

THE KINETICS OF SOLVENT EXTRACTION
BY TERTIARY AMINES

by

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ABSTRACT

The kinetics of solvent extraction of iron (III) from chloride solutions (HCl and HCl-LiCl) by tri-n-octylamine hydrochloride (TOAHCl) in toluene has been studied in a stirred cell.

The evaluated rate parameter was the initial specific iron (III) extraction or stripping rate. A chemical reaction rate controlling mechanism was indicated by the effects of stirring speed and temperature on the mass transfer rate. It was found that there is a range of chemical composition where chemical control cannot be attained. It was found also that when the viscosity of the aqueous phase increased, the Reynolds number was a reasonable criterion of hydrodynamic similarity in the mixing conditions. The linear dependence of the mass transfer rate on the specific interfacial area was consistent with an interfacial process. The effects of aqueous (5×10^{-4} to 5×10^{-3} M) and organic (1.74×10^{-4} to 1.74×10^{-3} M) iron (III), TOAHCl (0.002 to 0.1 M) and aqueous chloride (1 to 7 M) concentrations on the initial specific mass transfer rate were investigated. The extraction rate is first order with respect to the total aqueous iron (III) and monomer TOAHCl concentrations, whereas the stripping rate is first order with respect to the organic iron (III) concentration and inverse first order with respect to the total TOAHCl concentration. The extraction rate is dependent on the aqueous chloride concentration, whereas the stripping rate is independent on this parameter. A mechanism for the reactions involved is presented. The experimental results could be represented with a rate equation based on the proposed mechanism. Because it was not possible to determine with certainty which chlorocomplex(es) was involved in the extraction process, due to lack of reliability and consistency of the published values of the stability constants, further experiments were carried out using radioactive chloride (^{36}Cl as HCl). The experiments were designed so as to offer the possibility of detecting the transfer of neutral or anionic iron (III) species. Experiments were carried out in the range 1 to 7 M Cl^- . It was found that mixed (neutral and anionic) transfer is the most likely possibility.

To Terezinha,
Marcos and Francis
with love

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CHAPTER I

INTRODUCTION

Solvent extraction is one of the most important processes in hydrometallurgy for separation, purification and concentration of metal ions. However, until two decades ago this unit process was relatively unknown and was restricted in application to the nuclear field and to some less common metals. Relatively few extractants were available and the process was considered expensive and unlikely to be of general interest without the development of cheap extractants. The development of the chemistry of the process had just begun and very little was known about kinetics and mechanistic aspects. Today, there is little doubt that this unit process has gained wide acceptance as a proven technology in extractive metallurgy.

Since the sixties, the increasing concern about pollution, caused mainly by copper smelters, has directed the attention of metallurgists to solvent extraction routes. It was thought that with the new alternative method, the pollutants would be concentrated in solutions, kept and processed in closed circuits so that the environmental effects could be localized. Solvent extraction has also other advantages. The ability to treat concentrated as well as dilute solutions is of paramount importance, as this enables the economic extraction of metals from low grade ores, process effluents, dump ore heap leaching, mine waters, scrap and wastes. Another field of metal recovery in which solvent extraction will probably find increased applicability is in the treatment of complex ores containing a variety of the base metals, some of which are lost or only partly recovered in conventional flotation/pyrometallurgical processing.

Besides copper and the nuclear field, solvent extraction has also found some applications in the metallurgy of cobalt, zinc and cadmium. However, solvent extraction has not gained widespread use in the extractive metallurgy of other base metals, although many new hydrometallurgical processes are being developed. The escalation in the costs of energy and petrochemicals has been a serious drawback. Solvent extraction plants have large power requirements from pumps and other equipment to agitate and move large quantities of liquids. They also have large inventories of expensive petroleum products tied up in the extractant. In some cases, pyrometallurgical processes have been improved by technological advances that help to produce more concentrated and readily handled effluents, and the smelting operations can satisfy a great deal of their own energy requirements from the heat generated by the process. Nevertheless, solvent extraction is solidly established for the many situations where it demonstrates clear advantages.

Long chain amines and quaternary ammonium salts found extensive use as extractants in the nuclear fuel process industry, in view of their reported stability towards radiation. Amines are also widely employed in uranium extraction. Other commercial applications of amines in metal extraction involve cobalt (separation from nickel), tungsten, vanadium and chromium extractions, just to give a few examples. Non-metallic applications include separation of acids from industrial effluents, pharmaceutical industry, etc. Amine extraction has been used increasingly for studying the properties of metal complexes. These extractants also find extensive applications in trace analysis of elements in geological samples, soils, sediments and natural waters.

The kinetics of an extraction process is very important in the design of an industrial plant. The kinetics of the system, along with the proper dispersion

and coalescence, will influence the choice of contacting equipment. Because kinetics may vary with agitation and therefore drop size, and the drop size, together with the mixing time, may in turn affect the coalescence rate, the selection of the most suitable contactor for the process is difficult and data require careful evaluation. The kinetics play an important role in comparing and evaluating contactor performance. Thus, kinetics together with coalescence and entrainment will dictate the choice and size of the equipment, so that it is essential for any rational design of industrial contacting equipment.

A great deal of information is available on extraction equilibria in amine systems, but very little work has been carried out on extraction kinetics and the fundamental chemistry of the extraction process. Little work has been done specifically on process kinetics because it is generally found that amines are fast extractants and investigators have not been troubled by slow extractions. The kinetics of some amine systems have been studied in attempts to understand the mechanism of the reactions involved. There is uncertainty concerning the nature of the extractable metal complexes and to date there is no sure way to know whether amines are neutral or anionic extractants, or both.

The purpose of this experimental work is to study the extraction mechanism of amines. This is best achieved by investigating the variation of the mass transfer rates under appropriate conditions. Experiments and equipment must therefore be designed in such a way as to give accurate and reproducible values of this parameter. The extraction of iron (III) chloride by tri-n-octylamine in toluene has been selected for experimental study not on account of its industrial importance amongst amine systems, but rather to test the relevant models and to measure various parameters

which make it suitable for the systematic study of the mechanism of amine extraction.

Understanding the extraction mechanism might be very useful in designing optimal conditions for metal extractions, as well as for aiding the use of amine systems in physicochemical investigations.

Equilibrium data are easy to obtain using readily reproducible experimental techniques but there is no standard method of studying the kinetics of liquid-liquid extractions. A stirred cell was used throughout this investigation. It is believed that this type of equipment offers some advantages when compared with other techniques.

The present work can be considered as a systematic investigation aimed towards the elucidation of the mechanism of amine extraction, as well as an attempt to gain some understanding about the hydrodynamics of the stirred cell. It is hoped that the results obtained from this study will be useful for those concerned with the chemistry of amine extraction and/or stirred cell kinetics.

CHAPTER II

LITERATURE SURVEY

The literature relevant to this investigation is extensive. For the sake of clarity it has been classified under the headings of:

- 2.1 Mass transfer theories;
- 2.2 Experimental methods used in the kinetics of solvent extraction;
- 2.3 Pure mass transfer in a stirred cell;
- 2.4 Mass transfer with chemical reaction;
- 2.5 Kinetics of amine systems

The physical chemistry of the studied system is discussed in Chapter III and the choice and description of the equipment used in the present work is presented in Chapter IV.

2.1 MASS TRANSFER THEORIES

Several models have been developed for mass transfer through an interface. The best known are:

- i) the film theory
- ii) the penetration theories
- iii) the film-penetration theory
- iv) the boundary layer theory
- v) the hydrodynamic theory

Whitman's¹ two film theory for gas absorption is frequently applied to mass transfer at the liquid-liquid interface. The film theory deals with mass transfer between a turbulent medium and the interface. It assumes the presence of a stagnant layer of the fluid

at the interface. The thickness of the film is calculated by assuming that the flux through it is due to molecular diffusion only. The films are assumed to be of sufficiently small capacity for the concentration profile to be established instantaneously.

Its mathematical formulation is given by the equation:

$$J = \frac{D}{\delta} (C_i - C_b) \quad (2.1.1.)$$

where J is the mass flux, D the molecular diffusivity, δ the thickness of the film, C_b the solute concentration in the bulk of the phase and C_i the concentration at the interface.

Defining a mass transfer coefficient K , as

$$K = \frac{\text{Mass flux}}{\text{Driving force}} = \frac{J}{C_i - C_b} \quad (2.1.2.)$$

then for the film theory,

$$K = \frac{D}{\delta} \text{ and hence } K \propto D.$$

The film theory provides a simple method for comparing the performance of processes operating under different steady-state conditions. It cannot be used satisfactorily for the prediction of mass transfer coefficients since the assumptions of a stagnant film and steady-state diffusion at the interface are rarely true in practice.

The penetration theory² considers the unsteady state molecular diffusion process at the interface. It assumes that large eddies penetrate the liquid interface and are thus constantly bringing elements of fluid from the bulk to the interface where they are exposed for a finite time before being replaced. The exposure time is

short, so the medium can be assumed to be semi-infinite in depth. After exposure the elements are mixed with the bulk fluid which offers no resistance to transfer. Each element will have a mass flux dependent upon its age and therefore the rate of transfer from the interface will be an average value dependent upon the surface age distribution function $\phi(t)$. $\phi(t)$ can be defined as the probability of elements in the interface having a surface age (t) .

Higbie² postulated a mode of surface renewal in which each element was exposed for the same length of time, t^* , before being replaced. This represents the case of the penetration theory with regular surface renewal. From the diffusion equation, using the appropriate boundary conditions and the concept of t^* for the surface age distribution, the mathematical formulation of the model is given by

$$\bar{J} = 2 \sqrt{\frac{D}{\pi t^*}} (C_i - C_b) \quad (2.1.3.)$$

where $\bar{J}$ is the average mass flux. Then for Higbie's penetration model,

$$K = 2 \sqrt{\frac{D}{\pi t^*}} \quad \text{and hence } K \propto D^{0.5}$$

Danckwerts³ considered that the rate of surface renewal is constant and independent of surface age, which can assume any value between 0 and ∞ . The assumption of a random surface renewal is a considerable improvement in the penetration theory, as it appears to be more representative of interfacial conditions existing in extraction equipment. It thus follows for Danckwert's model

$$\bar{J} = D s (C_i - C_b) \quad (2.1.4.)$$

where s is the fractional rate of surface renewal, then

$$K = \sqrt{Ds} \text{ and hence } K \propto D^{0.5}$$

Perlmutter⁴ modified the surface renewal model by introducing the concept of multiple capacitance. This is basically the penetration theory with the degree of mixing in the region of the interface being specified by a number of stirred vessels (n) in series. The Higbie ($n = \infty$) and Danckwerts ($n = 1$) models thus represent the limiting cases of mixing conditions in the surface zone.

Harriot's model⁵ assumes that eddies arrive in the region of the interface at random times and penetrate to within random distances.

Ruckenstein's model of gradual renewal⁶ postulates that elements of fluid which come into contact with the interface do not maintain their individuality as they flow along the surface, but that a certain part of them is replaced with liquid from the adjacent layers. This process is repeated at discrete intervals of distance advancing into the turbulent field.

Toor and Marchello⁷ showed the limitations of the film and the penetration models. In the case of purely physical absorption the two models are not separate unrelated concepts, but rather provide limiting cases of a more general model, the film-penetration model, and that the two theories are complementary and not mutually exclusive. The mass transfer into new elements reaching the interface follows the penetration theory whilst mass transfer into old elements is approximated by the film theory. The elements of intermediate age have the characteristics of both

theories. In another paper⁸, Marchello and Toor introduced a modification in the film-penetration model⁷, postulating layers of definite thickness, not necessarily in contact with the interface, which are uniformly mixed at random time intervals. Mass transfer from one layer to another then takes place by molecular diffusion.

Howarth⁹ has shown by analogy with heat transfer boundary layer solutions that

$$\frac{Kx}{D} \propto \left(\frac{\mu}{\rho D} \right)^{\frac{1}{3}} \left(\frac{U\rho}{\mu} \right)^{\frac{1}{2}} \quad (2.1.5.)$$

where U is the stream velocity, x the distance along the interface, μ the absolute viscosity and ρ density, hence,

$$K \propto D^{0.67}$$

Potter¹⁰ derived an approximate boundary solution for mass transfer across the plane interface between two co-current, parallel fluid streams of the form

$$Sh = 9 (S_c)^P (Re)^{\frac{1}{2}} \quad (2.1.6.)$$

For a stationary interface the solution shows that

$$K \propto D^{0.67}$$

It has been shown experimentally¹¹ that turbulence does not die out at a particular distance from the interface as predicted by the film¹ and boundary layer theories¹² but that it extends into the region of the interface. Then, for conditions of high intensity turbulence, there is a need to add the eddy diffusivity (ϵ) to the molecular diffusivity (D) throughout the whole diffusion path.

In general, in order to integrate the rate equation obtained, i.e.

$$J = -(D + \epsilon) \frac{dC}{dX} \quad (2.1.7.)$$

where X is the distance from the phase boundary, it is necessary to relate ϵ and X .

King¹³ has assumed that ϵ is proportional to some power, m , of the distance from the interface x . The mass transfer coefficient K will be proportional in some way to m but it will be difficult to calculate.

Kishinevskii et al.^{14,15,16} have assumed ϵ to be constant. The turbulence is supposed to extend to the interface, the new effective diffusion coefficient being the sum of the molecular and eddy diffusivities, as in equation (2.1.7.). The mathematical formulation of Kishinevskii's hydrodynamic model is very similar to Higbie's penetration model and is given by

$$\bar{J} = 2 \sqrt{\frac{D_{\text{eff}}}{\pi \bar{t}}} (C_i - C_b) \quad (2.1.8.)$$

where $D_{\text{eff}} = (D + \epsilon_D)$ and $\bar{t}$ is the average residence time of an eddy at the interface. So, under conditions of low intensity of turbulence

$$K \propto D^{0.5}$$

and for fully developed turbulence

$$K \propto D^{0.0} \text{ (independent of } D)$$

Sherwood et al.¹⁷ developed a turbulent boundary layer model. This model uses various analogies relating mass, heat and momentum transfer. ϵ is obtained indirectly

through its relation to eddy viscosity which is derived from velocity profiles.

Kolar¹⁸ pointed out the fact that the turbulent disturbances penetrating from the bulk phase towards the interface cause a flow near it and also its periodic renewal. It is assumed in this case that the controlling step is unsteady molecular diffusion into the elements forming the interface.

Prochazka and Bulicka¹⁹ developed a model based on theoretical Kolar model¹⁸. The influence of mass transfer across the interface on the rate of mass transfer was taken into account. This model predicts that

$$\frac{K_1}{K_2} = \left(\frac{D_1 \mu_1}{D_2 \mu_2} \right)^{\frac{1}{2}} \quad (2.1.9.)$$

which does not agree with most experimental results. Later²⁰ the same authors revised their theory on the assumption that disturbances affect both layers simultaneously in view of the perfect mobility of the interface. This gives a more acceptable relation²⁰:

$$\frac{K_1}{K_2} = \left(\frac{D_1}{D_2} \right)^{\frac{1}{2}} \quad (2.1.10)$$

A simple model based on Levich's theory²¹ was set up by Davies²². The Levich theory assumes steady molecular diffusion into a boundary layer whose thickness depends on the depth of the zone of deformed turbulence corresponding to the characteristic size of the eddies causing surface renewal.

All these models reviewed in this work are limited in their applications by the lack of information regarding the hydrodynamics at the interface.

COMPARISON WITH EXPERIMENTAL RESULTS

Table 2.1.1. summarises the dependence of mass transfer coefficients on diffusivity as predicted by the main theories of mass transfer and Table 2.1.2. indicates the range of values of n obtained experimentally.

MODEL	n
Film theory - eqn. (2.1.2.)	1.0
Penetration theory - eqns. (2.1.3.) and (2.1.4.)	0.5
Boundary layer theory - eqn. (2.1.6.)	0.67
Hydrodynamic theory - eqn. (2.1.8.) (for fully turbulent transfer)	0.0

TABLE 2.1.1. Theoretical models ($K \propto D^n$)

INTERFACE	$K \propto D^n$	References
Gas-liquid	$0.15 < n < 0.70$	23-25
Liquid-liquid	$0.0 < n < 0.67$	24,26-34
Solid-liquid	$0.5 < n < 0.83$	24,35,36

TABLE 2.1.2. Experimental results.

2.2. EXPERIMENTAL METHODS USED IN THE KINETICS OF SOLVENT EXTRACTION

In accordance with Whewell³⁷, the ideal method for measuring kinetics has the following attributes:

- (i) the apparatus is simple to initiate and to operate;
- (ii) the experiment enables easy isolation of variables;
- (iii) interfacial areas may be measured;
- (iv) lengthy calculations can be avoided;
- (v) the results can be interpreted in a plant context.

A number of experimental techniques have been used to study the kinetics of solvent extraction systems. No method passes all of these criteria listed above. Each technique has its own advantages, drawbacks and limitations and it is essential to keep these in mind when comparing results, especially when different techniques have been used and/or the geometry and hydrodynamic conditions in the equipment are different.

Yagodin and Tarasov³⁸ stress that only by knowing the interfacial area can correct conclusions be drawn regarding the extraction mechanism.

Fleming³⁹ pointed out the importance of an experimental distinction between diffusion and chemical rate control.

In addition to the criteria selected by Whewell³⁷ the following ones can be considered essential for better scope and flexibility in kinetic studies.

- (i) interfacial area and phase ratio must be measured and varied so that unambiguous conclusions can be derived;
- (ii) the hydrodynamic conditions must be kept constant;
- (iii) the two phases must be kept always separated, hence many problems associated with dispersion mixing, e.g. time lag between settling and chemical analysis, are avoided;
- (iv) continuous reading of chemical analysis in both phases, especially in the phase to which the species of interest are being transferred, as this greatly increases the precision of the method of initial rates, which is the most used to analyse the results.

The most important experimental methods used to study the kinetics of solvent extraction are outlined below.

2.2.1. Dispersion Mixing

This technique has been used since the earliest studies. It has been preferred by many authors as the closest to plant conditions. It involves agitation of two phases in a given phase ratio for varying lengths of time in a batch stirred tank. An unknown interfacial area is produced which depends on the hydrodynamics and chemical conditions. The degree of mixing cannot be varied independently without affecting other variables (e.g. interfacial area, drop size distribution, coalescence and redispersion of drops, etc.). Therefore it is difficult to investigate the dependence of the rate on the system variables. The separation of the phases before analysis takes time. This means the reaction continues to take place in the sample so that rates obtained are erroneous with the magnitude of the

error depending on the rate of the reaction. The lack of a standard design is a further disadvantage of this technique, as it makes very difficult the comparison of any result from different laboratories.

Some useful studies, usually plant engineering oriented, have been carried out using this technique. Ritcey and Lucas^{40,41} compared the rates of extraction of different metals from mixed aqueous solutions. Murray and Bouboulis⁴² studied the effects of diluents on extraction and stripping rates. Hartlage and Cronberg⁴³ evaluated the relative influence of additive concentrations for copper extraction and stripping.

The AKUFVE⁴⁴ apparatus overcomes some of the difficulties of the batch stirred tank. Being a standard piece of equipment, the results can be reproduced. The AKUFVE is basically a batch stirred tank connected in closed circuit with a centrifugal separator. Flett et al.^{45,46,47} and Spink and Okuhara⁴⁸ studied the extraction of iron, nickel and copper by some commercial extractants using a relaxation technique. The batch tank problem of changing concentrations is reduced by keeping the additions to the metal concentration so small that all the change in the other concentrations during the return to equilibrium can be considered negligible. This becomes a serious inconvenience as it is only possible to study the reaction near equilibrium, where the concentrations can be kept more or less constant. The problem of phase separation is avoided to some extent, but mass transfer does occur in the centrifuge. Phase recycling time must be controlled to give reproducible results. The time to reach equilibrium is usually less than one minute for most reported systems.

Cox and Flett⁴⁹ have shown that interfacial properties vary with pH, reagent concentration, diluent

type and temperature. The limiting dispersion size will certainly depend on these interfacial properties, hence even small changes in these parameters can dramatically affect the interfacial area and consequently affect the extraction rate as well.

Various methods have been used to measure drop size distribution or the average drop size, including: light absorption⁵⁰, a fast chemical reaction,⁵¹ photographic techniques⁵² and the Coulter counter.⁵³ Van Henven and Beek⁵⁴ discussed the advantages and limitations of these methods and proposed some improvements in the sampling methods, but as was shown by Giles et al.,⁵⁵ it is not easy to represent the population of different mean drop sizes. The assumption that the interfacial area is proportional in some way to the stirring speed⁵⁶ is not necessarily correct. The use of this type of correlation requires the use of a standard geometry, as well as a constancy of physical properties and especially interfacial properties. This is difficult to attain when a reasonable range of variation of the parameters is studied. If the interfacial area is not known, the absolute rate constants cannot be obtained.

Using the AKUFVE, it is usually found that increasing the stirring speed above a certain value, does not change the extraction rate. In this case, the rate apparently no longer depends on interfacial area, which is not likely for either mass transfer or chemically controlled interfacial reactions, or more likely a limiting dispersion size has been reached. The analysis of the results in terms of a chemical interfacial reaction requires the assumption that in the "plateau" region, stirring is strong enough to ensure that mass transfer considerations play no part in controlling the reaction rate. This is a serious

handicap for the use of the AKUFVE in kinetic studies, as it is not possible to know (unless complicated methods are used, e.g. photographs of the dispersion) whether a limiting dispersion size has been reached, hence a constant value for interfacial area, or whether the reaction rate no longer depends on the stirring speed. Yagodin and Tarasov³⁸ propose a method of determining if reaction or mass transfer is the rate controlling step in an AKUFVE type reactor.

The shake-flask technique is also another form of dispersion mixing. Here reactions are carried out using a number of flasks. Each flask is shaken for a given length of time and the combination of these experiments is taken to represent the course of the extraction. A major problem is the difficulty of standardizing mixing conditions, which in any case will be less representative of what might happen in commercial conditions. In some cases, conditions were standardized^{57,58,59} so that enough control could be exercised to ensure that the extraction rate was mainly limited by chemical reaction. However, the precise location of reaction site could not be isolated. This technique is restricted to slow reactions where equilibration times of over 20 minutes might be expected.

The use of any dispersion mixing technique in fundamental studies is questionable. Detailed mechanistic conclusions are not possible because of the unmeasurable effects of uncontrollable variables.

2.2.2. Single Drop

This technique has been widely used in kinetic studies of metal extraction. Both rising and falling drops have been employed. The apparatus is described

adequately in the literature^{60,61,62,63}. It is easily constructed and cleaned and the results should be reproducible from one laboratory to another. Concentration in the continuous phase can be kept essentially constant but concentrations in the dispersed phase (drops) can only be determined at the beginning and the end of the experiment. The interfacial area can be calculated but it is generally assumed that drops are spherical, which is not always the case.⁶³ The hydrodynamics of single drops is complex^{64,65} especially with respect to degree of internal circulation. Drops over 2 mm diameter are subject to oscillation and drag a wake⁶⁶ behind them, the nature of which depends on the internal circulation, amongst other variables. Because drop properties will depend on the physico-chemical properties of the system, drop behaviour should be investigated over the range of physico-chemical conditions, to ensure that the extraction rates obtained can be compared (e.g., variation of the chemical composition can affect interfacial tension, hence can affect drop size; variation of temperature will affect viscosity, which can affect the hydrodynamics, hence can affect the residence time, etc.). Although the hydrodynamics can be kept fairly constant, the experimenter has no sure way of independently varying the mixing conditions. Ellender and Lawson⁶⁷ used the drop technique to study the performance of different extractant systems. They found great difficulty in producing drops of the same size using different systems. Their results present some anomalies and their conclusions are contested by Cognet and Renon⁶⁸. Lawson⁶⁹ in a recent work made some improvements in the analysis of results, so that now they look more acceptable. The unquantified changes in hydrodynamics with drop size will make very difficult the comparison of the kinetics of different reagents. Whewell³⁷ analysed the problem of misleading and prejudiced comparisons.

Atwood et al.,⁷⁰ have pointed out some of the problems due to end effects in drop studies, that is, the extraction taking place during the formation and collection of the drop. This may account for a significant portion of the total extraction. However, some standard techniques have been developed to correct for it.⁶⁹

Hanson and co-workers^{62,71} have successfully used the single drop technique to study copper extraction by some hydroxyoximes. Davey et al.^{63,72,73} studied the kinetics of extraction of niobium (V) by a quaternary ammonium chloride salt using the drop technique.

Interfacially active impurities, if present, will accumulate at the interface and may affect seriously the mass transfer rate, leading to misleading results. Those impurities may play a more important role in the single drop systems than with dispersion mixing systems, where the interface is continually being broken up. Thus, reagent purity is essential to give the real rates of extraction, as well as for good reproducibility of the results.

A typical value reported for drop residence time is about 20 seconds. If the reaction rate is very slow, it is not possible to use the drop technique unless special analytical methods are used (which can detect very low concentrations) or alternatively very long columns are used. Very low concentrations are usually not easy to analyse, and such analyses are associated with large errors, hence the initial rates will reflect a large degree of uncertainty that must not be forgotten when the analysis of results is carried out. Usually, only initial rates are studied unless the dispersed phase is pre-loaded. Another inconvenience of the drop technique is that different lengths of columns will be

necessary in order to achieve different contact times. Even if a large number of these columns is available, the range is still limited.

Under certain conditions the drop technique may be useful for fundamental studies, but the single drop is far from plant conditions and the results obtained may be of little use for process considerations. The impossibility of identifying the rate controlling step by direct measurements of the rate of extraction is a further disadvantage of the method and its application in fundamental studies becomes very limited.

2.2.3. The Stirred Cell

The Lewis³²⁻³⁴ type stirred cell has been used to investigate a number of systems. The essential characteristic of the cell is that the interfacial area of contact between the phases is kept constant and well defined by the cell geometry. Stirrers in each phase ensure that the bulk liquid remains homogeneous while suitable baffles keep the interface quiescent. Slow or fast reactions can be studied and, depending on the concentration of the reactants, specific interfacial area (A/v) and stirring speeds, equilibration times from minutes to several hours can be attained. The duration of the experiments is readily varied. The extraction rate from time zero to near-equilibrium can be examined. Continuous analysis can be easily performed, provided a suitable analytical method is available. Another advantage is the possibility to connect reagent feeders in conjunction with on-stream analysis in order to keep certain concentrations constant, while the one of interest is allowed to change. Phase volumes or contact areas can be changed by a number of methods so that the variation of the rate with specific interfacial area can be investigated.

Some criticisms of the stirred cell centre on the complexity of the apparatus and the variety of designs, no standard equipment being available as with the AKUFVE. This complicates comparisons between different studies.

The hydrodynamics, particularly in the interfacial zone, are not accurately characterized. However, the stirring speed provides a controllable mode of altering the hydrodynamics. The problem of transport control can be avoided by working in a range of stirring speed where the extraction rate is independent of stirring speed. The ideal behaviour of the extraction rate as a function of stirring speed for an extraction with an interfacial chemical reaction is illustrated by Figure 2.2.3.1. As the stirring speed is increased from zero, the extraction rate should increase. In this range, mass transfer of reactants or products controls the mass transfer rate. Under these conditions, the chemical reaction at the interface would be in equilibrium. With increased stirring speed, a speed should be reached above which the extraction rate is independent of stirring speed. In this plateau region, chemical reaction is controlling the extraction rate. The stirring is strong enough to ensure that reactants are supplied to the interfacial zone and products removed faster than the reaction uses or produces them. The reaction is then not at equilibrium. At higher speeds the extraction rate again depends on stirring speed. The agitation is now so vigorous that the interface begins to ripple and then breaks up, increasing interfacial area and eventually mixing the phases. At very high speeds, it is possible that a second plateau is reached. This is where the limiting dispersion size has been attained. The AKUFVE operates on the second plateau.

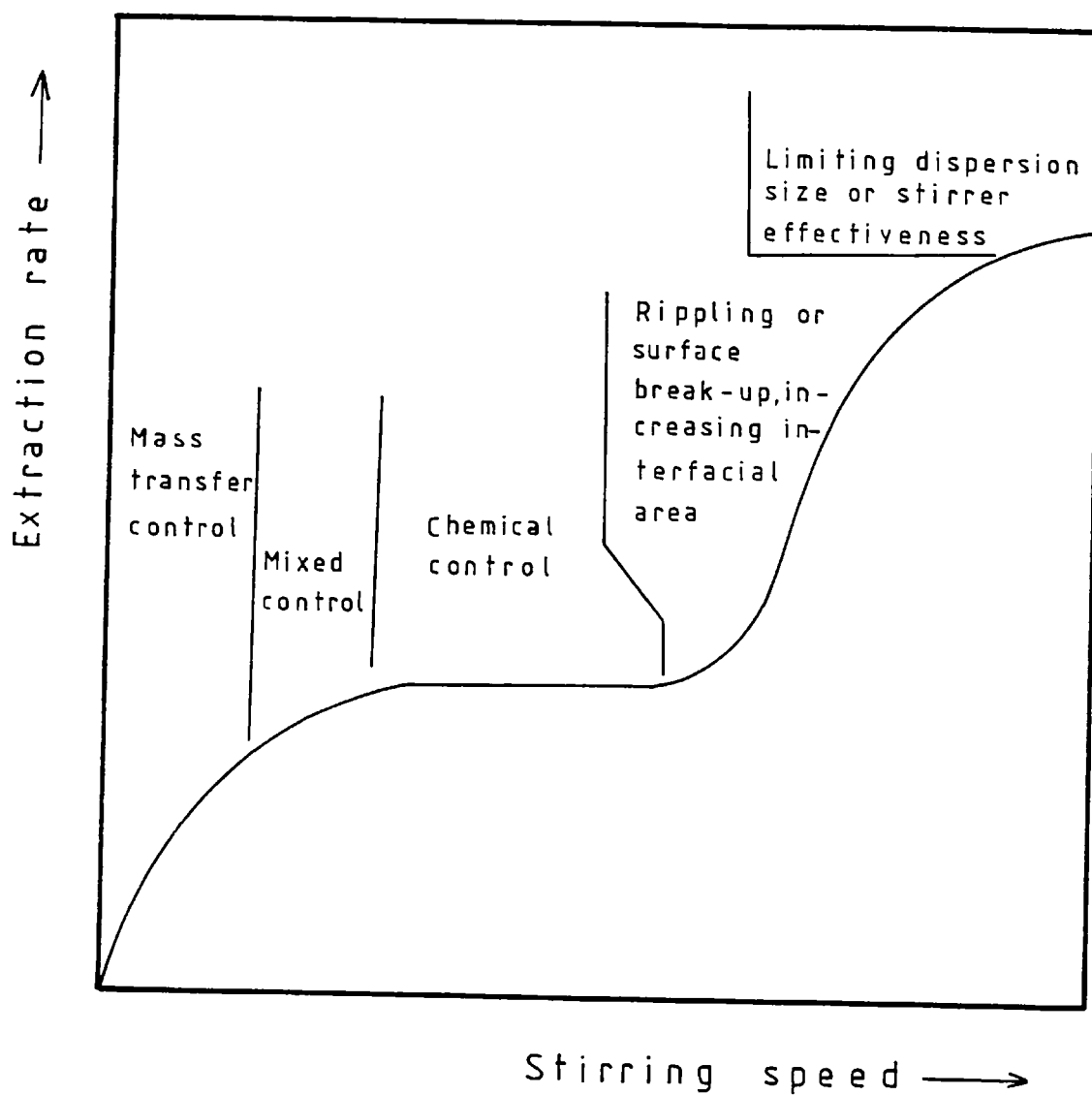


FIGURE 2.2.3.1. IDEALIZED RESPONSE OF EXTRACTION RATE TO STIRRING SPEED IN A STIRRED CELL.

The location and existence of the different zones will depend on the geometry of the cell and the properties of the system being studied. The first plateau may be absent in a completely unbaffled cell because the stirring may be so strong that the interface starts to break up before the plateau is reached. At the other extreme, a system with a very slow interfacial reaction may show no noticeable plateau. The location of the plateau with respect to stirring speed can shift with chemical and physical changes in the system. Nitsch and Kruis⁷⁴, studying zinc extraction by dithizone in various diluents, found that the length of the plateau region varies with the zinc concentration and it can disappear completely above a certain limiting aqueous zinc concentration, or on changing the diluent. Another problem is that the cell may be so heavily baffled that large increases in stirring speed do not affect the mass transfer significantly and any change may be confounded with the experimental error. This can also happen with very ineffective stirrers. In this case, there is no direct way to know whether the observed plateau in a chemical reaction system is due to chemical reaction control or to insensitivity of the stirring in the cell. If, however, the behaviour of a pure mass transfer system has been studied in the cell, this question can be sorted out. Thus, the preliminary study of a pure mass transfer system is of paramount importance for the understanding of the cell performance. This unnecessary complication and extra experimental work could be overcome with a standard cell. So far there is no sign of a standard design for the stirred cell and unfortunately it seems that the trend is that each experimenter designs a new type of cell, which makes the comparison of results rather difficult.

Olander and Benedict³¹ pointed out the fact that if an interface appears visually quiescent, this is no guarantee that there are no disturbances and conversely,

the visual appearance of ripples does not per se imply that the mass transfer rates are vastly different from those with seemingly undisturbed interfaces.

As with the single drop, the interfacial properties of the system are very important with stirred cells and so impurities, particularly surface active ones, may have large effects. Investigation of which, if any interfacial phenomena, such as Marangoni or gravitational instabilities, are present should be considered in order to fully characterize an interfacial process. Little work has so far been done on the effects of interfacial phenomena, but there is some evidence that these are now being investigated.⁷⁵

Contactors very similar to the Lewis cell in many respects have been used by McDowell and Coleman⁷⁵, Kataoka et al.⁷⁶, Tsuneuki et al.⁷⁷, Richter and Meinhold⁷⁸, Brisk and McManamey⁷⁹, Vandegrift and Horowitz⁸⁰, Danesi et al.⁸¹ amongst others. All these investigators correlated their results for metal extractions in the plateau region with an interfacial chemical reaction model, and, in the region where mass transfer affects the extraction rate, a mixed model was used to represent some of the observed results.

Prochazka and Bulicka²⁰ designed a stirred cell that presents some improvements compared with the Lewis type cell. High stirring speeds were attained without disturbing the interface. The cell has a cylindrical grid with 3 mm openings. Vertical baffles were also introduced into each phase. The grid and the baffles were mounted on the stator. The cell, however, has very little room for varying either the phase volumes or the interfacial area.

Landau and Chin⁸² reported on a stirred cell which is essentially a modification of the one proposed

by Prochazka and Bulicka²⁰. It presents considerable improvements over the latter especially in its flexibility to enable independent variation of phase volumes and contact areas.

Nitsch and co-workers^{74,83,84} designed a cell of the Prochazka type. It is claimed that speeds up to 600 r.p.m. have been obtained with the interface still stable. This is a considerable advantage. The design of the cell does not, however, allow the variation of the contact area.

Ajawin et al.⁸⁵ presented recently a new version of a Prochazka type cell. Apparently some limitations of previous designs of this class of stirred cell have been overcome. A high degree of flexibility was achieved that makes it suitable for kinetic studies. One possible disadvantage of this cell is the difficulty of circulating both phases out of the cell to enable continuous analysis.

Hancil et al.⁸⁶ described a new stirred cell in which vibrational mixing was used in both phases. The mixing was provided by two perforated plates fastened to the central driving shaft with one plate in each phase. It is doubtful whether reasonably high stirring speeds could be obtained without the disruption of the interface.

The use of any type of stirred cell is limited by the requirement of a stable interface and good mixing in each phase, so that there is always a maximum and minimum stirring speed where experiments can be properly carried out. In order to have a range of conditions where chemical control is attained, usually it is necessary to work with very low concentrations of the reactants. The mechanism of the reactions involved in these conditions

may not be easy to relate to what might be expected under plant conditions.

One remark often made when comparing extraction rates obtained using single drop and stirred cell techniques is that "the Lewis cell rates of extraction are an order of magnitude lower than single drop rates when area is taken into account." This remark has its merits and must be analysed in detail. It is true that because the equipment for the single drop technique is easily made and the technique itself very simple, the results obtained, assuming that proper care is taken, are reliable within the limitations of the method, as discussed previously. The same argument is not necessarily true with respect to stirred cell and indeed the results obtained with some types of stirred cell are not reliable at all, especially when the assumption of chemical reaction control is introduced, as there is little chance it was achieved. Some stirred cells have operated under such poor mixing conditions that the results must be compared with care. It is possible that a plateau may be reached, but only by comparison of the behaviour of the system under investigation with one where pure mass transfer occurred, in the same piece of equipment, can this problem be sorted out. Assuming that the experiment was carried out in a situation where the chemical composition of reactants were the same, two possibilities can happen. Firstly, if the reaction rate is off a "true" plateau in the stirred cell, that means a mass transfer or mixed control. In that case it is likely that the single drop technique will give a higher extraction rate. Nitsch et al.⁷⁴ defined a stirring speed equivalent to stirred cell conditions for the drop and found that the equivalent stirring for the drop is higher, which means that the stirring conditions around the drop are more efficient than at the interface in the stirred cell. Secondly, if the reaction rate is in a "true" plateau in the stirred cell, chemical control was

attained. In that case stirring speed has no effect on the extraction rate. Nitsch *et al.*⁷⁴ and Horner *et al.*⁸⁷ found no significant difference, within experimental error, when both techniques were used, provided conditions for chemical control were achieved.

2.2.4. Other Techniques

Scriven and Pigford⁸⁸ developed the laminar jet technique. This involves producing a jet of liquid of small diameter from an appropriate orifice. The jet length and the liquid flow rate can be varied, thus both the time of contact and area are controllable. The contact area is fixed for a given orifice, jet length and velocity. The influence of nozzle⁸⁹ and of mass transfer⁹⁰ on the stability of the jet have been discussed in the literature. The flow of the jet must be laminar and plug-like. This requires complicated procedures to control the flow and ensure its stability.

The laminar jet technique has been used mainly in the study of gas-liquid reactions^{91,92,93}. It has also found some applications in liquid-liquid extraction^{94,95}. In this case a further inconvenience is added, as the transfer of kinetic energy of the jet to the stagnant liquid induces circulation, hence local mass transfer is enhanced and this effect is not easy to correct.

The wetted-wall column has been used in gas absorption^{96,97}, as well as in liquid-liquid extraction^{98,99}. Under controlled conditions it is possible to maintain a well-defined interfacial area. In practice, many corrections have to be made in the use and interpretation of data.

The laminar jet and wetted-wall column techniques have the advantage of a better knowledge of the hydrodynamics

at the interface compared with the other techniques discussed previously. Due to the very short contact times attained by both techniques, they can be used only for fast reactions, as it would be very difficult to obtain reliable results for slow reactions.

The Hahn static cell¹⁰⁰ removes the problem of unknown hydrodynamics at the interface. The two phases are contacted in the cell without any stirring. Diffusion gradients are formed over long periods of time. Concentrations can be followed spectrophotometrically or by other means, but sampling is avoided as this will disturb the interface.

Hughes and Middlebrook¹⁰¹ used a Hahn type static cell to study the extraction of copper by LIX 64N. The use of this technique dictated a diffusion controlled reaction. The Hahn cell enables the study of the importance of diffusion in the kinetics of solvent extraction, but conditions are far removed from plant conditions. The usefulness of this technique is only to improve the understanding of mass transfer processes.

Austin¹⁰² used an unstirred cell coupled with a Schlieren apparatus to study interfacial instabilities (gravitational and Marangoni type), although the cell was stirred in some cases in order to enhance these effects.

Yagodin and Tarasov³⁸ discussed the aspects of experimental techniques applied to systems involving reaction kinetics in which it is difficult to predict the role of chemical processes beforehand. They showed the advantage of studying unsteady state mass transfer into an unstirred medium. They found that as contact times tend to zero, mass transfer rate is limited only by chemical reaction. They describe a cell for studying

mass transfer kinetics under short-time phase contacting. The technique has its merits but its application is restricted to some simple systems where the chemical analysis is feasible.

2.2.5. Conclusion

Of all the techniques, the stirred cell should best be able to provide absolute reaction rates, provided that suitable experiments are carefully done, and furthermore it offers enough flexibility to enable easy investigation of the different variables of the system. It is fairly easy to clean and operate and offers the possibility of continuous analysis. For these reasons a stirred cell was chosen for the present study.

2.3. PURE MASS TRANSFER IN A STIRRED CELL

The relation between mass transfer coefficient and the physical and/or hydrodynamic parameters is usually presented using empirical correlations of the type

$$Sh = \alpha Re^{\beta} Sc^{\gamma} \quad (2.3.1.)$$

where $Sh = \frac{KL}{D}$, $Re = \frac{NL^2}{\nu}$, $Sc = \frac{\nu}{D}$; K is the mass transfer coefficient; L is usually taken as the tip-to-tip stirrer length; D the molecular diffusivity, N stirring speed, ν kinematic viscosity, β and γ constants.

Lewis³² was the first to use a stirred cell in which the interface formed an annulus between two baffles. He correlated the individual mass transfer coefficient of a few partially miscible systems in terms of their physical properties and the Reynolds numbers of the phases. This correlation was used also to predict mass

transfer coefficients for the transfer of a solute between two immiscible phases³⁴, giving reasonable agreement in some cases and considerable deviations in others.

McManamey³⁰, in his studies on the interfacial resistances in liquid extraction of inorganic nitrates, used a stirred cell with no central baffle. He also correlated Lewis's data in a different form.

Mayers²⁹ recorrelated Lewis's data using a j-factor technique. His correlation was confirmed with new experimental data. His cell had a central baffle but no annular baffle.

Olander and Benedict³¹ repeated many of Lewis's experiments using a different type of cell and found that the results did not confirm Lewis's conclusions. It is possible that deviation was due to the absence of baffles, as well as for the different direction of stirring (co-rotating, instead of contra-rotating as used by Lewis).

Austin¹⁰², using a modified version of the Lewis cell (with additional vertical baffles), proposed two different correlations applicable for an undisturbed laminar interface (low Re) and for a surface-renewed interface (high Re). He also found a substantial dependence of the mass transfer coefficient on the direction of stirring speed (contra- or co-rotating). Grosjean¹⁰³ using the same equipment, repeated some of Austin's experiments and found no significant difference whether the stirrers were contra- or co-rotating.

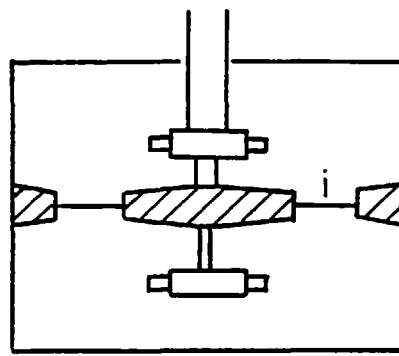
Prochazka and Bulicka^{19,20} developed a model based on the theoretical Kolar model.¹⁸ The influence of mass transfer across the interface on the rate of

mass transfer was taken into account. The model was applied to mass transfer studies using a different version of the Lewis cell. The stability of the interface was improved by the introduction of several vertical baffles and of a cylindrical grid in the proximity of the impellers.

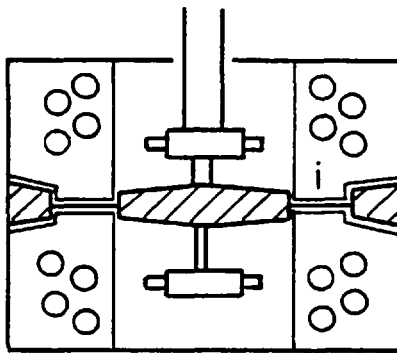
The various Lewis type cells used in the above studies are shown in scale drawings in Fig. 2.3.1 and the obtained correlations are given in Table 2.3.1. In all cases the hydrodynamics at the interface are entirely different. This eliminates the possibility of a direct comparison of results. However, comparison can be made between correlations with respect to the effect of certain variables on the process. Table 2.3.1. indicates the magnitude of the discrepancies existing for the effect of molecular diffusivity on the mass transfer coefficient. A similar discrepancy exists for the effect of Reynolds number in each phase. The interaction which occurs across the phase boundary can be assessed from the correlations. The results are equally inconclusive.

Some criticisms of all these correlations are related to the excessive scatter and irreproducibility of coefficients that could well be sufficient to mask any dependence of the transfer coefficient on diffusivity and confuse the mechanism of interaction across the phase boundary. It is also doubtful whether the interfacial area is sufficiently well defined in the equipment to make the coefficients precise enough for use in fundamental correlations. The interface is often disturbed by ripples. The extent of the rippling, which will affect the transfer area, is a function of the interfacial tension and density difference of the solvents and will therefore vary from one system to another. Others^{30,104} have criticised the use of

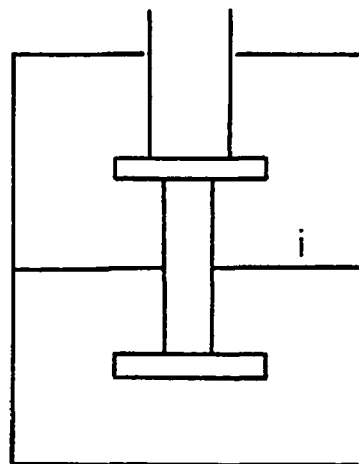
Scale
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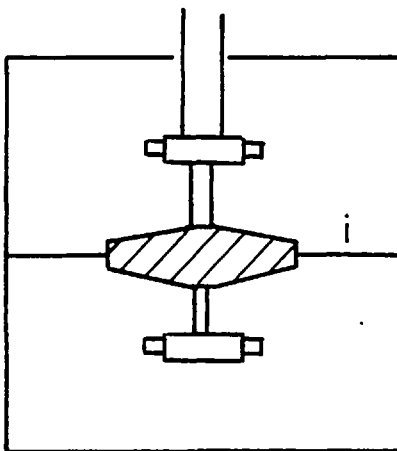
(Contra-rotating)
LEWIS



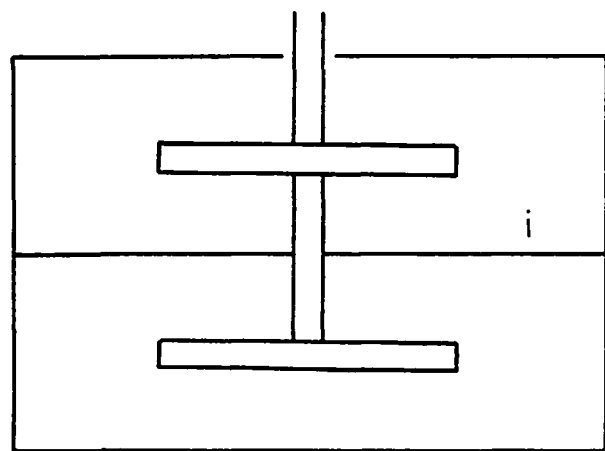
(Contra-rotating)
AUSTIN



(Contra-rotating)
McMANAMEY



(Contra-rotating)
MAYERS



(Co-rotating)
OLANDER and BENEDICT

FIGURE 2.3.1. COMPARISON OF THE STIRRED CELLS USED IN THE FORMULATION OF CORRELATIONS.

AUTHOR	CORRELATION	$K \propto D^x$	$\frac{K}{\nu} \propto N^y$
Lewis (32)	$\frac{60K_a}{\nu_a} = A \left[(Re)_a + (Re)_o \frac{\mu_o}{\mu_a} \right]^{1.65} + 1$	$X = 0.0$	$Y = 1.65$
McManamey (30)	$\frac{K_a L}{\nu_a} = \frac{B(Re)_a^{0.9}}{(Sc)_a^{0.37}} \left[1 + \frac{\mu_o(Re)_o}{\mu_a(Re)_a} \right]$	$X = 0.37$	$Y = 0.9$
Mayers (29)	$\frac{K_a L}{D_a} = C [(Re)_a (Re)_a]^{0.5} (Sc)_a^{0.83} \left[\frac{\mu_o}{\mu_a} \right]^{0.9} \left[E + \frac{\mu_o}{\mu_a} \right]$	$X = 0.17$	$Y = 0.5$
Olander & Benedict (31)	$\frac{K_a}{\nu_a} = \frac{F}{(Sc)_a^{0.42}} \left[\frac{N}{\nu_a} \right]^w$ Low $(Re)_a$ $w = 0.67$ High $(Re)_a$ $w = 1.70$	$X = 0.44$	Low $(Re)_a$ $Y = 0.67$ $Y = 1.70$ High $(Re)_a$
Prochazka & Bulicka (19)	$(Sh)_a = G(Re)_a^{0.75} (Sc)_a^{0.5}$	$X = 0.5$	$Y = 0.75$
Austin (102)	$(Sh)_a = 1.5(Re)_a^{0.5} (Sc)_a^{0.33} - 400$ for $300 < (Re)_a^{0.5} (Sc)_a^{0.33} < 800$ $\ln \left[\frac{K_a}{D_a} \right] = \frac{N_c}{300} + H$ for $(Re)_a^{0.5} (Sh)_a^{0.33} > 800$	$X = 0.67$ $X = 0.5$	$Y = 0.5$ $K \propto e^N$

A, B, C, E, F, G, H = Empirical Constants

Re = Reynolds Number

N = Stirring Speed

Sc = Schmidt Number

L = Characteristic Length

Sh = Sherwood Number

D = Diffusion Coefficient

K = Mass Transfer Coefficient

ν = Kinematic Viscosity

μ = Dynamic Viscosity

TABLE 2.3.1. STIRRED CELL CORRELATIONS. BINARY LIQUID MASS TRANSFER SYSTEMS.

annular baffles in the Lewis type cells where, because of the unknown contact angle of the phases of the baffles, the interfacial area cannot be measured accurately. However, this problem can be minimized by the use of large interfacial areas.

It is quite unreasonable to expect a correlation with fixed exponents such as in equation (2.3.1.) to cover a variety of systems and hydrodynamic conditions. Such types of correlation can only be of limited applicability and may not always be of fundamental significance. Inherent to the correlation is the assumption that the hydrodynamic conditions close to the interface, that is in the region where most of the resistance to transfer is located, are described by the bulk Reynolds number. With reference to the interface, it is assumed that either the interface does not interfere with the transfer process or affects it in a very simple manner by the presence of an interfacial resistance. Such resistance is taken as constant in magnitude, as often happens when an insoluble surfactant is added to the system. Problems arise when interfacial instabilities, such as gravitational or Marangoni type, are present. In this situation the bulk Reynolds number can no longer be used to represent hydrodynamic conditions existing in the close vicinity of the interface and all the correlations presented in Table 2.3.1. cease to describe the mass transfer process satisfactorily. The subject of interfacial phenomena is treated in more detail elsewhere¹⁰⁵.

To conclude, it must be stressed that all the correlations are valid only for a narrow range of parameters over which the experimental data were obtained and for a given size and type of equipment, as well as being limited to a given system or a set of systems (and only stable systems).

2.4. MASS TRANSFER WITH CHEMICAL REACTION

Dancwerts⁹⁷ reviewed the theories of mass transfer with chemical reaction in heterogeneous systems.

Astarita¹⁰⁶ reported the general state of knowledge on mass transfer with chemical reaction in an excellent book. Gas absorption with chemical reaction has been studied extensively. This was justified by its industrial importance as well as its suitability for theoretical treatment, as the chemistry of the studied systems was well established. The lack of a good knowledge of the chemistry of many important liquid-liquid reactions has posed as a serious problem for a better understanding of mass transfer in these systems and liquid-liquid reactions have only recently received much attention. During ISEC 77 and 80, some papers about kinetics of metal extraction were presented and apparently there is a considerable interest in this subject at the present. The study of kinetics of metal extraction is complicated by its complexity and the uncertainty of the chemistry of extraction.

Hanson¹⁰⁷ and Hanson et al.¹⁰⁸ in a critical review analysed existing works dealing with mass transfer with chemical reaction in liquid-liquid systems. Their main points can be summarized as follows:

- (i) Until recently many of the industrial operations in liquid-liquid extraction have been classified either as mass transfer controlled or chemically controlled processes, the influence of the other effect being generally neglected;
- (ii) This assumption was discussed for several processes (e.g. aromatic nitration), and has been shown to be doubtful. The importance of the role of chemical kinetics or of mass transfer resistance was demonstrated;

(iii) The effect of various parameters, such as agitation, temperature, phase ratio, space time, phase inversion and surfactants was indicated for purposes of easier recognition of the type of control;

(iv) The case of interfacial reactions was reported, but attention was particularly drawn to a model based on Astarita's model for a fast reaction. The reaction is assumed to take place in a zone in the aqueous phase adjacent to the interface. This was considered more likely in the case of metals extraction. The possibility of true interfacial reactions was dismissed, as this would require a complete immiscibility of the two phases or reactants. The model also assumes the overall reaction to be the rate controlling step for the chemical reaction. This is not the case in many situations. In a later paper¹⁰⁹ a more realistic approach was used.

Some of the possibilities of liquid-liquid reactions are illustrated in Fig. 2.4.1. The position and depth of the reaction zone depends on the reaction velocity and the mass transfer rates (which depend on both the diffusivities of the various components and the degree of agitation imposed on the system).

Fleming et al.¹¹⁰ studied the extraction of copper by LIX 64N and Kelex 100. A model was developed to explain the extraction process. The extraction rate is limited by mass transfer. Interfacial concentrations involved in the model were eliminated by using an equilibrium constant, so that, the rate equation could be related to bulk concentrations of reactants and products. The mathematical model is complex but it was simplified under certain limiting conditions and useful qualitative predictions were possible. The film theory was used throughout the basic assumptions.

REACTION: $A + B \rightarrow \text{PRODUCTS}$

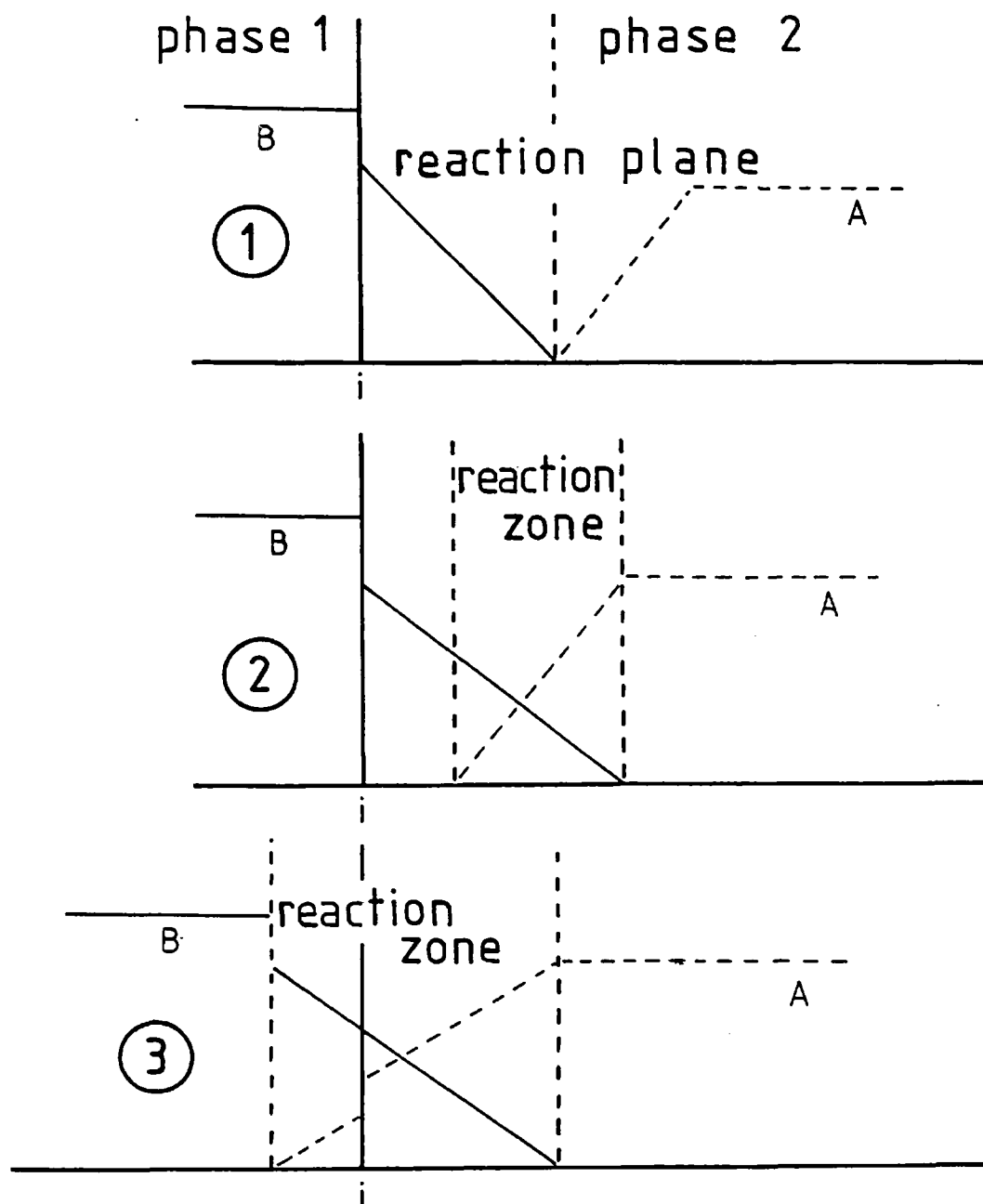


FIGURE 2.4.1. CONCENTRATION PROFILES FOR MASS TRANSFER WITH CHEMICAL REACTION. (1) - instantaneous reaction; (2) - reaction at finite rate, reaction zone limited to one phase; (3) - reaction of finite rate, reaction zone extends into both phases.

Chapman et al.¹¹¹, derived a similar model for the case of bivalent metal solvent extraction. The reaction is assumed to be fast and interfacial. The mass transfer coefficient calculation is based on the surface renewal theory. They were able to show that some apparently slow extraction rates which may be thought to indicate chemical control can be explained by a mass transfer model which shows how the transfer rates of the different components interact through the chemical equilibrium. Extraction rates as low as 0.02 times the value predicted by the mass transfer model were found for the extraction of copper by Kelex 100.

Baumgärtner and Finsterwalder¹¹² studied the extraction of uranium and plutonium by TBP. The single drop technique was used and the experimental results were explained in terms of a model based on Langmuir isotherms. The reaction was assumed to take place at the interface through the formation of an interfacial complex between the metal and TBP. It was assumed that the interfacial complex was the same regardless of the phase of origin, that it occupied equal effective areas in both phases and had equal probability of entrance into either phase. This technique assumes in advance that the rate of the process is first order with respect to the metal concentration.

Danesi et al.⁸¹ developed a model on similar lines to that of Baumgärtner and Finsterwalder¹¹² but identified the rate determining step as interfacial. The film model was used to relate mass transfer coefficients to the diffusivities. Basic assumptions used were: a) steady state conditions at the interface throughout the mass transfer process; b) H^+ concentration at interface the same as its bulk concentration; c) H^+ and extractant concentrations are much larger than the metal concentration, hence constant; d) mass transfer

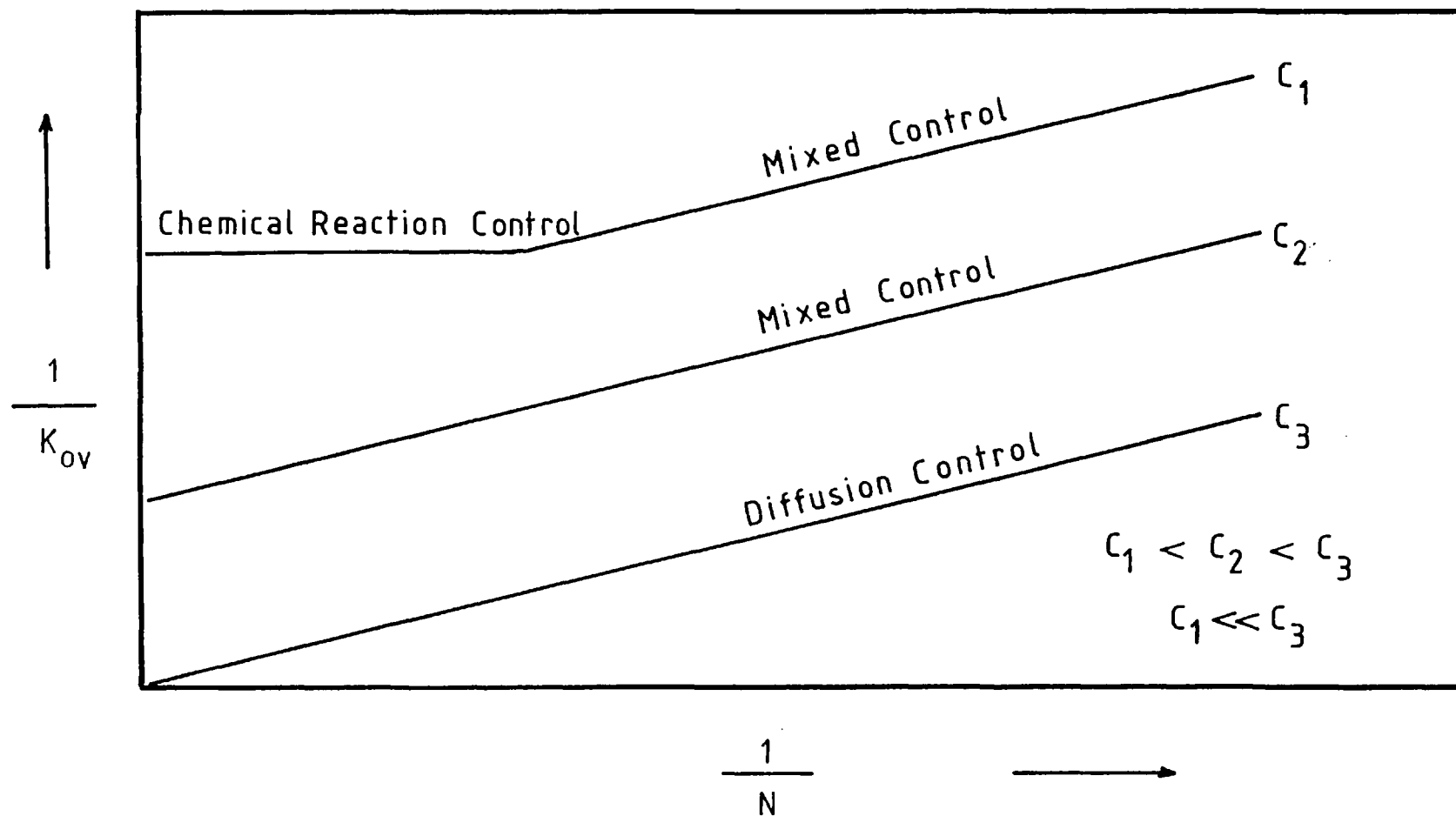


FIGURE 2.4.2. DEPENDENCE OF THE OVERALL MASS TRANSFER COEFFICIENT ON STIRRING SPEED AND CONCENTRATION (NITSCH AND KRUIS, Ref. 74).

coefficient for all the reactants, except for the proton, are equal. The last assumption can be, at best, approximate. A mixed model was derived to predict extraction rates.

Pratt¹¹³ showed the effect of a slow chemical reaction at the interface. His results indicated that the chemical reaction is represented by an additional resistance term in the equation for the overall mass transfer coefficient. This relation serves to emphasize that the transition from transport control to kinetic control is a smooth one. The plateau region described previously in relation to stirred cells is one where mass transfer resistance is small compared to chemical resistance.

Nitsch and Kruis⁷⁴ have derived a model during their study of zinc extraction by dithizone under conditions in which both diffusion and the rate of chemical reaction are comparable in magnitude. They pointed out the effect of concentration on the rate controlling step when the hydrodynamic conditions are kept constant. They were able to derive a model where transport resistances were separated from the resistance of the interfacial reaction. The model is shown schematically in Fig. 2.4.2. It can be seen that chemical control is attained only at low concentrations and high stirring speeds. The mass transfer coefficients of all the species were assumed equal and proportional to the stirring speed of the phases. The latter seems to contradict results on pure mass transfer.¹⁰²

Ortiz et al.¹¹⁴ developed a model relating the mass transfer coefficients to diffusivities through the penetration theory. The model was applied to rationalise the rate measurements of copper by hydroxy-oxime extractants, obtained by different experimental techniques.

Kondo et al.¹⁵⁹ studied the extraction of copper by benzoylacetone in a stirred cell. By assuming that the reaction takes place in the aqueous phase they developed approximate solutions of the diffusion equation. This approach is of limited utility as there are no exact analytical or numerical solutions available to the differential equations which result.

The applicability of the mixed models is limited by their complexity and the need to estimate empirical constants introducing sometimes large errors. Under limiting conditions they can be reduced to simpler forms which will give some indications of the behaviour of the system.

In practice most solvent extraction processes involve reactions under conditions when the extraction rate is affected by both diffusion and chemical reaction. There is a need to be able to predict the rate in terms of easily measurable parameters. Unfortunately, there is no single accepted method to fulfil this need to date. Van der Zeeuw¹¹⁵ pointed out that "If one wishes to have the problem of kinetics solved, the correct order of action would be to separate diffusion and chemically controlled systems, resolve the relations there, and then tackle the intermediate cases".

If the rate control is entirely by a slow reaction at the interface, the bulk concentration will be uniform up to the region of the interface. If the control is by diffusive transport through resistance, the rate will increase with increase of either agitation or interfacial area, if by interfacial reaction only, the rate will increase with increasing area but will be independent of agitation; and if by homogeneous reaction only, the rate will be independent of both agitation and area. When there is mixed control, these distinctions

are not clear; dependence of rate on agitation shows that there is at least some control by transport but does not preclude some control by slow reaction and of course large changes in the area and/or degree of agitation can cause a shift from one control regime to another.

It has been pointed out¹⁶⁰ that in control by a slow interfacial reaction, since the local solution properties are not identical to the bulk properties and not necessarily even simply related to them, the exact mechanism, coefficients and constants cannot in principle be determined from bulk-phase measurements. While certainly true, this does not mean that useful kinetic information cannot be established.

The treatment of the kinetic results from solvent extraction experiments is complicated by a number of factors. The chemical reaction is reversible. Complex interactions between the components being transferred to or from the interface as a result of the interfacial reaction may be present. The mass transfer is influenced by the interfacial activities of the reactants and products which in turn are affected by the bulk properties of the phase, such as the nature of the diluent and modifiers. Physico-chemical parameters such as diffusivity and viscosity can vary widely depending on the composition of the phases and these variations will complicate the comparison of results. Some criteria of similarity must be introduced. All these effects will have an influence on the extraction rate, particularly under those conditions where mass transfer is the predominant step. All these complications are a warning against long extrapolations from studies over only limited ranges of conditions in such systems.

2.5. KINETICS OF AMINE SYSTEMS

In contrast to some other extraction systems, relatively little attention has been given to the kinetics of amine systems. The rate of extraction has been of no concern in process developments as investigators have not been troubled by slow extractions. When rate limitations have been a problem they have been mainly from slow phase disengagement rather than slow equilibration. Although, some rate information has been recorded, mainly in a qualitative form, during exploratory and process development work, the majority of kinetic studies have been directed specifically towards elucidation of extraction mechanisms.

Most of the evidence that amine extractions are fast have been reported as very short contact times necessary to reach equilibrium during shaking-test experiments. Table 2.5.1. shows some of these results.

Coleman and Roddy¹²⁹ developed a general model that has been used successfully in process development and preliminary guidance of scale-up of uranium extraction by some amines. The model assumes beforehand the forward and reverse rates are both first order with respect to the extracted solute and the mechanism remains unchanged as the system progress to equilibrium. The mathematical formulation of the model is given by:

$$ak_1 = \frac{1}{t} \left[\frac{\phi D_{Me}}{(\phi+D)(\phi+1)} \right] \ln \left[\frac{1}{1-F} \right] \quad (2.5.1.)$$

where a is the specific area (interfacial area A divided by the total volume V), k_1 is the forward ($A \rightarrow O$) rate constant, D_{Me} is the bulk equilibrium O/A distribution coefficient, ϕ is the A/O phase ratio and F the fractional approach to equilibrium $(C_{init} - C_t)/(C_{init} - C_{eq})$. When data are derived from continuous instead of batch extraction,

SOLUTE	MEDIUM	EXTRACTANT	DILUENT	EQUILIBRATION TIME	REF
Co (II)	chloride	TOA	benzene	<1 min	116
Cu (II)	"	TOA	"	"	117
Fe (III)	sulfate	DDA	"	"	118
Pa (V)	chloride	Aliquat 336	xylene	"	119
Lan (III)	nitrate	PrJM-T	kerosene	"	120
"	"	LA-2	"	"	120
"	"	TOA	"	"	120
Th, Pa (V), U (VI)	"	LA-1	"	"	121
"	sulfate	"	"	"	121
"	chloride	"	"	"	121
U (VI)	sulfate	DDA	benzene	"	122
U (VI), Pu (IV)	nitrate	Alamine 336	Solvesso 100	"	123
"	chloride	TIOA	xylene	<30 sec	124
"	acetate	"	"	"	125
"	nitrate	LA-1	cyclo- hexane	"	126
Act (III)	thio- cyanates	Aliquat 336	xylene	<15 sec	127
Zn (II)	chloride	DEHA	"	"	128
Cu (II)	"	"	"	<10 sec	128

TABLE 2.5.1. Equilibration times for some Amine Systems
(Shaking Tests)

equation 2.5.1. is modified to

$$ak_1 = \frac{1}{t} \left[\frac{\phi D_{Me}}{(\phi+D)(\phi+1)} \right] \left[\frac{F}{1-F} \right] \quad (2.5.2.)$$

where ϕ is now the flow ratio Q_A/Q_O .

Fomin's equation¹³⁰ for determination of the rate constant and reaction order becomes similar to equation (2.5.1.) after some mathematical manipulations. This equation was derived for a system where a slow homogeneous reaction in the bulk aqueous phase is the rate controlling step.

Rate control by homogeneous aqueous-phase reaction is not unlikely with some extractants, reactions and conditions used in analytical chemistry and in physicochemical investigations. However, for metal process extractions of any commercial application, diffusion, mixed or chemical reaction control at the interface is much more likely, because of the extremely low aqueous solubility of practicable extractants. Danesi and Chiarizia¹³¹ found that the solubility in the aqueous phase of TLAHCl (in toluene) was about 10^{-6} M. This is usually considered the order of magnitude of the solubility of high molecular weight amines in aqueous solutions. Flett¹³² studied the feasibility of a mechanism where homogeneous aqueous phase reaction was the rate controlling step, in view of the very low aqueous solubility of commercial metal extractants, which is necessary to prevent their loss in the extraction circuits. The homogeneous route was ruled out because it implies unrealistic rate constants when the low solubility of the extractants is taken into account. The interfacial nature of amine extraction has been confirmed in studies^{133,134} where the rate has been shown to be directly proportional to the specific interfacial area (A/V).

It is well established that amine extractants are strongly surface active and several studies^{133,135,136,137,138} have shown that the amine salts are more surface active than either the metal-amine salt complexes or the free-base amines. The highly oriented dense layer of amine-salt at the interface probably imposes a special order for a small distance into each phase, causing locally different values of the physical properties and activity coefficients. Vandergrift et al.¹³⁷, studying the interfacial activity of quaternary ammonium salts, concluded that reaction occurred at the interface. They found also that the interface was saturated mainly with the monomeric species of the extractant.

Since almost all metal extractions by amines involve amine salts as the actual extractant and since some stripping methods utilize hydrolysis of the amine salts to free-base amines, acid extraction and stripping are of fundamental importance.

Danesi et al.¹³⁹ studied the extraction of HCl by TLA in toluene. For the situation where the interface was saturated with free-base TLA, they concluded that the rate control was by protonation of the interfacial TLA to TLAH^+ and in replacement of TLAHCl at the interface by new TLA, with the intervening reaction of Cl^- to form interfacial TLAHCl being fast.

Nakashio et al. studied the extraction of HCl by LA-2 in n-hexane using several techniques^{77,140,141}. They found that the rate control was by turbulent diffusion, mainly in the organic side of the interface, with the interfacial reaction being instantaneous at amine concentrations above 0.2 M and mixed control below that concentration.

Kataoka et al.^{76,142} also found control by diffusion with instantaneous interfacial reaction, in extraction of HCl by LA-2 in benzene.

Harada et al.¹⁴³ using Schlieren optics detected a reaction plane in the organic phase near the interface in the extraction of HCl by TOA in benzene.

In view of these results, including the fact that amine salts are more surface active than the free-base amines, the interface would be expected to become saturated with the salt soon after the start of the acid extraction. Then there would be two parallel paths for further salt formation: (i) the (unfavourable) displacement of salt by free-base molecules coming to the interface followed by direct protonation, vs (ii) association of additional acid with the interface salt to be carried in that form to the bulk free base. Since the sorbed salt must be oriented with the anion toward the aqueous phase, hydrolysis of amine salt at the interface in stripping of acid should be straight-forward and rapid and the free-base molecules formed are readily displaced by amine salt coming from the bulk organic phase.

Chiarizia and Danesi¹³³ studied the kinetics of Iron(III) chloride extraction by TLA. The effect of stirring speed of the phases, specific interfacial area and chemical composition of the system were examined. Benzene and toluene were used as diluents. Tests were run at a plateau in the stirring rate where chemical reaction control occurred. The initial rates in both directions of transfer were first order with respect to the iron concentration; the forward rate was directly proportional to the specific area of the interface; the diluents benzene and toluene (which induce different aggregation behaviour of TLAHCl) gave similar results. Comparison of the initial forward rates at different HCl concentrations with the corresponding aqueous iron species indicated that the neutral complex FeCl_3 was the kinetically reactive aqueous iron species. A rate equation was derived and the rate constants of the

interfacial reactions evaluated. The proposed mechanism assumed that rate control was by reaction of (probably) FeCl_3 with interfacial TLAHCl monomers, followed by reaction with further TLAHCl (monomers and polymers) during transfer into the bulk organic phase, with the interfacial iron complex at steady state. With fitted constants, the rate equation accounted for the experimental distribution coefficients and extraction curves, which indicated that the mechanism was unchanged to equilibrium.

Chiarizia et al.¹⁴⁴ examined the kinetics of Pu(IV) transfer in both directions between HNO_3 and TLA in *o*-xylene in a study very similar to their studies with iron (III) chloride¹³³. Preliminary tests established that the stirring speed was in the plateau region and that the initial rates in both directions were first order with respect to the plutonium concentration. Based on their previous study¹³³, control by interfacial reaction was assumed. They concluded that the reactions steps were (i) interaction of aqueous plutonium, $\text{Pu(NO}_3)_4$ or another species proportional to its concentration, with the interfacial TLAHNO_3 monomer and (ii) removal of the plutonium complex from the interface by reaction with more of the extractant (monomer or polymer), with the interfacial Pu complex remaining at steady state. This model, with fitted values of the constants, accounted closely for the experimental distribution coefficients and for the experimental extraction curves, which indicated that the mechanism was unchanged as the extraction progressed to equilibrium.

Fomin and Leman¹⁴⁵ studied the kinetics of Pu(IV) extraction from HNO_3 solutions by TOA in decane-octanol diluent. They reported that control was initially by interfacial reaction in the tests that had low interfacial area or low TOA concentration, and initially by diffusion in the other tests, but that all the tests shifted eventually to control by homogeneous bulk reaction as the

aqueous plutonium concentration decreased. This implies that all interaction between TOA nitrate and plutonium nitrate occurred in the aqueous phase and also that when control was by interfacial reaction, the slow step was not the transfer of plutonium to the organic phase but the transfer of TOA nitrate to the aqueous phase. These results contradict the study of Chiarizia *et al.*¹⁴⁴. It seems unlikely that a high molecular weight amine salt could be extracted into and dispersed through an aqueous phase to associate homogeneously with plutonium nitrate more readily than the plutonium nitrate could move to the interface and associate with the amine salt densely sorbed there. The initial levels of Pu_{aq} reported by Fomin and Leman were in the range $10^{-6} - 10^{-5}$ M. Such extremely low concentration levels might account for the discrepancies between these studies.

Inoue *et al.*¹³⁴ studied the extraction kinetics of zinc chloride with Amberlite LA-2 in n-hexane by the single drop technique. The extraction rate mechanism was explained by the Handlos-Baron model. The effect of extractant, zinc and chloride concentrations were investigated. They found that extraction rates were first order with respect to zinc concentration and not influenced by the extractant and chloride concentrations in the range of chemical composition studied. The proposed mechanism assumes that the neutral species ZnCl_2 is extracted and that the interfacial reaction involves the dimeric species of the extractant. No experimental evidence, based on the kinetics of the system, was shown to support these assumptions. Apparently, all the conclusions were based on the stoichiometry of the overall reaction which was derived from equilibrium studies¹⁴⁶. It is very dangerous to infer mechanistic assumptions based on the overall reaction as this is not the case in many situations.

Fuersternau et al.¹⁴⁷ investigated the kinetics of extraction of Copper(II) chloride by Aliquat 336 in xylene. The effect of extractant, copper and chloride concentrations, as well as stirring speed and temperature, were studied. They found that extraction rates were first order with respect to extractant and copper concentrations. They concluded that the anionic species CuCl_4^{-2} was the extractable one and the apparent activation energy was essentially zero. The proposed model assumed equilibrium at the interface, which was not the case, as the rate controlling step was supposed to be interfacial chemical reaction (the experiments were carried out in the plateau region). The rate equation does not fit the experimental data particularly well. It appears that the assumption that the neutral species CuCl_2 was the extractable species, would lead to a better fitting. The apparent activation energy calculated contradicts most of the results found in the literature for interfacial reactions^{46,59,148,149,150}. It seems very unlikely that the activation energy of the reaction - which is the rate controlling step - will be essentially zero.

Davey et al.^{72,73,151} studied the kinetics of the transfer of Niobium(V) from chloride solutions by BTHAHCl in chloroform, carbon tetrachloride and benzene, using the single drop method. A first order dependence of the rate on both the metal and stoichiometric concentration of extractant was observed for the extraction, while the stripping rate was found to be independent of chloride concentration and first order with respect to metal concentration. The proposed mechanism involves an interfacial chemical reaction between monomeric BTHAHCl and anionic species NbCl_6^{-} as the rate controlling step. The data provided estimates of the equilibrium constants for the process transfer.

Allen¹⁵² investigated the kinetics of uranyl sulphate extraction by TOAS in benzene. The organic phases were essentially identical (TOAS 0.1 M + 12% excess H_2SO_4). The aqueous phases were made of a series of H_2SO_4 - Na_2SO_4 solutions to give different concentrations of UO_2^{2+} , UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$. The complex $\text{UO}_2(\text{SO}_4)_3^{4-}$ was essentially zero in all cases. The results showed that the extraction was in the regime of control by diffusion and the rate was first order with respect to maximum concentration, and they also suggested that the controlling diffusion was principally or entirely on the aqueous side of the interface. As the concentration of sulfate ion was increased, the rate constant decreased in close parallel to the decreasing UO_2^{2+} concentration, in contrast to the patterns of the UO_2SO_4 and $\text{UO}_2(\text{SO}_4)_2^{2-}$ concentrations, showing qualitatively that the uncomplexed uranyl ion was much more effective, mole for mole, than either of the complexes in transporting uranium to the interface. On the assumption that first-order rate constants for the individual species should combine linearly to give the observed total rate constant, graphic analysis gave values of the individual constants that were in ratios of about 6:1:1 for the uranyl ion, the monosulfate and the disulfate complexes respectively. In combination with the changing proportions of the three species, these reproduced the observed rates fairly well.

McDowell and Coleman¹³⁶ studied the kinetics of uranium sulphate extraction by DDAS in benzene. They combined interfacial-tension measurements with stirred cell kinetics using radioactive labelled sulphur (S^{35}) to obtain more explicit details of the uranium transfer mechanism. A primary objective of the extraction kinetic study was to distinguish between true anion exchange and true neutral-species transfer. The extractant (DDAS) in benzene, exists in the bulk solution

as loosely bonded aggregates of about 40, while the extracted uranium species are monomeric. The interfacial tension study showed that $(R_2NH_2)_2SO_4$ is strongly surface active (necessarily de-aggregated at the interface), the bisulfate $R_2NH_2 HSO_4$ is slightly less surface active, the free base R_2NH is only weakly surface active and the extracted uranium species, mainly $(R_2NH_2)_6(SO_4)_4UO_2$, are intermediate. The interfacial tension rises somewhat above the low DDAS value when uranium loading is nearly complete, but only when it is nearly complete, indicating that the uranium species move away from the interface as long as a significant amount of uncomplexed DDAS is available to cover the interface. The resulting model of the extraction is that the kinetically active uranyl species interacts with the interface amine sulfate to form a uranyl sulfate species. Being less surface active than the amine sulfate, this is readily displaced from the interface and travels into the bulk organic phase, associating with further amine sulfate to form the final $(R_2NH_2)_6UO_2(SO_4)_4$. The kinetic study was in the region of mass transfer or mixed control. A model was developed to correct for the self-diffusion of S^{35} . It was found that the uranyl extraction proceeded through a neutral transfer at low sulfate concentration and anionic exchange at high sulfate concentration, with probably some bias toward anion exchange. The contribution of McDowell and Coleman was very significant for the understanding of the mechanism of amine extraction, as they introduced a method of investigation, more or less "in situ", of the nature of the extractable species. Large experimental errors were involved (up to 70%), probably due to the lack of keeping constant the hydrodynamics of the stirred cell (the equipment used was extremely simple), so that the range of their conclusions were limited.

Winfield¹⁵³ studied the kinetics of Cobalt (II) chloride extraction by TOAHCl in benzene. The approach was very similar to the one used by McDowell and Coleman¹³⁶. Radioactive labelled chlorine (Cl^{36}) was used instead. The suggested mechanism of extraction involves the anionic species CoCl_3^- . The large scatter of the experimental results was possibly due to the lack of keeping constant the hydrodynamic conditions (the stirred cell used was very simple; no baffles, not good stirring control, etc.). The chemical composition of the studied system was perhaps not adequate for this type of study (the extraction curves for chlorine tracer (Cl^{36}) - with and without cobalt were very close, so there was no clear differentiation of the extraction process). Another possible reason for the lack of reliable results was due to the analysis of the chlorine tracer, as the colour quenching problem was not investigated, which can have a significant effect in the analysis. Most probably, cobalt chloride may not be suitable for this type of investigation, because of the high chloride concentrations necessary to produce neutral and anionic species and the high activity of chlorine tracer, associated with the experimental method, necessary to produce a reasonable count rate, when the samples are analysed, and the lack of information and reliability regarding the stability constants of the cobalt chlorocomplexes.

Although no mass transfer transfer problems have been reported concerning extraction by amines, there have been reports of slow stripping.

Ryon et al.¹⁵⁴ studied the stripping of $\text{U}(\text{NO}_3)_4$ in LA-2 in a mixed aromatic-aliphatic diluent by HNO_3 . According to the known distribution coefficients, this uranium should have stripped readily, but it did not. The problem was overcome by using a mixture of HNO_3 and

acetic acid. Apparently, the extracted uranium had been hydrolysed to colloidal UO_2 , which was dispersed in the organic diluent, but was not surface active, nor significantly associated with labile amine species. The HNO_3 was entirely associated with the amine and did not make contact with the dispersed UO_2 . The acetic acid, while mainly associated with the amine, was also sufficiently soluble in the hydrocarbon diluent to reach the UO_2 and bring it back into equilibrium with the acid solution.

The extractability of Pu (IV) nitrate by tertiary amines is so high even at low nitrate concentrations that water stripping is not feasible, at least from amines at the concentrations ordinarily used. Reducing and/or complexing agents are used to facilitate stripping and even with these the stripping may be slow.

Chesne et al.¹⁵⁵ reported direct comparison of the rates of plutonium extraction from 2 M HNO_3 and stripping into 0.5 M H_2SO_4 with 0.32 M TLA in dodecane. The contact time necessary to reach equilibrium is about 2 minutes for extraction and 5 minutes for stripping. They considered this extraction and stripping rate fast enough for mixer-settler operation, with the implication that it could cause trouble in some other types of contactors.

Other investigators have reported slow stripping rates; Gourisse and Battelier¹⁵⁶ on the stripping of plutonium nitrate from TLA; Shmidt et al.¹⁵⁷ on the purification of Np (IV); Cao et al.¹⁵⁸ on plutonium stripping from Alamine 336 in Solvesso 100.

To conclude this section it must be said that there is no reported case of slow rates during amine

extraction, although some cases of slow kinetics for the stripping have been found. The kinetic studies have been directed towards the mechanism of extraction. No further experimental evidence was found in the literature to support Allen's conclusion¹⁵² that amines are cationic extractant (as well as, neutral and anionic). It is possible that this sort of conclusion was reached by not using the right set of stability constants of complexes, or because those are not reliable and may give just a rough estimate of the distribution of the complexes. The controversy whether amines are neutral or anionic extractants continues, although the work by McDowell and Coleman¹³⁶ brought some light to this matter, but due to a large experimental error no far reaching conclusion was possible. Apparently, amine extraction occurs via a neutral or anionic transfer, most probably both, depending on the availability of both species.

CHAPTER III

THE PHYSICAL CHEMISTRY OF THE BIPHASIC SYSTEM

TOAHCl IN TOLUENE/IRON (III) CHLORIDE-HCl

(LiCl) IN WATER

The literature published during the past two decades on the extraction of metals by amines is very extensive. Several reviews have appeared periodically on the use of these extraction systems¹⁶¹⁻¹⁶⁸.

Comprehensive reviews of the work up to 1968 are given by Marcus and Kertes¹⁶⁹ and up to 1971 by Shmidt¹⁷⁰. Another excellent review has been published recently by Rao and Sastri¹⁷¹ including work up to 1979. A comprehensive list of amines and quaternary ammonium compounds available commercially and their manufacturers is presented, as well as extraction details of many amine systems. Commercial applications of amine systems are discussed by Ritcey and Ashbook¹⁷².

The kinetics of amine systems have been studied in attempts to understand the mechanism of reactions involved in the process. Little work has been done specifically on process kinetics because it is generally found that amines are fast extractants. Fundamental studies of extraction kinetics have examined the effects of a number of variables and some rate law expressions for the chemical reactions involved have been proposed. It has now been accepted that the reaction takes place at the interface. This is an important consideration in the formulation of a model. Some studies have considered the nature of the extracted metal species. Both neutral or anionic transfer have been considered as possible, but no clear conclusion has been reached so far and the subject is still an

open question. This matter is of paramount importance in some physicochemical investigations, i.e., determination of the stability constants of metal complexes¹⁷³, using data from amine extraction. It is usually assumed that one species is the extractable one. The results obtained would be useless if wrong assumptions are introduced, as to date there is no sure way to be certain of the nature of the transferred species.

The purpose of this experimental work is to study the extraction mechanism by amines. This is best achieved by investigating the variation of the mass transfer rates under appropriate conditions. Experiments and equipment must therefore be designed in such a way as to give accurate and reproducible values of this parameter. The choice and design of suitable equipment is presented in Chapter IV. A suitable amine-diluent-metal-ligand system must be selected in order to fully characterize the kinetics and mechanism of the process.

Experience has shown that for practical solvent extraction applications, an amine has to fulfil certain basic requirements, such as compatibility with a practical diluent, sufficient extraction power, rapid phase separation, low aqueous solubility and sufficient chemical stability. A practical diluent has to be cheap, with negligible losses and should have good solubility for extractants and their various compounds.

3.1. CHOICE OF SYSTEM

Previous work carried out in the Hydrometallurgy Group at the Royal School of Mines involving metal extraction by amines, have used tri-n-octylamine (in short, TOA, or its chloride salt, TOAHCl) as the

extractant. The advantages of using TOA are that it is available commercially with a reasonable degree of purity, or alternatively it can be purified fairly easily (as this condition is extremely important in fundamental studies), as well as the fact that it is used in a number of industrial processes (which give some practical significance to the studies). Although all these works have been under equilibrium conditions, a good amount of information and experience has been accumulated regarding the chemistry of amine extraction, which makes TOA suitable for this study.

The diluent should be easily available in a pure grade and be non-toxic, as well as practically immiscible in the aqueous phase and with a good capacity to dissolve the amine. Third phase formation, very common in some amine systems, should be avoided, as it would cause an unnecessary complication - the effect of the modifier would have to be introduced. Toluene is considered as a suitable diluent for TOA, satisfying all these requirements.

The metal and ligand ions to be extracted should have their chemistry in aqueous solutions well established and fully known. The metal ions should be also practically unextractable by the pure diluent and the chemical analysis should be easy to perform accurately in a simple manner, giving continuous readings of concentration as a function of time of extraction (or alternatively using small samples of solution). The system should also have relatively high extraction rates at reasonably low ligand concentrations so that it would be highly sensitive to changes in the hydrodynamics in the interfacial region and to chemical composition, therefore the interfacial phenomena could be examined in detail. For practical reasons, it would be also desirable to work with a common metal. A number of

systems were considered, none of them satisfying all these requirements. For example, mercury (II) chloride could be considered the ideal system, but it is very toxic and difficult to dispose of in large quantities and its chemical analysis is not easy to perform in a continuous basis, since the mercury-amine complex is colourless. Zinc, cadmium and antimony chloride-amine complexes are also colourless and therefore cannot be analysed by spectrophotometry. An electrochemical method of analysis, as used by Danesi *et al.*⁸¹ could be possible, but there was little room in the designed equipment for the special electrodes necessary.

Copper (II) and cobalt (II) chloride form strong coloured complexes with TOAHCl, but require high chloride concentrations in order to reach maximum extraction levels. Ferric chloride forms a coloured complex with TOAHCl and requires relatively low chloride concentrations to give high extraction levels and although not the ideal, could be considered suitable for the purpose of this study. Some complications would arise at low chloride concentrations because many aqueous complexes would be present, but this could be avoided by working at moderate concentrations. There is some information regarding the stability constants of iron (III) chlorocomplexes. The chemical analysis can be performed easily and continuously using a spectrophotometric method in either the aqueous or the organic phase. Another complication would arise if the support electrolyte (ligand) was HCl, as above a concentration of 3.5 M, there would be a competition reaction between HCl and iron extraction. This problem can be avoided using HCl concentrations below that limit and lithium chloride (or another chloride such as CaCl_2 , NaCl, etc.), as the support electrolyte is not extracted by TOAHCl¹¹⁶. Lithium chloride has also the advantage that its activity coefficients are very close to the activity coefficients

of HCl, so major corrections of this parameter are usually not necessary. The use of chloride solutions have the inconvenience of being highly corrosive, requiring the use of glass and PTFE materials for the construction of the parts of the equipment in contact with them.

The extraction of iron (III) chloride by TOAHCl in toluene has been selected for experimental study not on account of its industrial importance amongst amine systems, but rather to test the relevant models and to measure various parameters which make it suitable for the systematic study of the mechanism of amine extraction.

3.2. THE NATURE AND PROPERTIES OF THE AMINE

The extraction by high molecular weight amines is considered to take place by the formation of an amine salt. This amine salt is the actual extractant. Then, before metal extraction, the amine is converted to the amine salt by the reaction



where the bars denote organic phase species.

Several methods have been used to prepare the amine salt. Dissolution of the amine in benzene or petroleum ether and bubbling hydrogen chloride through the solution, followed by several recrystallization cycles from organic solvent mixtures, leave an anhydrous and non-hygroscopic white waxy substance^{174,175,176}. Neutralization of an alcoholic solution of the amine with aqueous hydrochloric acid¹⁷⁷ and subsequent recrystallization from alcohol or acetone is an

alternative method. A very efficient method, giving a higher yield, used the equilibration of the amine in petroleum ether solution with aqueous hydrochloric acid¹⁷⁸. Several recrystallization cycles are needed to obtain the pure compound. If the amine is already reasonably pure, the amine salt can be prepared easily by bringing an excess of diluted aqueous hydrochloric acid (0.2-1.0 M) into contact with a diluent solution of the amine¹⁷⁹.

Bertocci and Rolandi¹⁸⁰ studied the extraction of HCl by TOA in benzene at equilibrium conditions. They found that the ratio TOA/HCl in the organic phase was always about one, provided that the aqueous acid concentration was below 3.5 M. Above that value the amine extracted excess acid and the ratio TOA/HCl was bigger than one. The amine concentration had no significant effect on that ratio, in the range of concentrations studied (0.0095-0.5 M).

Several values have been reported for the equilibrium constant of TOA-HCl in toluene: $\log K_{HA} = 3.80$ ¹⁸¹, 4.00 ¹⁸² and 4.87 ¹⁸³. In all cases, the extracted compound was TOAHCl.

Aggregation of amine salts, which occurs when they are dissolved in organic diluents, is an interesting feature of amine extraction systems and frequently affects the metal extraction considerably. The properties of the diluent, the nature of the ammonium cation and anion, and their concentrations, determine whether the salt is dissociated, ion paired, or highly aggregated in the organic phase. Aggregation into dimers is a general phenomenon and it is generally attributed to ion-quadruple formation, which reduces the polarity of the monomeric ion-pairs of the amine salt. Aggregation into polymers higher than the dimer is

observed in most amine salt-diluent systems as the concentration is increased. Amine nitrates appear to form trimers quite readily in many diluents, whereas for most other amine salts, dimer formation appears to be the basic unit from which higher aggregates are formed¹¹⁶. Coleman *et al.*¹⁸⁵ suggested that the amine salts may interact among themselves or with the solvent in the organic phase through hydrogen bonding, leading to the formation of colloidal aggregates and resulting in constant activity for the amine salts. Interfacial tension measurements made by McDowell and Coleman¹⁸⁵ and Orlandini *et al.*¹⁸⁶ also point strongly to the possible formation of aggregates containing as many as 40 monomers.

The experimental techniques that have been used to study aggregation include vapour pressure osmometry, light-scattering measurements, cryoscopy, two-phase e.m.f. titrations, and distribution measurements. Marcus and Kertes¹⁶⁹, Shmidt¹⁷⁰ and Monhemius¹¹⁶ reviewed the experimental work on aggregation of amine chlorides and this will not be repeated here.

The extent of aggregation of the amine salt is mainly responsible for the lack of knowledge on the variation of the activity coefficients of the organic phase, making it very difficult to provide a quantitative description of the distribution equilibria. Qualitatively, it may therefore be stated that if the extractant is largely associated to a q-mer, the concentration of the monomer ($R^+ A^-$) is proportional to $C_R^{1/q}$ and if q is large, ($R^+ A^-$) varies very little for large variations of C_R ¹⁷⁹. On the other hand, if the aggregates are open structured, so that the ion-pair end of the long chain amine is mobile, relatively independent of its neighbour, the amine phase resembles an anion exchange resin with variable capacity. However, even in such systems, aggregation has been experimentally indicated¹⁸⁷.

The existence of polynuclear species in amine salts in various diluents has been established by several investigators. Danesi et al.¹⁸⁸ attempted to give a semi-quantitative explanation for the slope analysis in terms of the polynuclear species formation equilibria in the aqueous or organic phase for the system $\text{ZnCl}_2 - \text{LiCl} - \text{TLAHC1}$.

Aggregation of the metal amine complexes is even more difficult to explain quantitatively, but is less likely than the aggregation of the simple salts, since aggregation occurs normally when one ion pair is large and the other small. In any case, this can be neglected at trace metal concentrations.

The extraction of metal complexes by amine extraction systems depends mainly on the extent of aggregation of both the extractant and the metal complexes and also on the concentration of the free amine salt. These factors need to be carefully considered in order to draw definite conclusions about the mechanism of extraction with the amine system.

The activity coefficients of amines have been reported in different ways. Kertes¹⁷⁶ determined the solubility of TOAHC1 in various organic solvents (including toluene). The solubility parameter of the amine hydrochloride was evaluated and used to calculate its activity coefficients. The activity coefficient equation used refers to the standard state of monomeric solutes. It is assumed that any non-ideality is included in the derived activity function and that, as evaluated, it refers to an arbitrary species existing in solution. The deviation from ideal behaviour of the systems is explained as being due not only to aggregation of the solute molecules, but also to the non-specific non-ideality of the monomeric species. It was found that

below 0.01 M, TOAHCl in toluene exists mainly as a monomeric species. Sato and Kato¹⁷³ determined the activity coefficient of TOAHCl in benzene using a vapour pressure method. A thermodynamic relationship was used to calculate the activity coefficient in a manner similar to Kertes¹⁷⁶. Monhemius¹¹⁶ studied the aggregation of TOAHCl in benzene using vapour pressure osmometry. The results were expressed in terms of a dimerisation constant. The basic assumption was that the non-ideal behaviour was due to aggregation. All the various species in solution were assumed to behave ideally. This simplifying assumption may be questionable, but it explained satisfactorily the experimental results up to approximately 0.1 M TOAHCl.

No reported value for the aggregation constant of TOAHCl in toluene was found in the literature. Some values for TOAHCl in benzene and TLAHCl in benzene and toluene are given in Table 3.2.1. These values may give an idea about the expected values for TOAHCl in toluene (which are presented in Appendix B).

Amine salt	Diluent	$\log K_2$	T (°C)	Reference
TOAHCl	benzene	1.11	25	189
"	"	1.39	32.5	116
"	"	0.91	37	117
TLAHCl	"	1.72	25	186
"	"	1.3	"	190
"	"	1.27	"	179
"	"	1.70	"	191
"	"	1.48	37	191
"	"	1.65	"	131
"	Toluene	1.75	25	131

TABLE 3.2.1. Dimerisation constant (K_2) of TOAHCl and TLAHCl.

3.3. EXTRACTION OF WATER

The extraction of water does not seem to greatly affect the extractive capacity of amine salts. The extraction of water by amine salts qualitatively obeys many relationships which are typical of extractions by an addition mechanism. It is probable that the extraction of water is due to the formation of hydrogen bonds with the anions of the amine salt.

Monhemius¹¹⁶ found that TOA in benzene is essentially unhydrated. TOAHCl, when formed by equilibration of TOA solution with diluted HCl, extracted considerable amounts of water and a ratio $\frac{[\text{TOAHCl}]}{[\text{H}_2\text{O}]}$ of about 1 was found. Similar results were obtained by Bertocci and Rolandi¹⁸⁰ with TOAHCl dissolved in xylene and by Muller and Diamond¹⁹⁰ for TLAHCl in benzene. Although amine hydrochlorides may be monohydrated when in equilibrium with dilute aqueous solutions, where the water activity is close to unity, Frolov *et al.*¹⁹² have shown that the degree of hydration varies with the water activity of the equilibrium aqueous phase. They derived an equation that expressed the solubility of water in solutions of TOAHCl in toluene as a function of salt concentrations and activities of water. The equation also gave a good fit for other amine salts in a variety of diluents.

Gardener and McKay¹⁹³ derived an expression that described the dependence between organic phase, water and metal concentrations.

Fomin¹⁹⁴ examined the effect of water activity in solvent extraction processes. An equation is given for the hydration number as a function of metal and ligand concentrations, and the activities of the extractant, the salt in the aqueous phase (mean activity), .

the salt in the organic phase and water in the aqueous phase. According to Fomin's equation, the concentration of metal in the organic phase must decrease with decreasing water activity in the aqueous phase if the activity coefficient of the ligand and the activity coefficient of the organic complex remain constant.

Variations of concentrations and activities in the aqueous phase change the activity of water. Different salting-out agents would have different degrees of hydration. Biray¹¹⁷ studied the effect of water extraction during copper (II) chloride extraction by TOAHCl in benzene from HCl, LiCl and CaCl₂ solutions. It was found that at equal initial concentrations of chloride and metal, different contents of water were extracted. The results showed a maximum of water extraction when the aqueous chloride concentration was 3 M for LiCl and NaCl, and 4 M for HCl. This corresponds roughly to the point at the beginning of the plateau of maximum extraction of copper. It is suggested that at high metal concentrations of the aqueous phase, water is not taking part in the extraction process. Monhemius¹¹⁶ found that TOAHCl solutions in benzene, fully loaded with cobalt (II) chloride, were essentially unhydrated. The lack of data about activity coefficients and the lack of reliable data for the stability constants of chlorocomplexes and the lack of knowledge of which complexes take part in the extraction process do not allow a more complete analysis of the results.

It is possible that hydration in the organic phase depends on the changes in the activities and the types of extractable ions in the aqueous phase when the amine concentration in the organic phase is kept constant. If that happens, a kinetic study of water extraction during metal extraction might throw some "light" on the mechanism of the extraction process. So far, this approach has not yet been attempted.

In spite of the rather complex behaviour of water in amine chloride systems, it is generally agreed that the presence of water in the organic phase has very little effect on the aggregation of the amine salts, or on the extraction process itself. The relationship governing the extraction of water with amine salts during metal extractions have not yet been studied in sufficient detail, and the question has not been adequately clarified, probably owing to the fact that its practical significance is small.

3.4. EXTRACTION EQUILIBRIA

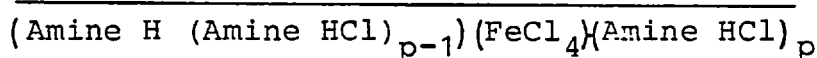
It is known that Fe (III) is readily extracted by amines from chloride solutions and the extraction is appreciable even at relatively low chloride concentrations.

The stoichiometry of the extraction of Fe(III) by amines from HCl solutions was first studied by the spectrophotometric method¹⁹⁵. The absorption spectrum of the organic phase showed that the extracted amine - Fe(III) compound contained $(\text{FeCl}_4)^-$ anions. This has been confirmed by a number of investigators¹⁹⁶⁻¹⁹⁸. Loading experiments have shown that solutions of amines in many diluents gave the ratio $(\text{Amine}) / (\text{Fe(III)}) \approx 1$, that led to the conclusion that Fe(III) is extracted by amine hydrochlorides in the form of compounds of the type $(\text{Amine H})^+ \text{FeCl}_4^-$. However, it was found that the slope of the plot of $\log D_{\text{Fe}}$ versus $\log (\text{Amine HCl})$ was linear, being about 2 for benzene, toluene, cyclohexane, chloroform and carbon tetrachloride and 1 for nitrobenzene¹⁷⁰. At first, it was thought that this second power dependence could be explained by assuming that $(\text{FeCl}_5)^{2-}$ was involved in the organic phase, but no experimental evidence was ever found to support this assumption. The other alternative was to assume that

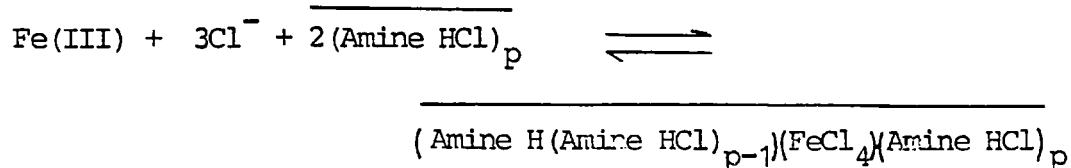
the organic phase contained $\text{Amine H}^+ (\text{FeCl}_4)^-$.

Amine HCl . In this case, the amine would be associated with the iron complex either as dipole-dipole head-to-tail association of $\text{Amine H}^+ \text{Cl}^-$ with $\text{Amine H}^+ \text{FeCl}_4^-$, or as having two Amine H^+ cations hydrogen bonded to one iron chloride anion. The existence of the $\text{Amine H}^+ (\text{FeCl}_4)^-$ Amine HCl compound has been confirmed using Raman spectroscopy by Michel *et al.*¹⁹⁹. They showed that at low iron (III) organic concentrations in equilibrium with the aqueous phase, $\text{Amine H}^+ (\text{FeCl}_4)^-$ Amine HCl is the compound formed, whereas at saturation, $\text{Amine H}^+ (\text{FeCl}_4)^-$ is formed. This explains the difference between saturation and distribution experiments (here trace concentrations are normally used).

The extraction mechanism of iron (III) chloride is very complex and so far no generalized conclusion has been reached. However, it is known¹⁷⁰ that if the diluent is of low polarity and is unable to solvate the anion of the extracted compound, the latter can be solvated only by the amine salt associates which are present in solution, with formation of compounds of the type



The addition of the second associate $(\text{Amine HCl})_p$ does not affect the inner sphere of the iron (III) complex and represents a solvation. Nevertheless, the associates $(\text{Amine HCl})_p$ are expended in the formation of the extracted compound by the reaction



The dependence of the distribution coefficient (D_{Fe}) on the chloride concentration of the aqueous phase has been found to be not simple. The curves $\log D_{Fe} \times \log [Cl^-]$ have a slope of about 3 at low chloride concentrations, decreasing steadily at higher concentrations, being 0 at about 8 M HCl (and further to a negative value at higher HCl concentrations), but being not negative in HCl-LiCl solutions. This behaviour can be explained when the aqueous phase species Fe^{3+} , $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$, $FeCl_4^-$ are considered to be formed consecutively as the HCl concentration is increased. However, if the values of the stability constants, that have been used successfully to account for TBP extraction and for anion exchange distribution, are employed¹⁶⁹, the D_{Fe} curve for a given amine concentration cannot be reproduced. Moreover, the $\log D_{Fe}$ versus $\log [Cl^-]$ curves for different amine concentrations are not parallel¹⁷³, as they should be, so that the distribution data cannot be used to give a definite set of stability data. The dependence of D_{Fe} on amine concentration is also not regular, since it can vary from about second power to first power as the amine concentration is increased, contrary to expectation. This may be connected with the aggregation of the amine salt and iron (III)-amine complexes, but this should then be rather independent of chloride concentration, but it is not.

The distribution coefficients were found to be independent of iron (III) concentration up to a loading as high as 10% and independent of acidity at constant chloride concentration in (H, Li)Cl solutions up to 9 M¹⁶⁹.

Another common phenomenon in some amine extraction systems is the extraction of excess acid (the amount of acid after neutralization of the amine). The excess acid

dissolution in the organic phase is due to the solvation by the acid of the anion extracted by the amine in a manner similar to water solvation. The ease of solvation of anions by molecules of acid varies with the diluent in the same manner as hydration of the anion itself. The possibility of competitive extraction between the excess acid and the metal has to be considered when these acid systems are used for the extraction of metal complexes unless the acid concentration is kept below the point where excess acid extraction can happen. For TOAHCl in toluene excess acid extraction occurs above 3.5 M HCl, regardless of the amine concentration¹⁸⁰.

The literature about amine extraction equilibria is extensive and no attempt is made to review all the available literature as this can be found elsewhere¹⁶⁹⁻¹⁷¹. Only a few investigations relevant to this work will be cited briefly here.

Very little work involving specifically the extraction of iron (III) in chloride solutions by TOAHCl in toluene was found in the literature, but some systems very similar to this one have been studied extensively and they may give a good indication of the expected physicochemical behaviour of the system under study in this work. These systems include the extraction of iron (III) in chloride solutions by TOAHCl in benzene or TLAHCl in benzene or toluene.

In solvent extraction technology, the diluents occupy an important place in the economy of the process. The diluent used in the process has to be cheap, with negligible losses and should have good solubility for the extractants and their various compounds. The effect of diluents on the extraction of metals with amine systems has been studied by many workers.

Smulek and Siekierski²⁰⁰ studied the extraction of iron (III) from HCl solutions with a series of diluents. For the case of TOAHCl, the extraction coefficient (D_{Fe}) was high and about the same in benzene, toluene, o-xylene, chlorobenzene and o-dichlorobenzene media, about the same in n-heptane, n-octane and carbon tetrachloride, and low in chloroform. The effect of the diluent on the activities of the amine and the activity coefficients of the complex was found to vary linearly with dielectric constant and dipole momentum of the diluent. Toluene, benzene and o-xylene showed similar behaviour.

Juznic²⁰¹ studied the extraction of iron (III) from HCl solutions by TOAHCl in benzene. The effect of TOAHCl, HCl and iron (III) concentrations were studied. These results followed the trends described previously. Water extraction was also studied. It was found that TOAHCl in equilibrium with diluted HCl extracts water forming the compound $TOAHCl \cdot H_2O$. The water content of the organic phase decreased with increasing HCl concentration, being essentially unhydrated when iron (III) saturates the organic phase. Aggregation studies were also performed using ebulliometric measurements. It was found that at low iron (III) concentrations monomeric $TOAHFeCl_4$ is the main species and at high iron (III) concentrations $TOAHFeCl_4$ is formed with average aggregation number ($\bar{n}$) equal to 1.4 and independent of further increases in the organic iron (III) concentrations.

Bagreev et al.²⁰² studied the simultaneous extraction of micro- and macro amounts of several metals in HCl solutions by TOAHCl and Aliquat 336 in benzene. A decrease in the extraction of the microelements in the presence of extractable macroelements was shown to occur. Saturation experiments showed that the molar ratio

iron (III)/TOAHCl was 0.86, indicating that free amine was solvating the iron (III) organic complex and under these conditions the compound $(\text{TOAHFeCl}_4 \cdot 0.16\text{TOAHCl})_n$ was formed.

White *et al.*²⁰³ studied the extraction of iron (III) in chloride solutions by TOAHCl in benzene. Their results could be represented by the mathematical equation

$$D_{\text{Fe}} = 3200 \frac{(\text{Cl}^-)^3 (\text{TOAHCl})^2}{1 + 4.57 (\text{Cl}^-)} \quad (3.3.1.)$$

They claimed that "the investigation is the first to give positive evidence that the negatively charged FeCl_5^{2-} complexes are formed in the organic phase in the form of $(\text{TOAH})_2\text{FeCl}_5$ ". It is now known that this is not correct. The fact that the slope of $\log D$ versus $\log (\text{TOAHCl})$ is about 2 is because $\text{TOAHFeCl}_4 \cdot \text{TOAHCl}$ is formed instead of the compound mentioned above. Their results showed that the slope of $\log D_{\text{Fe}}$ versus $\log [\text{Cl}^-]$ is 3.0 when $(\text{Cl}^-) \rightarrow 0$ and about 2.0 at high (Cl^-) concentrations. It is known that this slope is 0.0 at HCl 8M, so that equation (3.3.1.) is not of general validity and at best it explains the experimental results only in the studied range of chemical compositions.

Nelson *et al.*²⁰⁴ studied the extraction of iron (III) in HCl solutions by TOAHCl in nitrobenzene. They found some rather complicated behaviour in this system and they pointed out that "it is not possible to draw meaningful conclusions about the composition of the extracted species from equilibrium extraction data alone."

The validity of slope analysis depends on the applicability of the law of mass action to the system under consideration. Since most metal extraction reactions

are reversible equilibria, the law of mass action will apply, providing the activities of the reactants and products are known or can be obtained. In many extraction systems, it is possible to avoid the difficulties of activity measurements by firstly, maintaining constant aqueous activity coefficients, and secondly, assuming ideal behaviour of solutes in the organic phase.

In amine extraction systems, only exceptionally can either of the above assumptions be used. Generally high anion concentration in the aqueous phase are required to bring about metal extraction. This makes impracticable the application of the constant ionic strength method. In the organic phase it is known that, in many diluents, amine salts behave non-ideally in that they aggregate to form polymeric species. This slope analysis in this type of system has to be applied with care.

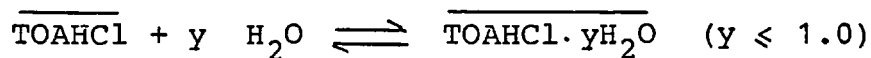
The use of slope analysis to establish reaction mechanisms in metal extraction systems was often used until some years ago and has been very criticized, but nowadays it is practically abandoned. The proper use of slope analysis in the case of extraction by amine salts has to take into account the non-ideal behaviour exhibited by these salts in many solvents. At best slope analysis will give the stoichiometry of the overall reaction.

Typical reactions of the system $\text{TOAHCl-Fe(III) - HCl(LiCl)}$ are presented in Table 3.4.1.

i) Acid extraction:

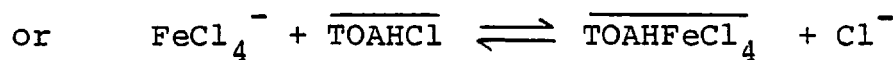
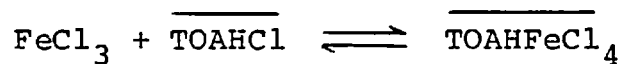


ii) Water extraction:



$$y = 1, \text{HCl} \rightarrow 0$$

iii) Iron (III) extraction:



at low Fe(III) concentrations:

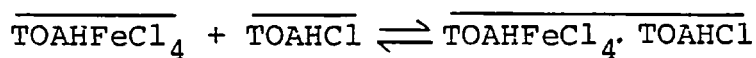


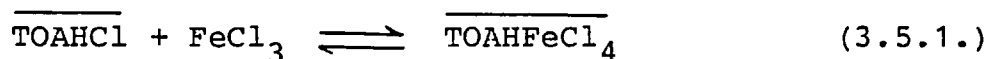
TABLE 3.4.1. Reactions of the system TOAHCl-Fe(III)-HCl(LiCl)

3.5. MECHANISM OF EXTRACTION

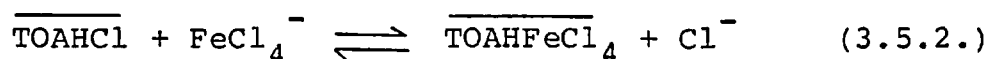
In amine extraction systems, the amine salt should be regarded as the extracting agent rather than the free base amine itself. In fact, most of the metal extractions are performed from acidic aqueous media, so that if the organic phase initially contains the free amine, it is first converted to its salt. Even if the amine salt is used in the initial organic phase, it is still necessary to keep the aqueous phase acidic to prevent the hydrolysis of the amine salt, with consequential liberation of the free amine. The amine salt can be reconverted to the free amine simply by shaking the organic phase with an aqueous solution of sodium hydroxide or sodium carbonate. This procedure is commonly followed for the recovery of metals from the organic phase. These limitations on the aqueous phase conditions do not apply when quaternary ammonium salts are used as extractants, which can be employed in neutral, slightly alkaline or acid solutions.

In accordance with Shmidt ¹⁷⁰ the mechanism of extraction by amine salts may involve addition, anion exchange or several simultaneous reactions of addition and anion exchange. So, for the system Fe(III)-Cl-TOAHCl the following reactions are possible:

(i) addition mechanism:



(ii) anionic transfer

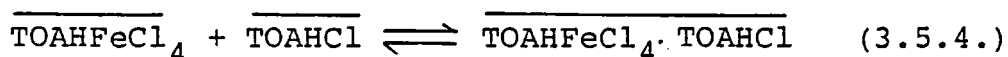


(iii) addition and anionic transfer:



where the minimum value of n is $n = 0$ and the maximum is $n = 4$. It is obvious that this mechanism (equation (3.5.3.)) would reduce to addition or anionic transfer at some stage of the reaction, or it would require a third or fourth order reaction, which is not likely, as this type of reaction is very rare or non-existent. So, the most probable mechanisms for iron (III) extraction would involve addition and/or anionic transfer.

As has been discussed before, at low organic Fe(III) concentrations, the amine salt would solvate the extracted Fe(III) - TOAHCl complex. In this case a second reaction would happen in the organic phase



Since reactions (3.5.1.) and (3.5.2.) yield the same reaction product, while the metal compounds in the aqueous phase are in mobile equilibrium with one another, the position of the extraction equilibrium is independent of the particular reaction responsible for the formation of the extracted compound, whatever the phase composition. As a result, equilibrium studies would not show with certainty which particular reaction is involved in each individual extraction of metal salts with amine salts, even though extensive experimental material on the subject is available.

In the initial period of amine extraction studies it was the general opinion that the extraction of metal salts with amines would take place only if the metal ions in the aqueous phase were present in the anionic form; as a result, it was believed that the optimum conditions for the extraction of metal salts with amines and neutral extractants were different. It is known¹⁹⁴ that the optimum conditions for extraction with

neutral extractants corresponds to a maximum yield of neutral metal complexes in the aqueous phase. It was found²⁰⁶ that the relationships between the distribution coefficient of the metal and the composition of the aqueous phase during the extraction of metal salts are the same for extractions with amine salts and with neutral extractants of the TBP type.

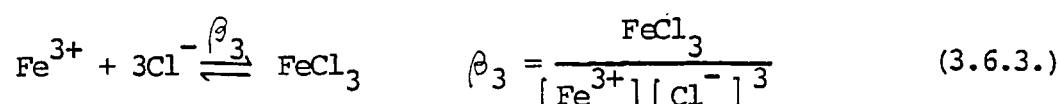
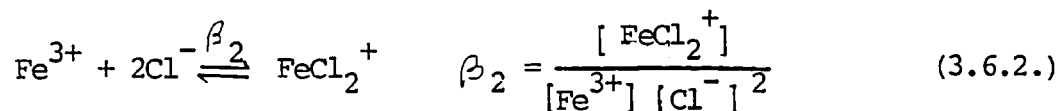
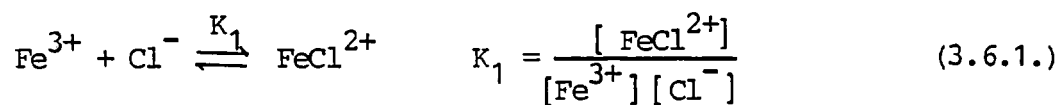
It has been shown²⁰⁷ that even though the extracted compounds of the metal salts may exist as complex anions, it is also possible to extract metals from aqueous solutions in which no such anions are present. Lindenbaum and Boyd¹⁹⁶ showed that a number of metals were readily extracted with amine salts without forming any anionic complexes in the aqueous phase, disproving the view held at that time that anionic metal complexes must be present in the aqueous phase for the metal to be extractable with amine salts. In all these cases, the doubt whether amines are anionic or neutral extractants remains to a certain extent, as all the evidence has been essentially circumstantial. The interfacial reaction may involve, at some stage, one or other species and the bulk properties of the aqueous phase may not represent, or may even be totally different from, the conditions at the interface. It is now generally accepted, without formal evidence, that both the anion and neutral mechanisms are possible and the one which predominates depends largely on the composition of the aqueous phase and possibly on the amine type. So, a kinetic study is essential for the solution of this problem if indeed it is possible to solve it.

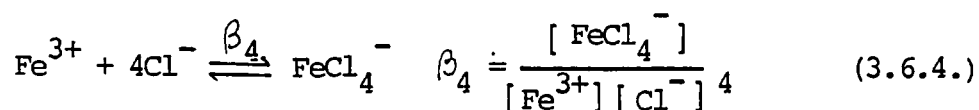
3.6. IRON (III) CHLOROCOMPLEXES

The complexing that occurs between iron (III) ions and chloride ions in aqueous solutions is the subject of

much controversy. The determination of the stability constants of these complexes is complicated by several factors. The uncomplexed aqueous iron (III) ion is octahedrally co-ordinated with six water molecules, whereas the highest chlorocomplex is the tetrahedrally co-ordinated ion, FeCl_4^- . However it is not clear which of the intermediate complexes are octahedral and which are tetrahedral. The result is that the number of complexes that have to be considered is uncertain, since the possibility exists of pairs of intermediate complexes which have the same number of chloride ligands but different numbers of water molecules due to different co-ordination states of the central ion, e.g. $\text{FeCl}_3(\text{H}_2\text{O})_3$ (oct.) and $\text{FeCl}_3(\text{H}_2\text{O})$ (tet.). In addition to the uncertainty concerning the number of chlorocomplexes that occur, the fact that the stabilities of these complexes in aqueous solution are low, leads to difficulties in the interpretation of experimental data. The constant ionic strength method cannot be used in the determination of the higher stability constants since high ligand concentrations are required. Thus various assumptions have to be made about the activity coefficients of the ions in the system and the validity of the stability constants becomes very dependent on the validity of the assumptions.

The association of iron (III) ion with chloride ions in aqueous solutions may be represented, according to Bjerrum's theory of complex formation¹⁶⁹ and neglecting the hydration of the metal and complex ions, as follows:





where [] denotes activity of the involved species. The neglect of the hydration of ions in these equations is equivalent to the assumption that the activity of the water molecules occupying the unfilled co-ordination positions of the ions is the same as the water activity in the bulk of the solution. Using this convention it is not possible to distinguish between the formation of octahedral and tetrahedral species, i.e., $\text{FeCl}_3(\text{H}_2\text{O})_3$ and $\text{FeCl}_3(\text{H}_2\text{O})$, as both are written as FeCl_3 . For cobalt (II) chloride this simplification has been found to lead to the best overall fit of the experimental results, when calculating stability constants¹¹⁶.

Several experimental methods have been used to study the complexing in this system. Spectrophotometry has been the most widely used. A comprehensive compilation of the stability constants of metal-ion complexes (including iron (III)-chloride) is presented by Sillen and Martell²⁰⁹. A full set of stability constants for the iron (III)-chloride system is not available and data refer to K_1 and K_2 mainly, so that it is not possible to select a complete set, as they refer to different ionic strengths and/or experimental conditions (medium, temperature, etc.).

Gamlem and Jordan²¹⁰ investigated the nature of the chloro-complexes of iron (III) in concentrated HCl solutions. Values for K_3 and K_4 were determined. In a critical review, they selected the most likely values for K_1 and K_2 , so that a full set of values for the stability constants was available. This set of data has been often quoted and used in the literature and apparently it is the most reliable one, although not entirely consistent with the experimental evidence. The analysis of the results is complicated by the fact

that there is no wave-length at which only one species absorbs. In order to overcome this difficulty some simplifying assumptions were introduced. For instance, in the range of chloride concentration investigated it was assumed that only FeCl_3 and FeCl_4^- species were present, but when calculating the distribution of the chlorocomplexes in that range of concentrations, considerable amounts of other species were found, so that the initial assumption was not quite correct. The values given for the stability constants were:

$$K_1 = 30 \quad K_2 = 4.5 \quad K_3 = 0.73 \quad K_4 = 0.0105$$

Conditions: $T = 25^\circ\text{C}$ and $I = 0$

A feature of these results is the apparently low value of K_4 , and the reason for this result may be sought by calculating the "ligand effect" by Bjerrum's method²¹¹. In this treatment the ratio of the stepwise equilibrium constants is regarded as the product of the statistical (S) and ligand (L) effects:

$$\log \frac{K_n}{K_{n+1}} = S_{n,n+1} + L_{n,n+1} \quad (3.6.5.)$$

where $S_{n,n+1} = \log [(N-n+1)(n+1)/(N-n)n]$.

Calculation of $L_{n,n+1}$ for a co-ordination number (N) of 6, the values 30, 4.5, 0.73 and 0.0105 being used for K_1 , K_2 , K_3 and K_4 , respectively, gives

$$L_{1,2} = 0.44 \quad L_{2,3} = 0.52 \quad L_{3,4} = 1.59$$

Alternatively for a co-ordination number of four

$$L_{3,4} = 1.41$$

For a given series of complexes the ligand effect should be a constant, as shown by Bjerrum²¹¹ for several systems. The reasonable agreement between $L_{1,2}$ and $L_{2,3}$ appears to indicate that K_1 , K_2 and K_3 may be regarded as "normal" values. On the other hand, $L_{3,4}$ is much higher and K_4 much lower than would be expected. Such behaviour may be attributed to a change in the co-ordination number of the central ion from six to four, i.e. from $\text{FeCl}_3(\text{H}_2\text{O})_3$ to FeCl_4^- , or perhaps to the existence of an intermediate complex. If this statement is correct, the values of $L_{3,4}$ have no theoretical significance, since in the ratio K_3/K_4 the two equilibrium constants refer to different structures or to some missing intermediate complexes.

Marcus^{212,213} investigated the iron (III)-chloride complexes using the anion exchange method. The range of chloride concentrations studied varied from 1.0 to 12 M in HCl-LiCl solutions. A corrected distribution curve was constructed showing the complexes FeCl_2^+ , FeCl_3 and FeCl_4 , with stepwise equilibrium constants:

$$K_2 > 0.2 \quad K_3 = 0.04 \quad K_4 = 0.012$$

The interpretation of the results was complicated by the lack of experimental data on the activity coefficients of HCl-LiCl mixtures or a reliable method of estimating the activity coefficients for these mixtures, at that time.

Hegelson²¹⁴ in a critical review of the stability constants of some systems, selected from the literature the following values for the iron (III)-chloride system:

$$K_1 = 0.033 \quad K_2 = 0.224 \quad K_3 = 10 \quad K_4 = 0.616$$

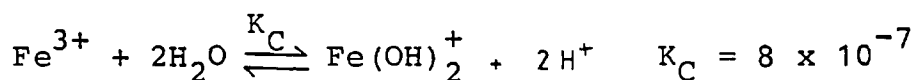
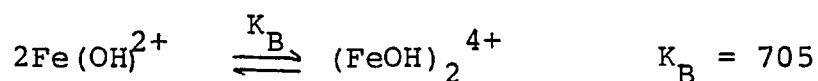
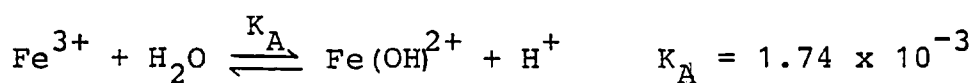
Dousma et al.²¹⁵ quoted the following values for the stability constants:

$$K_1 = 4.02 \quad K_2 = 0.045 \quad K_3 = 0.339 \quad K_4 = 0.0105$$

They investigated also the influence of chloride ions on the hydrolyse of iron (III) compounds. At $\text{pH} > 2$ chloride ions hydrolyse to form compounds of the type $\text{Fe}_4\text{O}_3(\text{OH})_5\text{Cl}$.

Michel et al.¹⁹⁹ studied the nature of iron (III)-chloride complexes using Raman spectrometry. The range of chloride concentrations investigated varied from 0.5 to 10 M HCl. FeCl_4^- was detected only at concentrations above 5 M, whereas below that only FeCl_3 was found. It seems remarkable that no FeCl_2^+ or FeCl^{2+} could be found in this range of concentrations, especially at low concentrations, as would be expected from the stepwise formation of the complexes.

Solutions of ferric chloride in water contain, in addition to the chlorocomplexes, the hydroxy-complexes $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_3$ which have been extensively investigated²¹⁶. The equilibrium constants are given by:



A summary of the stability constants for the system iron (III)-chloride is given below:

K_1	K_2	K_3	K_4	Reference
30	4.5	0.73	0.0105	210
-	>0.2	0.04	0.012	212
0.033	0.224	10	0.616	214
4.02	0.045	0.339	0.0105	215

The discrepancy of the data is a reflection of the inherent difficulty of the system. An interesting discussion about the "Reality of Complexes" is presented by Marcus and Kertes¹⁶⁹.

The general form of the stepwise equilibrium constants K_n , activities being written in terms of concentrations and activity coefficients, is

$$K_n = \frac{(\text{FeCl}_n^{3-n})}{(\text{FeCl}_{n-1}^{4-n})(\text{Cl}^-)} \frac{\gamma_n}{\gamma_{n-1} \gamma_{\text{Cl}}} \quad (3.6.6.)$$

where γ_n and γ_{n-1} are the activity coefficients of the n th and $(n-1)$ th complexes, respectively, and γ_{Cl} is the activity coefficient of the chloride ions. These activity coefficients are not known, except for FeCl_3 , which Nachtrieb and Fryxell²¹⁷ found to be approximately 1.0 at concentrations up to 0.1 M in 5 M HCl. An exact treatment without the introduction of non-thermodynamic assumptions is therefore not possible. The approximation generally made²¹¹ is to assume that a single mean activity coefficient, F , may be used to replace the activity coefficient term in equation (3.6.6.), i.e.,

$$\frac{1}{F} = \frac{\gamma_{\text{FeCl}}^{2+}}{\gamma_{\text{Fe}}^{3+} \gamma_{\text{Cl}^-}} = \frac{\gamma_{\text{FeCl}_2^+}}{\gamma_{\text{FeCl}_2^+} \gamma_{\text{Cl}^-}} = \frac{\gamma_{\text{FeCl}_3}}{\gamma_{\text{FeCl}_2^+} \gamma_{\text{Cl}^-}} = \frac{\gamma_{\text{FeCl}_4^-}}{\gamma_{\text{FeCl}_3} \gamma_{\text{Cl}^-}} \quad (3.6.7.)$$

This approximation is equivalent to assuming that

$$\frac{\gamma_n}{\gamma_{n-1}} = C \quad (3.6.8.)$$

where C is a constant, i.e., that the activity coefficients of the complexes change uniformly throughout the series. As Bjerrum²¹¹ pointed out, this is not an unreasonable assumption for solutions of high ionic strength for which chemical structure rather than charge determines the value of the activity coefficients. Bjerrum²¹¹ expresses F by the equation

$$\log F = A + B (Cl^-) \quad (3.6.9.)$$

in which A and B are constants for a particular system. This equation is of the form required by the extensions of the Debye-Hückel theory for concentrated solutions²¹⁸, and corresponds to the approximate empirical equations which hold for the activity coefficients of HCl and LiCl at concentrations greater than 3 M:

$$\log \gamma_{HCl} = -0.42 + 0.18 (Cl^-) \quad (3.6.10)$$

$$\log \gamma_{LiCl} = -0.43 + 0.23 (Cl^-) \quad (3.6.11)$$

Introducing the "Guggenheim assumption"²¹⁸ that $[Cl^-] = [HCl]$, equation (3.6.6.) can be rewritten in the form

$$K_n^* = \frac{(FeCl_n^{3-n})}{(FeCl_{n-1}^{4-n})(Cl^-)} \cdot \frac{1}{\gamma_{HCl}} \quad (3.6.12)$$

in which K_n was replaced for K_n^* for the stepwise equilibrium constants, since non-thermodynamic assumptions have been introduced. This procedure has been found to give values of the equilibrium constants (K_n^*) not

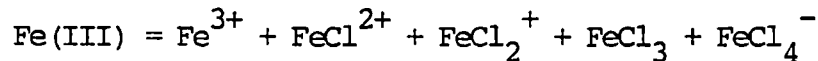
significantly different from that of the true constant $(K_n)^{211}$, so that $K_n \approx K_n^*$.

The values of K_n selected from the literature may be used to calculate the distribution of iron (III) amongst its various complexes as a function of chloride concentration.

The fraction α_n of iron (III) presented as the n th complex is given by

$$\alpha_n = \frac{\text{FeCl}_n^{3-n}}{\text{Fe(III)}} \quad (3.6.13)$$

A balance on the total quantity of iron (III) present in the aqueous phase can be written as:



It may be simply shown that if $\alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 1$ and $\text{Fe(III)} \ll \text{Cl}^-$ then:

$$\alpha_n = \frac{K_n [\text{Cl}^-]^n}{1 + \sum_{n=1}^4 K_n [\text{Cl}^-]^n} \quad (3.6.14)$$

where $[\text{Cl}^-] = [\text{HCl}]$ or $[\text{LiCl}]$ or $[\text{HCl-LiCl}]$, depending whether HCl, LiCl or HCl-LiCl solutions respectively have been used. But, because K_n values have been determined for a certain aqueous chloride medium, it may be more sensible to use the activity of that medium to calculate the distribution of the different chlorocomplexes and then afterwards relate in some way the activities of the two different aqueous media with the calculated α_n values.

The activities of HCl and LiCl are available in the literature¹⁶⁹ and presented in Appendix B-2. The activities of HCl-LiCl solutions can be calculated using Bromley's²¹⁹ or Kusik and Meissner's²²⁰ correlations. The Bromley method has been used successfully to calculate activity coefficients up to an ionic strength of about 6, whereas Kusik and Meissner's method can be applied up to saturation depending on the precision required. They provided the following equation for a three ion system (two cations and one anion):

$$\log \Gamma_{12} = \log \Gamma_{12}^0 + 0.5 X_3 \log \left(\frac{\Gamma_{32}^0}{\Gamma_{12}^0} \right) \quad (3.6.15)$$

where $\log \Gamma_{xy} = \frac{1}{z^+ z^-} \log \gamma_{xy}^+$

$\Gamma_{xy}^0 = \Gamma_{xy}$ for a pure binary electrolyte of the same total ionic strength;

X_3 is mole fraction of cation 3.

The reduced activity coefficients for HCl and LiCl as function of ionic strength are presented in Figure 3.6.1. The reduced activity coefficient of HCl-LiCl mixtures would be between the HCl and LiCl reduced activity coefficients at equivalent total ionic strengths. As these values are close, the reduced activity coefficient of HCl-LiCl mixtures may be approximated to the value of the reduced activity coefficient of the major component of the solution, in this study LiCl. As the molalities of HCl and LiCl are basically the same at same concentrations, it is reasonable to assume that the mixtures would have the same molality at equivalent total ionic strength. In this case, the activities of LiCl at equivalent total ionic strength may be used as a reasonable approximation of the activities of HCl-LiCl mixtures.

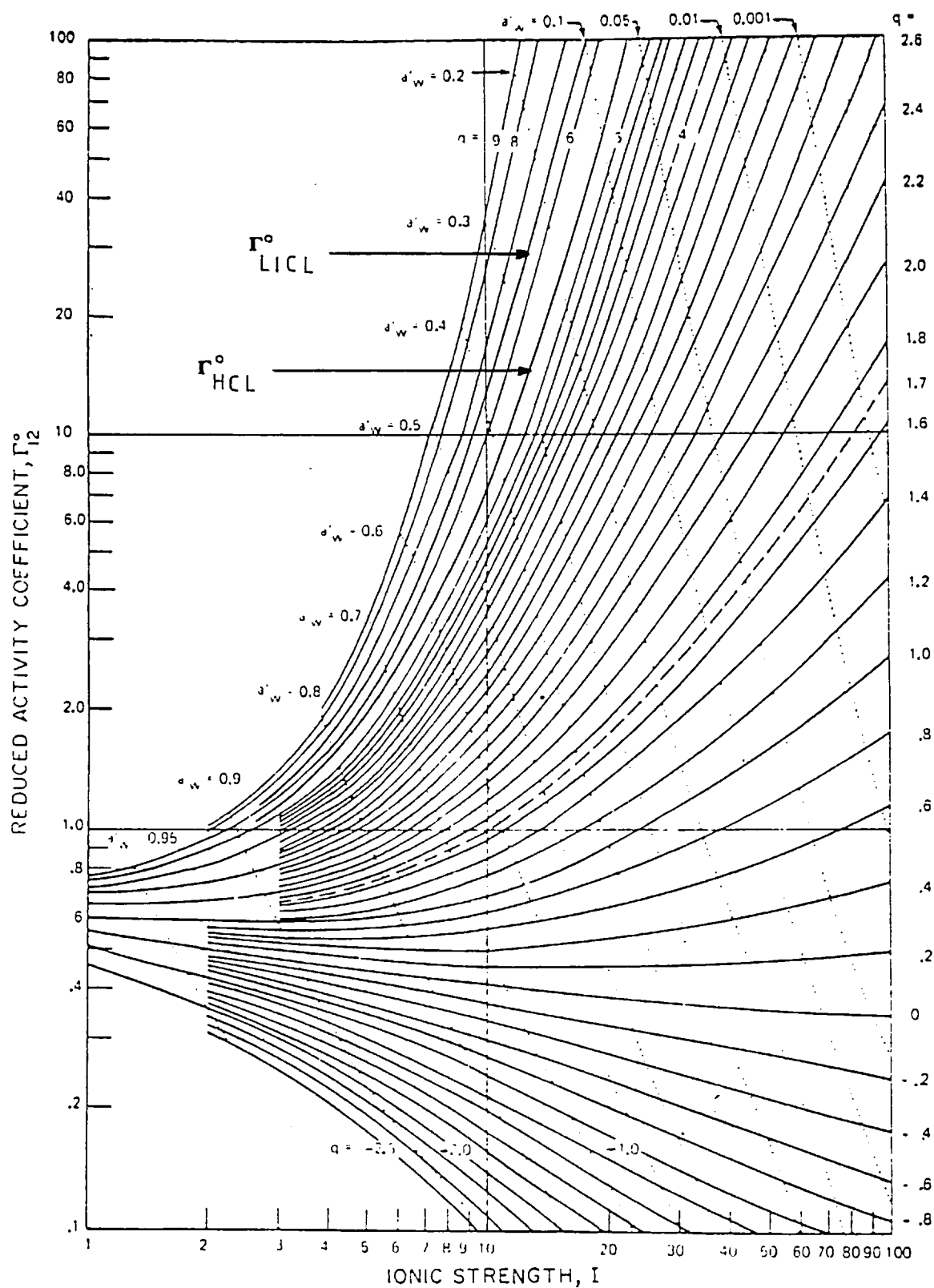


FIGURE 3.6.1. KUSIK-MEISSNER DIAGRAM FOR ISOTHERMS OF REDUCED ACTIVITY COEFFICIENTS VERSUS IONIC STRENGTH⁽²²⁰⁾.

The distribution of chlorocomplexes of Fe (III) were calculated using equation (3.6.14). A comparison of the distribution of the chlorocomplexes as a function of chloride ion concentration for some sets of stability constants is shown graphically in Figure 3.6.2. Calculated values are given in Tables B.2.1. to B.2.4. (Appendix B). There is no agreement at all amongst the results. It is not possible to decide which one is the most reliable or most representative of what might happen in practice.

A comparison of the effect of the chloride activity on the distribution of chlorocomplexes as a function of chloride ion concentration is shown graphically in Figure 6.3.3. Calculated values are given in Tables B.2.1., B.2.5. to B.2.6. Apparently there is a reasonable agreement amongst the results and any of the calculated values would give a fair idea of the system, provided the set of stability constants used throughout the calculations is reliable.

To conclude, it must be stressed that the calculated distribution of the chlorocomplexes may give just a rough indication of the complexes really predominating in solution (like in a Pourbaix diagram), because of the lack of reliability of the values and meaning of the stability constants. The non-thermodynamic assumption introduced that the ratio of the activity coefficients is equal to one, is an oversimplification to say the least, but to date there is no other method of calculating the distribution of the chlorocomplexes.

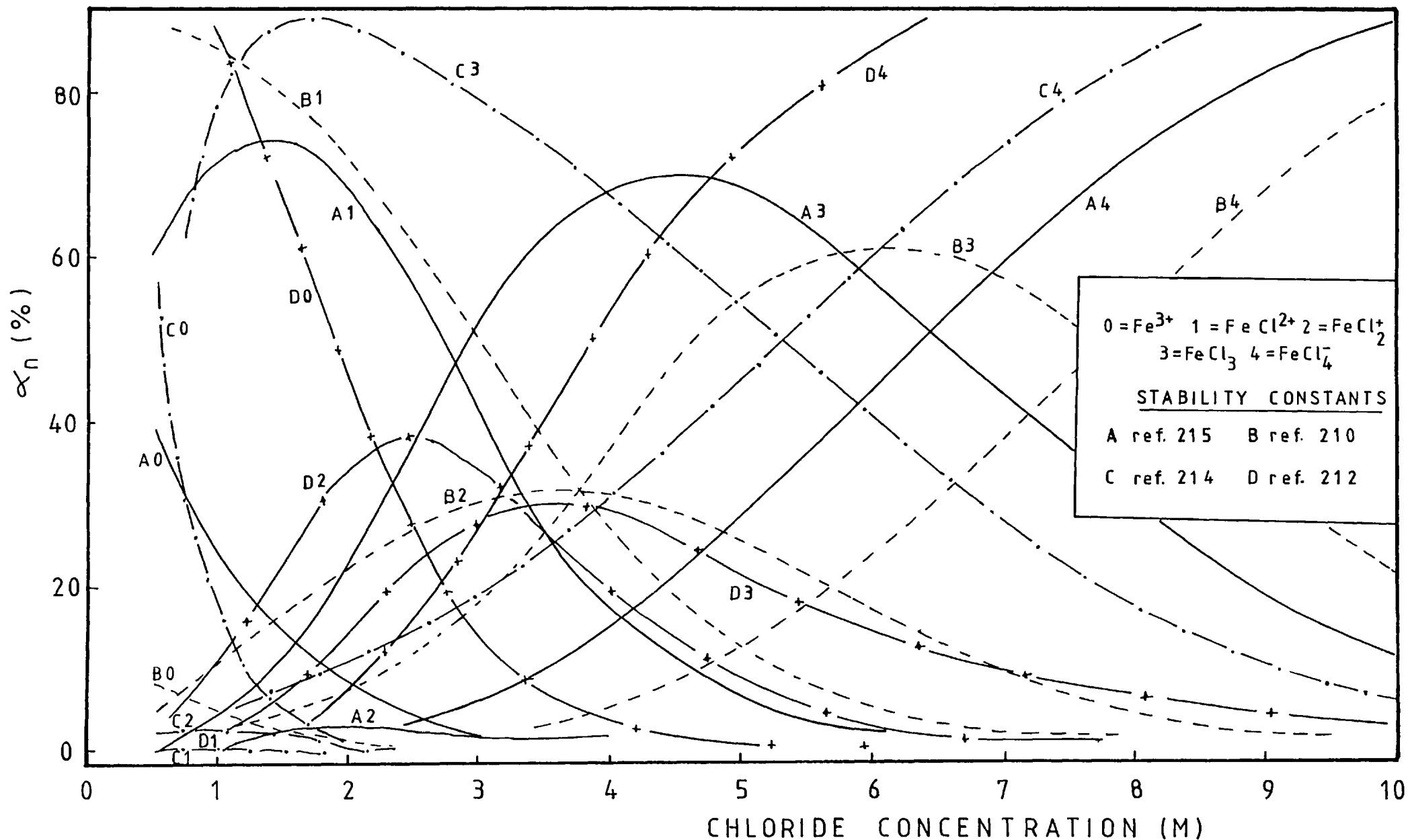


FIGURE 3.6.2. COMPARISON OF THE DISTRIBUTION OF THE CHLOROCOMPLEXES OF Fe(III) AS A FUNCTION OF CHLORIDE CONCENTRATION FOR SOME SETS OF STABILITY CONSTANTS.

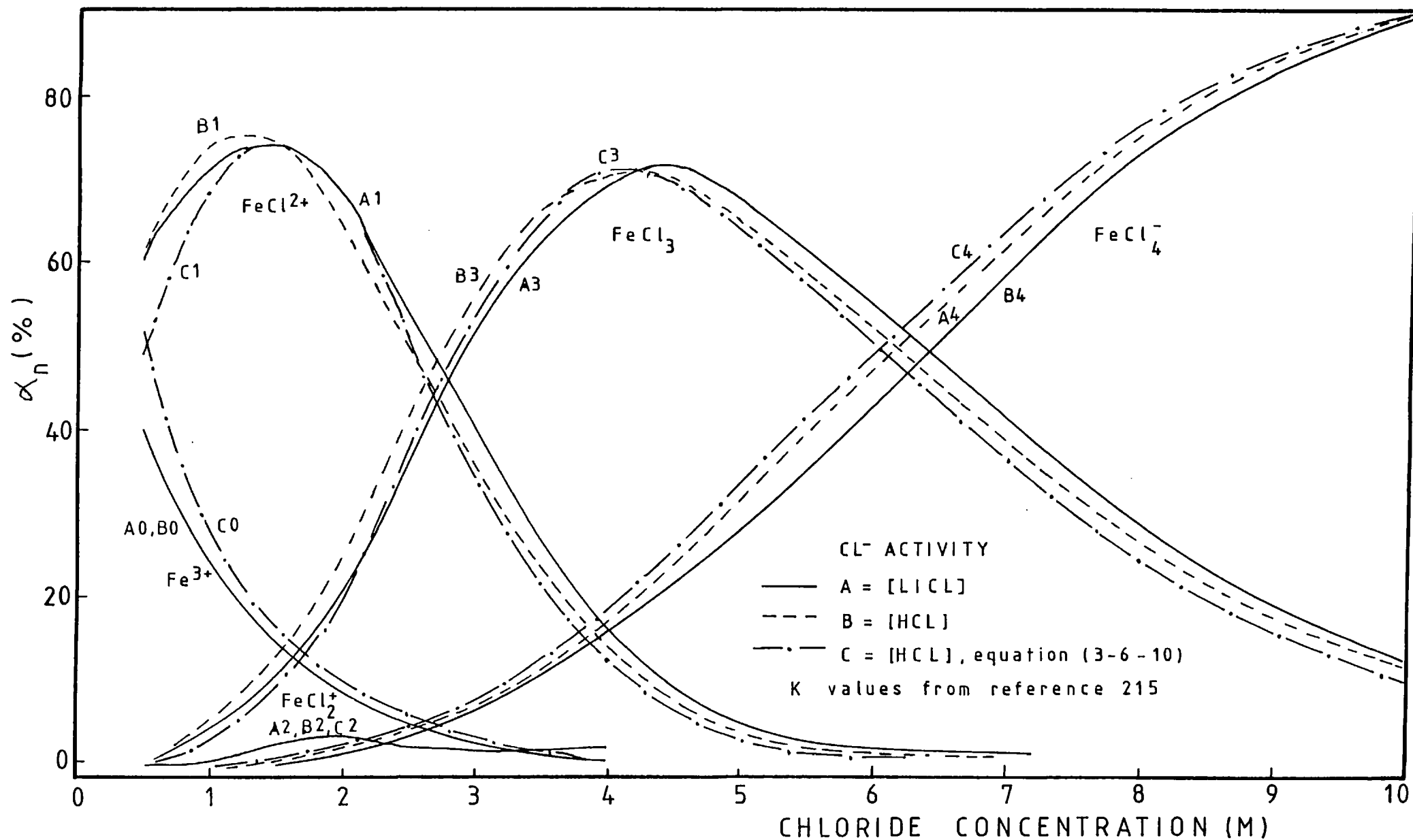


FIGURE 3.6.3. COMPARISON OF THE DISTRIBUTION OF THE CHLOROCOMPLEXES OF FE(III) AS A FUNCTION OF CHLORIDE ION CONCENTRATION. $[Cl^-]$ ASSUMED AS EQUAL TO $[HCl]$, $[LiCl]$ OR CALCULATED FROM EQUATION (3.6.10).

3.7. PHYSICOCHEMICAL PROPERTIES

The densities of toluene and water at 25°C under conditions of mutual saturation are:

$$d_{\text{toluene}} = 0.864 \quad d_{\text{water}} = 0.997 \quad (\text{gm/cm}^3)$$

The variation of these densities with temperature over the range of conditions used in this study can be considered negligible.

The density of pure TOA at 25°C is 0.8086. The effect of TOAHCl on the density of the organic phase was found to be negligible, as only dilute solutions were used (maximum 0.1 M).

The densities of HCl-LiCl solutions at 25°C were determined. The results are presented in Figure 3.7.1. where they are compared with the densities of pure HCl and LiCl solutions. Regression analysis of the results gave the following equation

$$d_{(1\text{M HCl} + x \text{ M LiCl})} = 1.08 + 0.0213(\text{LiCl}) \quad R_c^2 = 0.99 \quad (3.7.1.)$$

The effect of Fe (III)-chloride on the density of the aqueous phase was found to be negligible, as only trace concentrations were used.

The viscosity of toluene (saturated with water) at 25°C is 0.56 cp. The viscosity of the organic phase with 0.1 M of TOAHCl was found to be 0.59 cp and this solution fully loaded with iron (III) chloride had a viscosity of 0.62 cp. The effect of the presence of the amine or the amine fully loaded with iron (III) did not affect significantly the viscosity of the organic phase and this small increase was neglected.

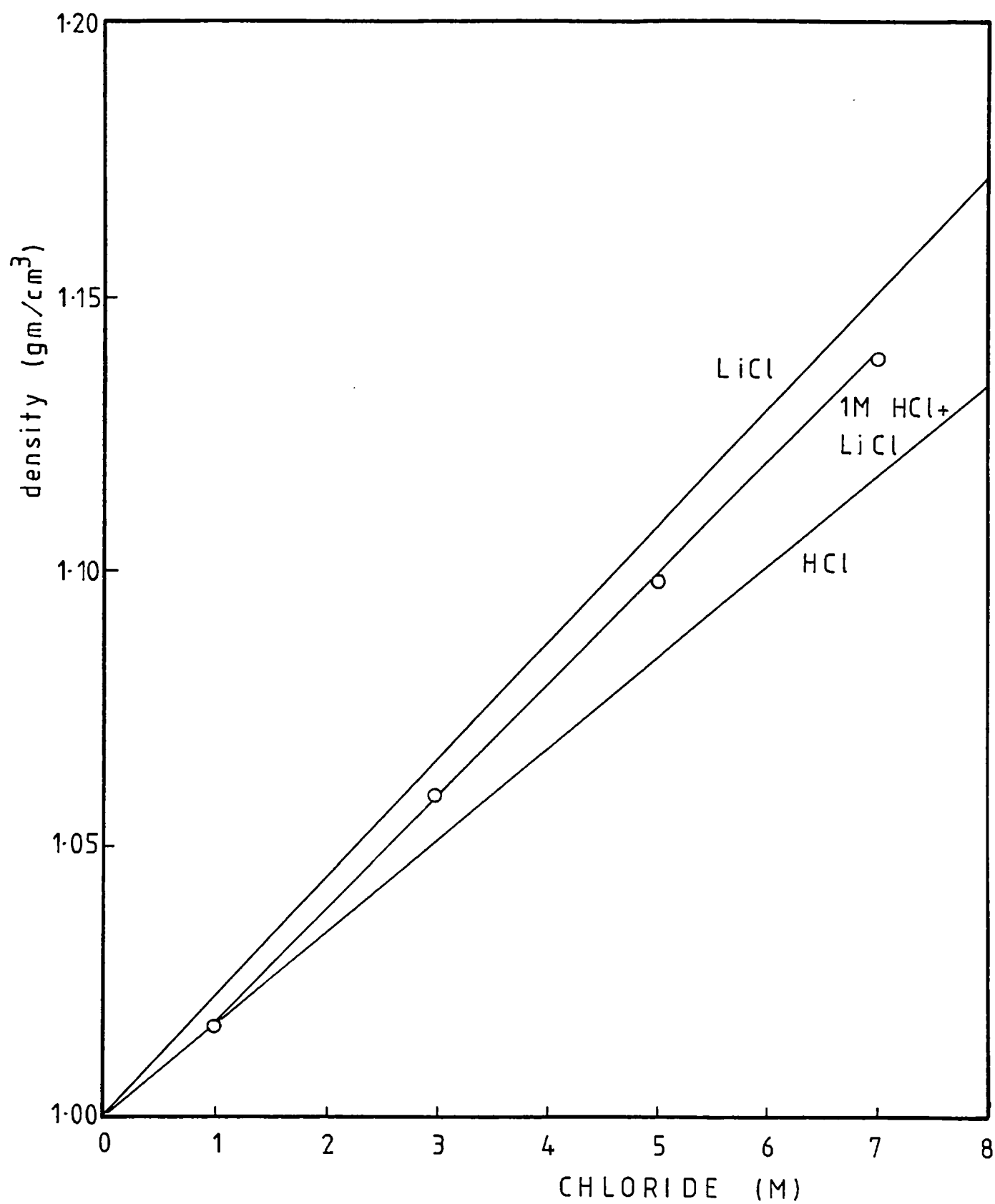


FIGURE 3.7.1. DENSITY OF LiCl, HCl AND (1 M HCl + x M LiCl) SOLUTIONS (25°C).

The effect of HCl, even at high HCl concentrations, does not affect significantly the viscosity of the aqueous phase. In contrast, the effect of LiCl is highly significant and viscosity increases considerably with concentration. This would be expected, as Li^+ is known to be a structure maker²²¹. This could have a significant effect not only on the hydrodynamic conditions of the system (affecting the Reynolds number) but also on the diffusivities of transferred species, so that it can affect significantly the mass transfer rates (affecting the Schmidt number), depending on the hydrodynamic conditions of the system. The viscosity of pure LiCl solutions²²⁵ at 25°C can be represented by the equation

$$\nu_{\text{LiCl}} = 1 + 0.0275 (\text{LiCl}) + 0.0233 (\text{LiCl})^2 \quad (3.7.2.)$$

$$R_c^2 = 0.99$$

The experimental results for the viscosity of HCl-LiCl solutions are shown in Figure 3.7.2. The results follow closely the viscosity of pure LiCl solutions and equation (3.7.2.) was assumed to represent the experimental results as well. The effect of Fe (III)-chloride on the viscosity of the aqueous phase was found to be negligible as only trace concentrations were used.

The interfacial tension (σ) between TOAHCl in toluene and HCl-LiCl aqueous solutions is not available in the literature. However, some similar systems have been studied, i.e., TOAHCl in benzene and HCl solutions⁷⁵ and TLAHCl in toluene and HCl solutions¹³⁵. Typical values are given in Table 3.7.1.

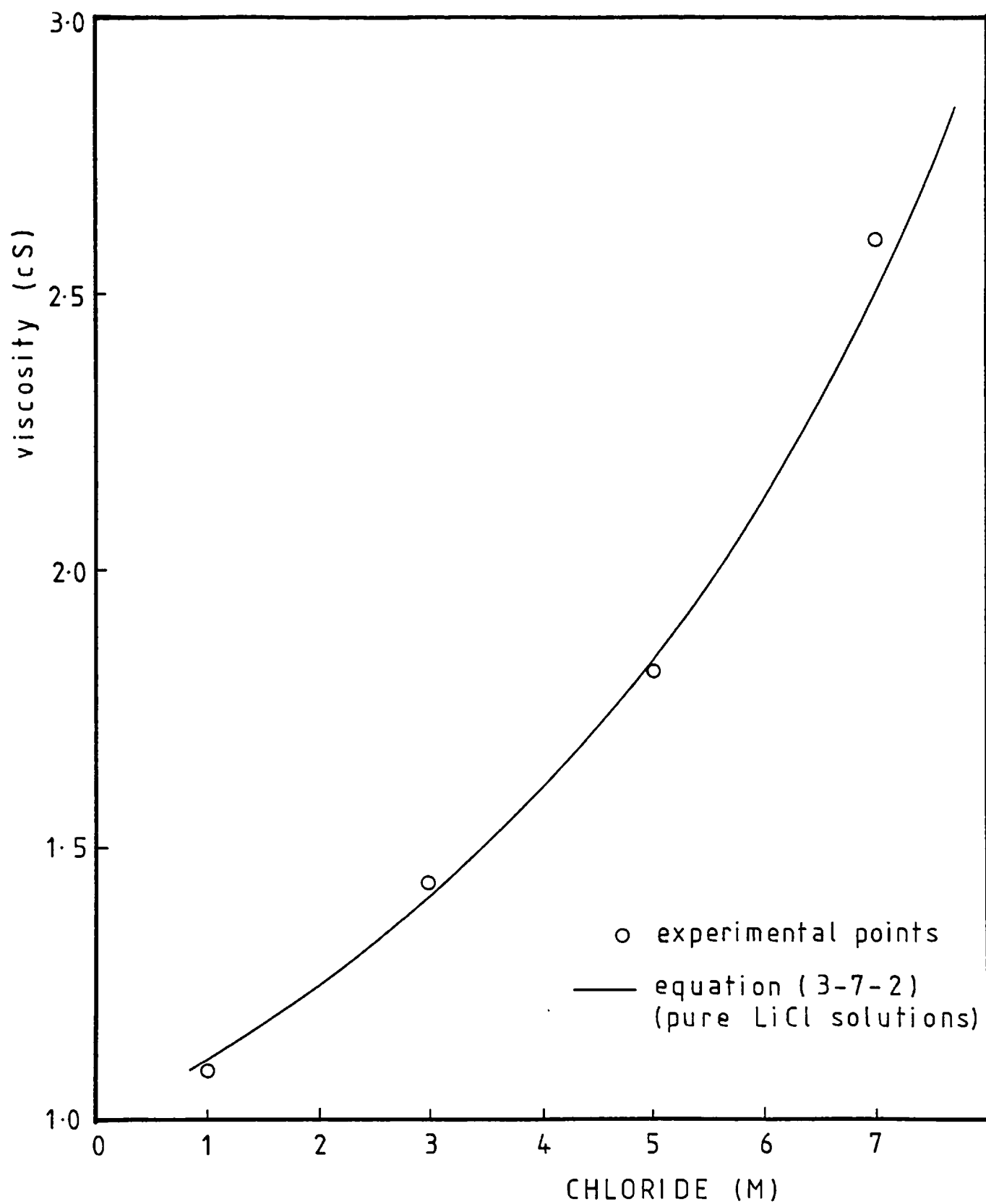


FIGURE 3.7.2. VISCOSITY OF CHLORIDE SOLUTIONS (25°C).

System	σ (dyn/cm)
benzene - H ₂ O	31.1
benzene - 0.01 M HCl	31.1
TOA (benzene) - H ₂ O	28.8
TOAHCl (benzene) - 0.01 M HCl	11.4
toluene - water	36.0

TABLE 3.7.1. Interfacial tensions (σ)

Pizzichini et al.¹³⁵ investigated the interfacial behaviour of TLAHCl in toluene with some chloride solutions. They found that the free amine TLA saturates the interface at about 10^{-3} M, whereas the amine salt TLAHCl is more surface active and saturates the interface at about 10^{-4} M. The cross-sectional area of the molecules at the interface were determined: TLA = $133 \text{ \AA}^2$ and TLAHCl = $180 \text{ \AA}^2$. The bulk organic concentration at which formation of aggregates starts to take place was found to be about 5×10^{-3} M. It was found also that only monomeric species can be absorbed at the interface. This conclusion is supported by the studies of Vandergrift et al.¹³⁷ Although this system is not the same as the one used in this study, it has been found^{75,135} that as far as interfacial tension is concerned the commonly used high molecular weight tertiary amines in benzene or toluene have similar behaviour when contacted with chloride solutions. Therefore the properties of the systems discussed here may give a fair idea about the interfacial behaviour between TOAHCl in toluene and HCl-LiCl aqueous solutions.

The solubilities of toluene in water and of water in toluene at 25°C are respectively 0.055^{and} 0.045 g/100 g

saturated solution. The solubilities of Fe (III)-chloride and LiCl in toluene was found to be negligible. A typical value for the ^{aqueous} solubilities of tertiary amine salts and their metal complexes is about 10^{-6} M¹³⁵, which can be considered negligible.

The accurate measurement of diffusion coefficients is difficult owing to the process being very sensitive to temperature fluctuations, vibration and turbulence and it is not always independent of solute concentration. Austin¹⁰² discussed the reliability of the experimental techniques available, as well as the theoretical and empirical correlations used to estimate this parameter. In general, these correlations perform poorly for liquids and basically are limited to stable binary systems. Amongst those found in the literature, the Sitamaran's correlation²²² gave most consistent results. For non-electrolyte solutions, the correlation gives reasonable results, whereas for electrolytes large errors were obtained. For a complex system like the present one, it is almost impossible to use any type of correlation, as the physicochemical parameters necessary are not available in the literature and are difficult to obtain.

The diffusion of dissolved electrolytes does not differ in principle from that of dissolved non-electrolytes, but two related factors should be taken into account which are absent in solutions of non-electrolytes. One of them is the electric potential gradient, caused by ions of different mobilities, which markedly alters the rate of the diffusion of ions by means of cross-effects. The other one is due to the electrostatic interaction between ions which does not allow macroscopic separation of ions of opposite charge. Both of them influence the mobility of ions.

Molecules of an electrolyte in solution dissociate into cations and anions, which because of their smaller size, diffuse more rapidly than the undissociated molecules. In solutions containing not more than one electrolyte, despite difference between the sizes of the positively and negatively charged ions, both types diffuse at the same rate, so that the electrical neutrality of a given solution is preserved. In the presence of other ions already in the solution, individual ions may diffuse at rates which are quite different from those of the previous case. Danckwerts⁹⁷ presented a good discussion on this subject.

Viscosity can have a significant effect on the diffusion coefficient. Kay²²¹ in a comprehensive review about ionic transport in water and mixed aqueous solvents discussed related phenomena.

A few experimental values for comparable systems are available in the literature. Juznic and Fedina²²³ investigated the self-diffusion and liquid-liquid interfacial transfer coefficients of Fe (III)-chloride in HCl with TOAHCl in xylene. At 25°C, the diffusion coefficients in the aqueous and the organic phase were determined, as well as the activation energy and the radii of iron (III) species. They are given below:

	Aqueous	Organic
$D \times 10^5 \text{ (cm}^2\text{/s)}$	0.611	0.29
$r \text{ (Å)}^0$	3.12	10.72
$E_A \text{ (kcal/mole)}$	1.3	1.4

Values for zinc (II) and antimony (III) chlorides were also determined. They are very similar to iron (III). So, it is likely that these values may give at least the order of magnitude of these parameters for the system under investigation.

Until recently most investigators have ignored the complications introduced by differences in ionic diffusivity. The difference between results is likely to be greatest when H^+ or OH^- are involved, as these have much greater mobilities than other species of ions. It is thus necessary to take into account these different diffusivities, particularly when transfer is diffusion controlled or alternatively to work in a range of conditions where mass transfer occurs under chemical control. In this case diffusion has little effect and could be ignored.

CHAPTER IV

THE STIRRED CELL

4.1. INTRODUCTION

The accurate determination of mass transfer rate requires that the transfer area is a constant, well defined interface and that the bulk phase is of uniform concentration. Facilities must also exist for a simple and quick analysis of the various concentrations in the two homogeneous bulk phases. The ideal method of analysis should be continuous, accurate and reproducible, especially at times close to the beginning of the experiment ($t \rightarrow 0$). The experimenter should also have means of keeping the hydrodynamics fairly constant, as well as be able to vary and control the mixing conditions from one experiment to another.

All these conditions can be satisfied by a stirred cell in which the two phases are stirred independently in a turbulent way, enough to homogenize both phases, yet the interface between the two fluids is smooth and well defined. Some designs of stirred cells have been shown schematically in Fig. 2.3.1.

The unbaffled cells, as used by some researchers^{29-31, 75-81} in this field, undoubtedly led to vortex formation and rippling of the interface at stirring speeds sufficiently high to produce good mixing in the bulk of the phases and to achieve chemical control. The stirred cell used by Lewis^{32,33} would appear to have some advantages over the unbaffled or partially baffled cells, since:

- (i) The annular baffle allows the bulk phases to be well stirred without disrupting the interface;

(ii) A well defined reproducible mass transfer area is produced;

(iii) The bulk phases can be assumed to be of uniform compositions;

(iv) The interfacial area is symmetrical to the stirrers and hence the surface age distribution will be independent of position.

The Lewis cell does however have the disadvantages that,

(i) The interface is partially obscured by the annular baffle;

(ii) Any surfactant present in the system will accumulate at the interface;

(iii) A mathematical analysis of the hydrodynamics at the interface is very difficult, perhaps impossible.

(ii) is surely true for any technique and (iii) applicable to all types of stirred cell.

Austin¹⁰² studied pure mass transfer in a Lewis cell and found that the cell has certain limitations, as follows:

(i) The interface rotated under most stirring speeds;

(ii) Injection of dye showed that when the bulk phases were well mixed the interface was disrupted with ripples and waves;

(iii) As mass transfer occurred, the level of the interface moved from the central position and advanced into one of the phases.

Austin¹⁰² found it necessary to make some modifications to Lewis's original design in order to stabilise the interface. He studied the effect of the depth of the interface well by using interchangeable central and ring baffles and concluded that a well depth of at least 1.905 cm ($\frac{3}{4}$ "), produced a smooth interface compatible with good bulk mixing for a reasonable range of stirring speeds. He also found that the addition of four vertical perforated baffles was necessary in each chamber of the cell to damp the swirl in the bulk fluids and to homogenize the bulk phases at lower stirring speeds. He added a level control cell which

acted as a variable volume reservoir of liquid for the lower chamber so that the interface could be located at the centre of the interface well and kept there as mass transfer proceeded.

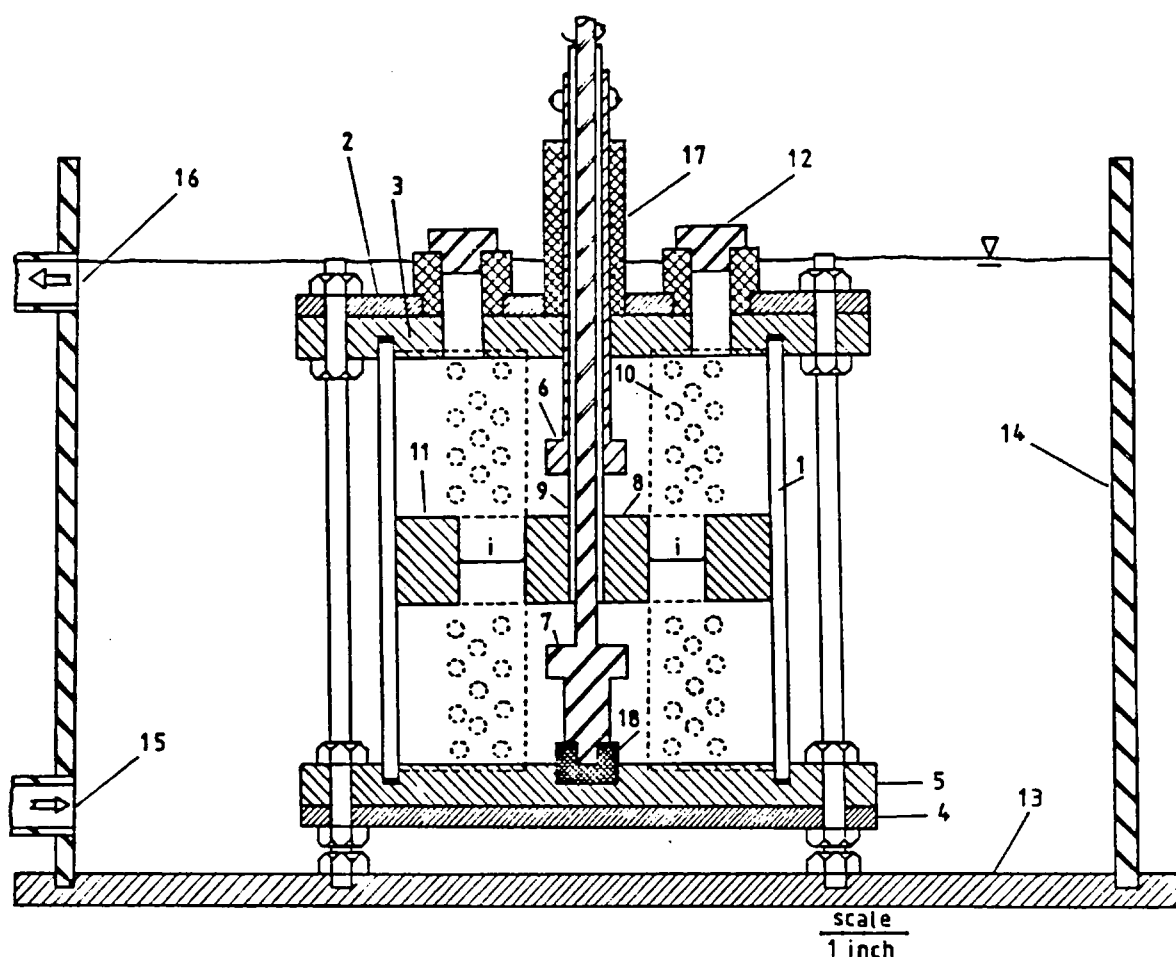
Grosjean¹⁶³ repeated some of Austin's experiments using the same equipment. He calculated the mean length of the eddies arriving at the interface and found these to be about the same dimensions of the perforations made in the vertical baffle at the level of the impellers. He concluded that the large scale flows propelled by the impeller blades through these holes produce large eddies whose length was equal to the diameter of the perforations. As pointed out by McManamey *et al.*³⁰ the eddy length is related to the scale of turbulence. So, it is undesirable to have large eddies at the interface as this would disturb it, causing ripples and waves. The best way to minimize this effect is to have many small holes in the vertical baffles, instead of a few big ones.

Molnar¹⁴⁹ studied the extraction of copper by Kelex 100 using a version of Austin cell with minor modifications. He found no need to use the level control cell as no significant variation in the level of the interface was noticed.

4.2. DESCRIPTION OF THE CELL

The basis of the design was the stirred cell described by Molnar¹⁴⁹. It was modified in various aspects to enable a systematic study of the kinetics of the system under investigation. An essential requirement was the use of materials which were chemically resistant to the chloride system, especially at high concentrations. All parts which were in contact with aqueous or organic solutions were made in glass, PTFE or Viton rubber, as required.

A diagram of the cell is shown on Fig. 4.1. and detailed drawings are presented in Appendix A. The apparatus is illustrated in Figs. 4.2 to 4.4.



NOTE: All parts are made of PTFE unless otherwise stated.
See Appendix A for detailed drawings.

- | | |
|----------------------------|------------------------------------|
| 1. Glass ring. | 2. Top plate (stainless steel). |
| 3. Top plate. | 4. Bottom plate (stainless steel). |
| 5. Bottom plate. | 6. Upper stirrer. |
| 7. Lower stirrer. | 8. Central baffle. |
| 9. Glass tube support. | 10. Vertical baffles. |
| 11. Ring baffle. | 12. Sampling/filling ports. |
| 13. Base plate (steel). | 14. Water jacket (perspex). |
| 15. Water from thermostat. | 16. Water to thermostat. |
| 17. Stirrer bearing/seal. | 18. Bearing. |

FIG. 4 - 1 - THE STIRRED CELL

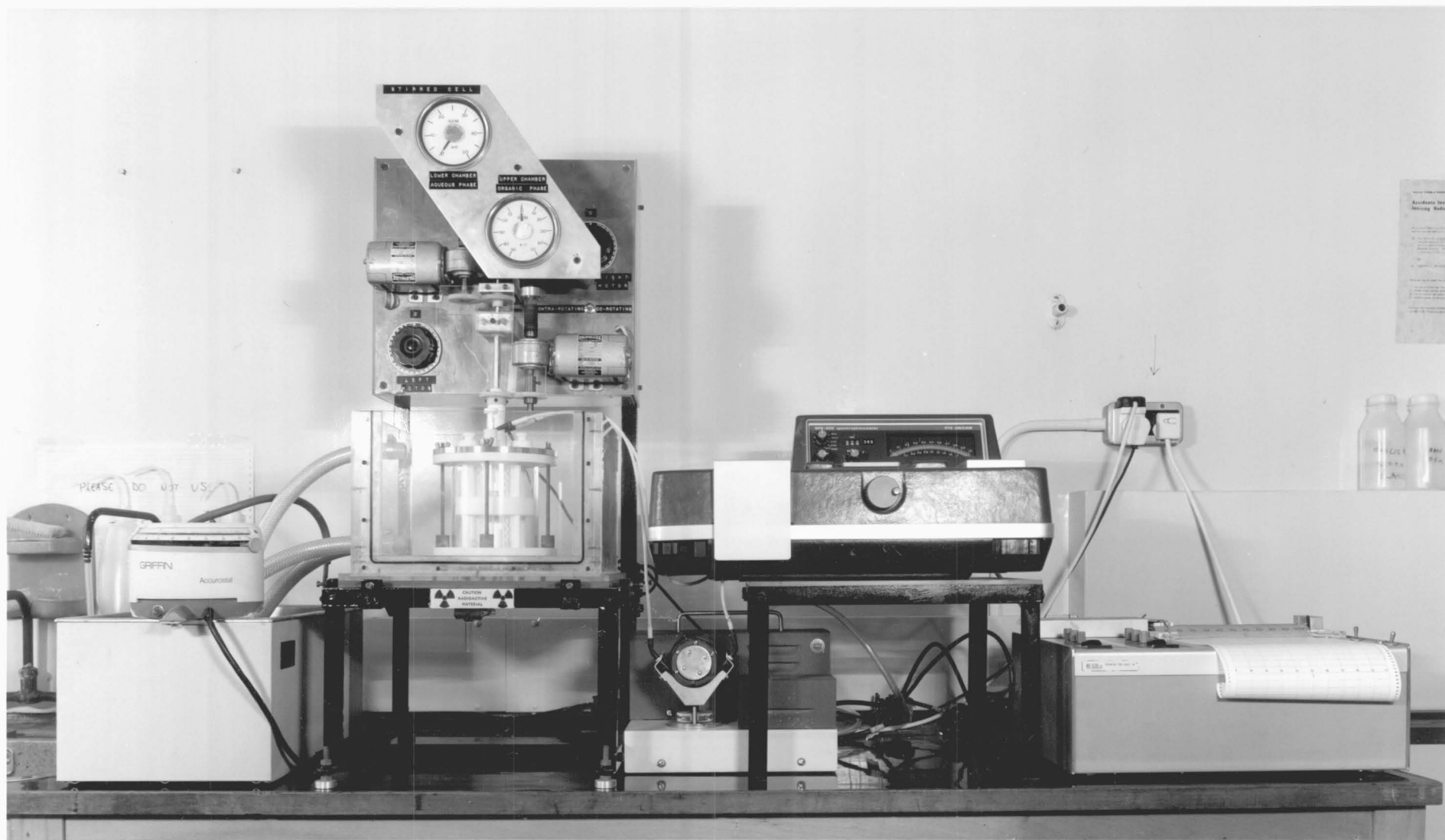


FIG. 4-2 - OVERALL VIEW OF APPARATUS

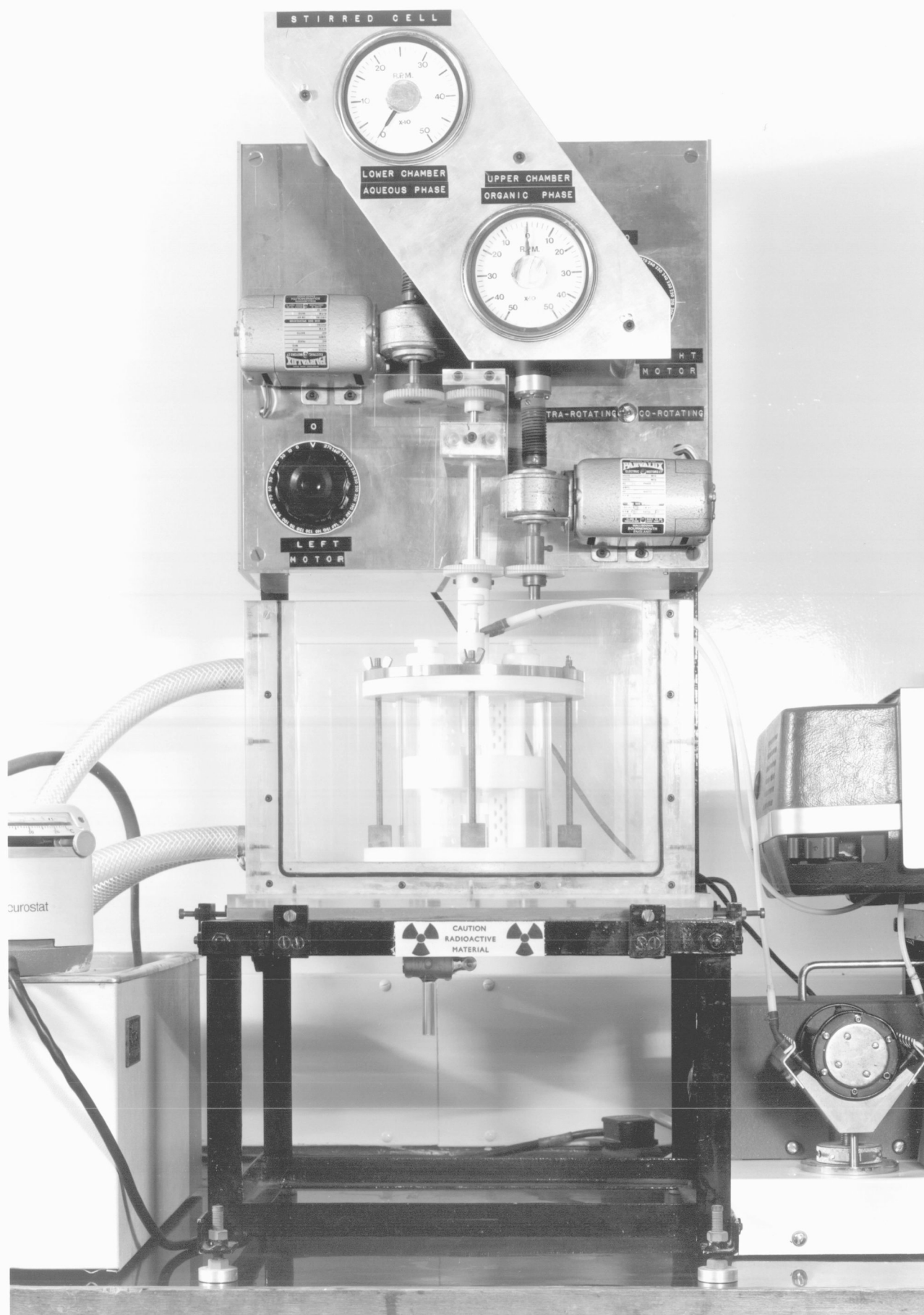


FIG. 4-3 - THE STIRRED CELL AND MOTOR BOARD



FIG. 4-4 - THE STIRRED CELL

The cell consists of a precision bore glass tube (125 mm diam.) clamped between two PTFE flanges by means of four stainless steel screwed rods and wing nuts. To give strength to the PTFE flanges, two stainless steel plates were used, as well. Viton rubber "O" rings were used to provide a good seal between the glass and the PTFE plates.

The stirrers and baffles were made of PTFE. The stirrers and central baffle were supported on three concentric shafts that passed through the centre of the top plates. The inner shaft was made of a stainless steel rod covered by PTFE tubing. It was fixed to the lower stirrer by press fitting. The tip of the inner shaft was machined to mate with a guide bearing that was press fitted in the centre of the bottom PTFE plate, to ensure that the stirrers rotated about the central vertical axis. The middle tube was made in glass and held the central baffle by press fitting. The upper chamber stirrer was machined from a PTFE rod. This stirrer and the outer tube was made in a single piece. A PTFE bearing, pressed into the outer tube at the stirrer end, supported this tube on the bearing support. The PTFE bearing support was pressed in the centre of the top plates. The middle shaft was clamped to the motor board in a mounting block and the shaft was positioned so that all shafts lined up exactly with the central baffle. A PTFE bearing pressed in the top of the inner stainless rod located the upper end of the inner shaft. This bearing was positioned by a mounting block screwed to the motor board. The two stirrers were driven through 1:1 Nylon 66 gears.

A set of lower stirrers were made so that it was possible to have different lower stirrer heights. A set of rings that mated with the outer tube was made, so that both upper and lower stirrers could be located

at different distances from the interface. The interfacial area could be varied easily by changing the central baffle. A set of central baffles were available. Interfacial areas of 20, 25, 30, 35 and 40 cm² could be used.

The vertical baffles were fixed using PTFE rods. Grooves in the upper and lower PTFE plates ensured their correct positioning. The ring baffle was fixed between the vertical baffles, guided by PTFE rods.

The base plate and motor board were fixed to a steel frame to ensure correct alignment. Two access ports were drilled in the base plate. The ports could be sealed either with PTFE plugs (with Viton rubber "O" rings) or glass drain stopcocks. The top plates also had six access ports which could be closed by PTFE plugs protruding about 1 cm above the water level. Two of these ports had direct access to the lower chamber, passing through the ring baffle, so that the interface would not be crossed. These ports were used both to add the aqueous solution to the lower chamber and also for circulating the solution out of the cell and through a spectrophotometer, using a peristaltic pump, so that the aqueous solution could be analysed continuously and the results recorded on a chart recorder. Alternatively, the same procedure could be carried out with the organic phase using two access ports in the upper chamber. The spare ports could be used to collect samples, add material, or to insert an electrode (e.g., pH electrode). In all extraction experiments the concentration of the transferred species was monitored in the organic phase, whereas in all stripping experiments, in the aqueous phase. The aqueous/organic solutions were circulated outside the cell using PTFE tubing. All the joints were made in glass or Viton rubber tubing.

Two Parvalux 1/12 H.P. single phase electric motors powered the stirrers. Each motor was controlled by a 0.7 amp Phillips Variac and the alternating current output of the variacs was converted to direct current using full wave rectifiers, as this afforded smoother operation, especially at low speeds. A reversing switch in the circuit of the upper stirrer motor permitted co- or contra-rotating operation. The double ended motor output shafts were connected at one end to the drive gears and at the other end to accurate Eddy-Current tachometers reading to within $\pm 1\%$ of full scale. The lower stirrer tachometer read 0 to 500 rpm (or 0 to 800 rpm if necessary, using another tachometer) in divisions of 10 rpm. The upper read 500 to 0 to 500 in divisions of 20 rpm. With this arrangement, once the motors were warmed up, stirring could be controlled from 20 to 480 rpm (or 20 to 780 rpm) with a fluctuation of less than ± 5 rpm.

A Tempunit heater-stirrer-pump in a water bath circulated water to the water jacket. The flow and water level in the water jacket were controlled by an inlet valve on the water jacket inlet and a pinch clamp on the return tubing. The system was operated to give the highest possible inlet pressure to maximize the stirring in the water jacket. Temperature was monitored in the water jacket. Temperature was monitored in the water jacket next to the cell, using an accurate mercury immersion thermometer reading to 50°C in 0.1°C divisions. The set temperature could be controlled to $\pm 0.1^{\circ}\text{C}$ without difficulty. The water bath provided a liquid reservoir to prevent sudden changes in the water jacket temperature. The level in the water jacket was maintained to immerse the top plate in about 10 mm of water using inlet and overflow valves. The cell was completely submersed. The water bath was also used to bring solutions to the appropriate temperature before a run was started.

The cell could be dismantled into its individual components, cleaned thoroughly and rebuilt, easily and quickly.

A spectrophotometer PYE-UNICAM SP6-200 was used for the iron (III) analysis. Flow cells of 5 mm and 10 mm path length were available, so that continuous readings of iron (III) concentrations as a function of time of extraction were obtained. Wavelengths of 325-1000 nm could be used. The accuracy of absorbance measurements in the range 0-1 absorbance units were found to be better than 1%.

A recorder Smiths Servoscribe RE 520-20 was connected to the spectrophotometer so that the reaction kinetics could be followed easily. A 10 mV output was used. The calibration accuracy, linearity and reproducibility was found to be within $\pm 0.5\%$ of the full scale. The chart speed accuracy was about $\pm 1\%$ on all speed ranges.

CHAPTER V

EXPERIMENTAL PROCEDURE

5.1. MATERIALS

5.1.1. Trioctylamine (TOA)

Technical grade TOA was obtained from Fluka AG. The molecular weight of this material, measured by vapour pressure osmometry was 353 ± 5 (Appendix B.1.5.), whereas potentiometric titration with standard HCl gave 352 ± 1.6 , indicating a high degree of purity (theoretical M.W. = 353.68).

A small amount of TOA was distilled under reduced pressure. The main fraction had a boiling point of 126°C at 0.1 mm Hg pressure. A middle fraction was collected as the purified reagent. In order to verify the purity of the TOA, the distilled fraction and the as-received material were compared using Infra-Red Spectrophotometry, which will identify different chemical bonds in an organic compound. The spectra of two samples were identical indicating that the as-received material contained no detectable extraneous chemicals.

In order to check the purity of the distilled and as-received material, mass spectrometry and gas chromatography were used. Both materials were run through the mass spectrometer, but the resulting spectra were complex and difficult to interpret. It was qualitatively observed that the spectrum of the purified material was simpler than that of the as-received material. In both cases it was noted that there was a large peak at M.W. = 353 and no peak above this value, indicating that the impurities in the as-received material, if any, would

have a M.W. lower than 353. Gas chromatography of the distilled material gave a single peak indicating good purity, whereas the as-received material produced three extra small peaks (probably of other amines) and had an estimated purity of 96%.

Purification of larger amounts of TOA by vacuum distillation proved to be unsatisfactory and gave a low yield and it was decided to use the as-received TOA.

Solutions of TOA in A.R. toluene were prepared as required and standardised by potentiometric titration with standard HCl.

5.1.2. Trioctylamine hydrochloride (TOAHCl)

Solid TOAHCl was prepared from TOA (Fluka product) by shaking a solution of 100 ml 0.5 M TOA dissolved in petroleum ether (b.p. 40-60°C) with three separate 100 ml volumes of 0.5 M HCl. The organic phase was washed three times with 200 ml of 1 M LiCl. The organic phase was cooled to -20°C. A precipitate was formed which was filtered off. The precipitate was redissolved in fresh petroleum ether and the solution cooled again. The recrystallization procedure was repeated at least twenty times. After the last filtration the precipitate was dried by removing the petroleum ether by vacuum distillation (10 mm Hg pressure). The final product was a waxy white solid with a melting point of 72-73°C. The molecular weight of this material measured by potentiometric titration with standard NaOH gave 320 ± 2.16 (theoretical 390.23).

Pure solid TOAHCl was obtained from Eastman-Kodak. The catalogue specifies a m.p. of 72-74°C. A melting point determination for this product gave 72-73°C,

indicating that the recrystallised TOAHCl (from TOA Fluka) had an equivalent purity.

Practical stock solutions of TOAHCl (0.1 M) were prepared from TOA (Fluka product) solutions in toluene A.R. The TOA solution was first equilibrated with an equal volume of 0.1 N NaOH in order to remove any metal trace from the organic phase. Then, the organic phase was shaken with three separate equal volumes of 1 M HCl, followed by washing with an equal volume of 1 M LiCl. Potentiometric titrations of both TOA and TOAHCl solutions with standard HCl and NaOH, respectively, within the experimental error, gave the same concentration (in a molar scale), indicating that during the process of preparation of TOAHCl, the losses, if any, would be negligible.

Vapour pressure osmometry measurements of practical TOAHCl, recrystallised TOAHCl and "pure" TOAHCl (Eastman-Kodak product) presented in Appendix B.1 showed no significant difference, indicating a similar behaviour for all these materials.

5.1.3. Lithium chloride

Concentrated stock solutions of lithium chloride were prepared by dissolving G.P.R. lithium carbonate in 10 M A.R. HCl until the reaction was complete. Unreacted solid was filtered off and the lithium chloride solution was purified by equilibrating equal volumes of concentrated LiCl solution with a practical solution of TOAHCl in toluene in order to remove metal traces from the aqueous solution. The LiCl solution was then standardised. The chloride content was determined by Volhard's method and the lithium chloride content was checked by density measurement (plot of density versus concentration is presented in Figure 3.7.1.). Two stock solutions were prepared during the course of the work, and their analyses

are given below:

	LiCl content	Cl content
1st stock solution	9.19	9.25
2nd stock solution	10.52	10.48

5.1.4. ^{36}Cl isotope

100 μCi of ^{36}Cl (half-life = 3×10^5 years) in 0.85 ml of 0.1-0.3 M HCl was obtained from the Radiochemical Centre, Amersham, U.K. The isotope solution was diluted to 100 ml with 1 M HCl, to give a stock solution with an activity of 1 μCi per ml. A second stock solution was prepared in the same way, but with an activity of 2 μCi per ml. These stock solutions were used in aliquots of 5-10 ml per 500 ml of aqueous phase to give a working solution of 10^{-2} to 4×10^{-2} $\mu\text{Ci/ml}$, as required.

5.1.5. Ferric Chloride

Stock solutions of iron (III) chloride were prepared by dissolving in 1 M HCl the calculated quantities of FeCl_3 . The solutions were then standardised by titration with standard sodium thiosulphate and excess potassium iodide with starch as indicator²²⁶. The aqueous solution was prepared by the proper dilution of the stock solutions.

5.1.6. Other reagents

All other reagents used were standard A.R. grade reagents.

5.2. KINETIC EXPERIMENTS

The kinetic experiments were carried out using the stirred cell described in Chapter IV. The extraction or stripping concentrations as a function of time under a variety of conditions were followed by analysing continuously iron (III) in the phase to which the species involved in the reaction process were being transferred, as this greatly increases the precision of the method of initial rates, which was the method used to analyse the results.

The aqueous phase consisted of iron (III) chloride dissolved in solutions of 1 M HCl plus variable concentrations of LiCl, to give chloride concentrations, as required. No attempt was made to control the ionic strength of the solution.

The cell was assembled at the start of each experiment, dismantled at the end of it and carefully cleaned. The cleaning procedure consisted of, firstly, rinsing with distilled water followed by soaking in "used" acetone; secondly, rinsing with fresh acetone, followed by soaking in fresh acetone and finally air drying. Compressed air was not used because it contains some dispersed oil that could upset the mass transfer measurements; instead an industrial heat gun was used with good results. When radioactive ^{36}Cl was used, the cell components were soaked overnight in 0.1 M HCl.

The organic phase consisted of TOAHCl ("pure", purified or practical) dissolved in toluene (practical TOAHCl solutions prepared by dilution of the stock solution).

The aqueous and organic phases were pre-equilibrated in a separating funnel, vigorously shaken for one minute

and then allowed to settle overnight at room temperature (20-25°C). At the start of an experiment, the phases were separated into glass stoppered flasks which were immersed in the water bath with the heater-pump adjusted to the required temperature, before the last soaking with fresh acetone and then dried and re-assembled for the next experiment.

To start the experiment, the cell was assembled and brought to the desired operating temperature (using water from the bath that contained the two equilibrated phases at the required temperature). The aqueous phase was transferred to the cell by measuring out the required volume and using a funnel connected to a glass tube (or a flexible PTFE tube in some cases). Special care was taken when loading the cell to avoid air bubbles, especially in the aqueous phase, as this would displace the interface level or could affect the hydrodynamics in some way. After the aqueous phase had been transferred to the lower chamber of the cell, the organic phase was transferred to the upper chamber using a funnel connected to a flexible PTFE tube bent at the open end. Extra care was taken when loading the organic phase in order to avoid any mixing of the phases or turbulence at the interface, which could cause the uncontrolled start of the reaction. When both phases had been transferred to the cell, the stirrer motors were started (which were allowed to warm up for about an hour in order to give constant speed, before the transfer of the aqueous and organic phase was begun) and timing was begun.

The chemical analysis in either the organic or aqueous phase, depending on whether it was an extraction or a stripping experiment, was performed by circulating the solution out of the cell and through a spectrophotometer equipped with a flow cell. A peristaltic pump was used for this purpose. The change in absorbance of the solution with

time was recorded on a chart recorder. Before the timing of the experiment had begun, the spectrophotometric flow cell was washed with absolute alcohol and all the PTFE tubing connected. In order to check if the pumping operation could be carried out efficiently with no leaks, absolute alcohol was circulated through the PTFE tubings and spectrophotometric flow cell. This was also found to be necessary in order to be sure that everything was well cleaned, with no contamination from previous experiments. The alcohol was removed by circulating pure toluene (or distilled water when stripping), followed by circulating the organic phase (or the aqueous phase when stripping) in order to correct for any zero drift in the spectrophotometer. Then, the standards were circulated through the flow cell and the absorbances recorded in the chart recorder. After this, the PTFE tubing were cleaned as described above, the zero of the machine checked, and the equipment was ready to record the kinetic of the reaction. At the end of the experiment, the PTFE tubing and flow cell were cleaned again and the standards were circulated through the flow cell in order to check the calibration curve for any drift in the absorbance. In all cases, an error of less than $\pm 0.5\%$ in the slope was found when comparing both calibration curves, so that the absorbance as a function of time recorded during the kinetic experiment could be considered reliable. It was found that the calibration curve did not vary significantly from one experiment to another, even if the period between those experiments was several months, provided that the cleaning operation of the PTFE tubing and spectrophotometric flow cell was carefully carried out.

The volume of the solution filling the PTFE tubing and flow cell was about 20 ml, representing a dead space of about 4% of the total volume of the phase, which was flowing at a rate of about 60 ml/min giving a time-lag

of about 10 seconds. It was found that the effect of dead space and time-lag could be neglected in most of the experiments.

The experiment was stopped when the absorbance reached a value of 1.0 unit or after 60 minutes. In some cases, longer runs were either recorded on the chart recorder or samples were taken and diluted - if the concentrations were off the scale of the instrument. In some runs, sample were taken from both phases and analysed by independent methods, in order to check the mass balance.

When radioactive ^{36}Cl was used in an experiment, 6 ml samples of organic solution were taken and the analysis of iron (III) was carried out using a spectrophotometric method and the chloride by liquid scintillation of the beta emission of ^{36}Cl . Both methods are described in the following section - "chemical analysis".

At the end of some runs equal volumes of both phases (25 ml each) were drawn from the cell and shaken together for about five minutes at room temperature (20-25°C) to determine the equilibrium distribution ratio (D).

Finally, the solutions were drained off and the cell was dismantled and cleaned for the next experiment, as described above.

5.3. CHEMICAL ANALYSIS

Chemical analysis was carried out continuously by circulating out of the cell the solution through the flow cell of a Pye UNICAN SP6-200 spectrophotometer.

5 mm and 10 mm path length cells were used depending on the experimental conditions.

Iron (III) chloride, when extracted by TOAHCl, forms a yellow complex of which a typical spectrum is shown in Figure 5.3.1. At $\lambda = 365$ nm a peak is observed. At this wavelength Beer's law is obeyed and a typical calibration curve is shown in Fig. 5.3.2. This calibration curve is linear up to 0.02 gm Fe/l when using 5 mm path length cell. When the concentration was off the scale of the instrument, samples of the organic phase were taken and diluted with toluene, as required. A stock solution for the standards was prepared by equilibrating equal volumes of 0.1 M of TOAHCl in toluene with 10^{-2} M of iron (III) chloride in 10 M chloride (1 M HCl + 9 M LiCl). Atomic absorption analysis of iron in the aqueous phase after extraction, showed that the residual iron concentration in the aqueous phase was below 0.1 ppm and 100% extraction was assumed. The standards were prepared by diluting the stock solution with solutions of TOAHCl in toluene, as required. Master standards were stored in tightly stoppered flasks and not used for longer than four weeks; comparison with freshly made solutions showed no deterioration during this time.

Attempts to analyse the organic phase by atomic absorption using absolute alcohol or MIBK as diluent were unsuccessful. Apparently, toluene does not burn completely and the results were not reproducible.

Quantitative stripping of iron from the organic phase with 6 M HNO_3 was possible. The aqueous phase was diluted to 0.6 M HNO_3 and iron analysed by atomic absorption. Reasonable results were obtained, although slightly scattered.

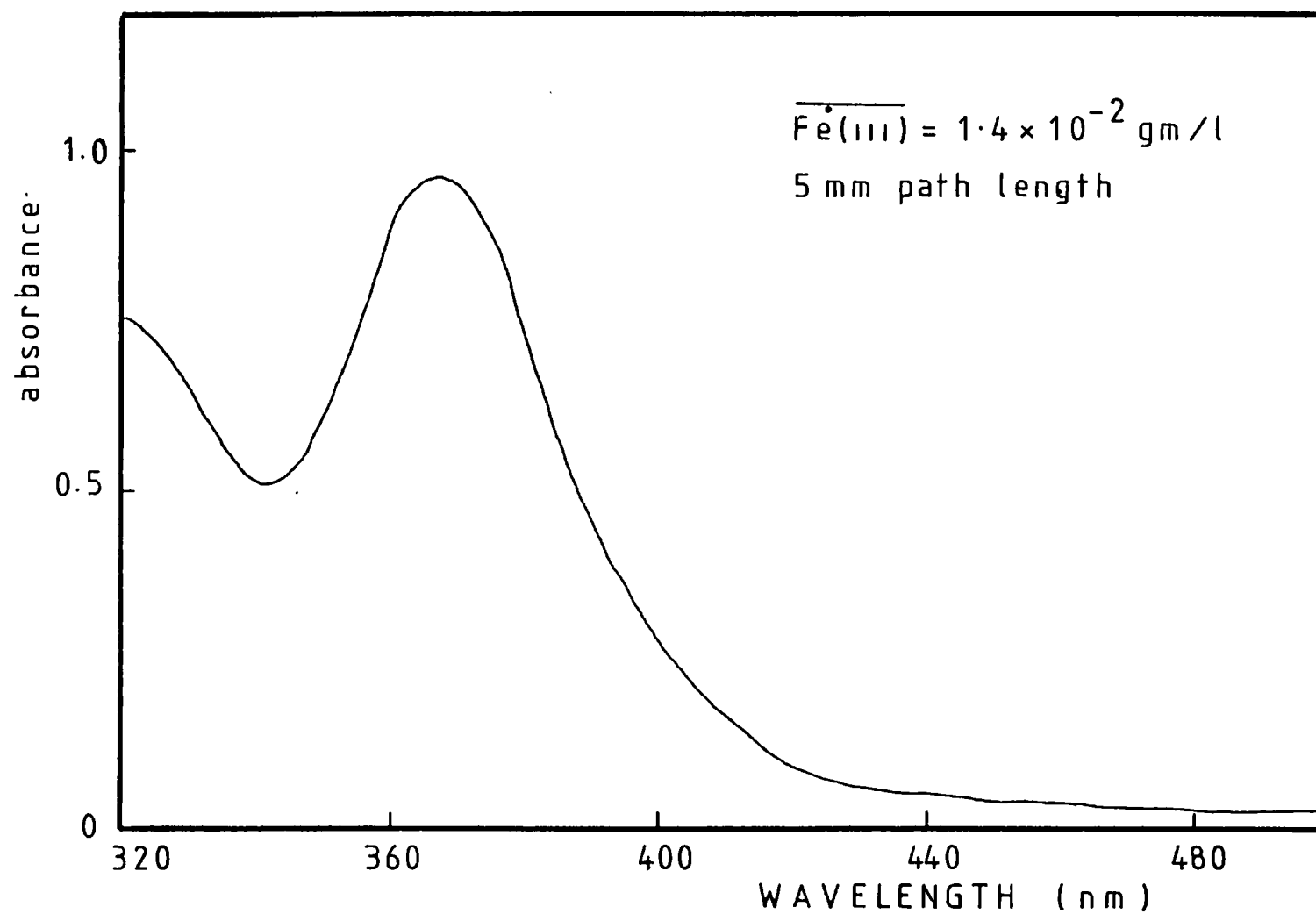


FIGURE 5.3.1. TYPICAL SPECTRUM OF THE SYSTEM Fe(III) - TOAHCl IN TOLUENE.

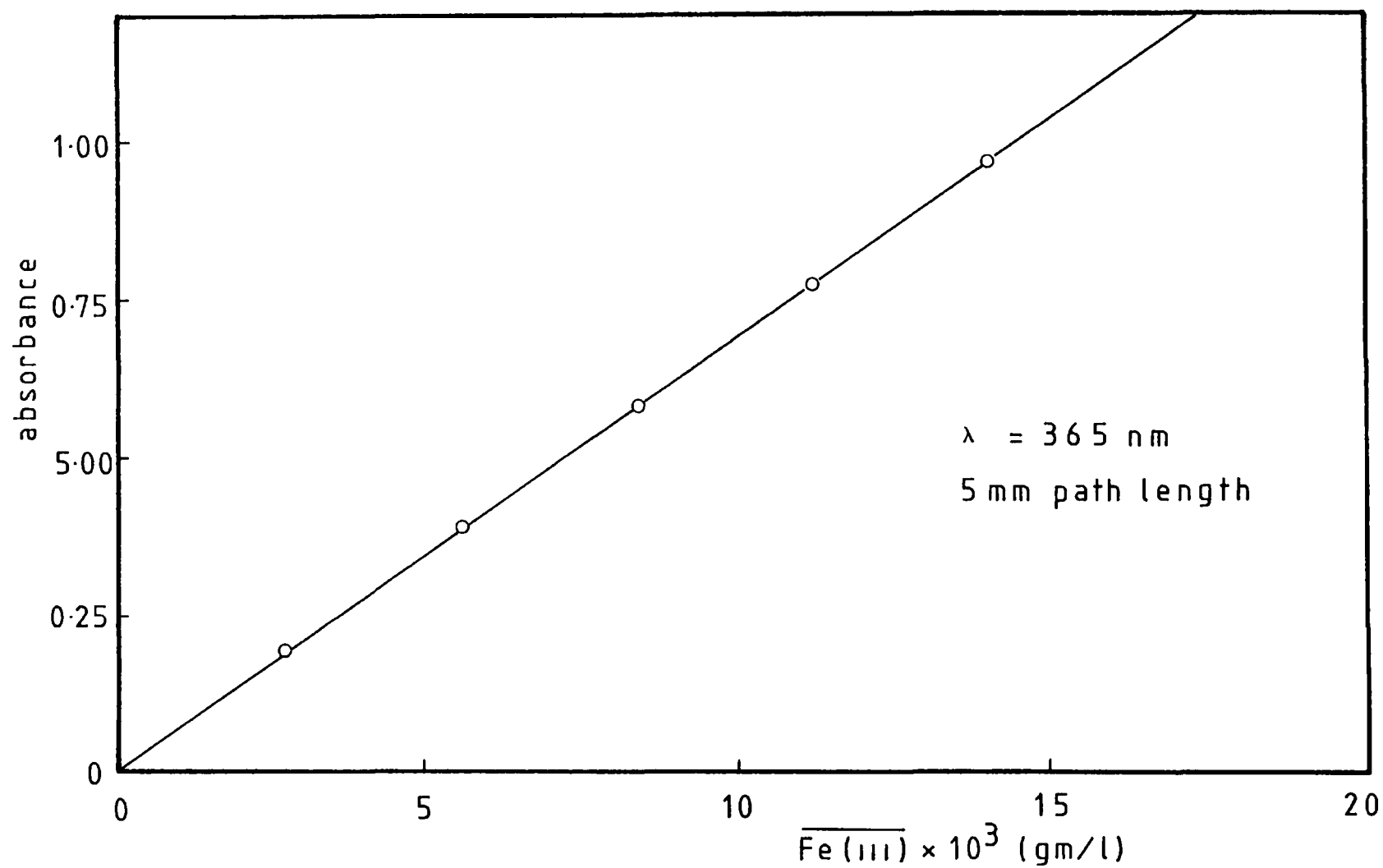


FIGURE 5.3.2. TYPICAL CALIBRATION CURVE FOR Fe(III) CONCENTRATIONS IN THE ORGANIC PHASE.

Typical spectra of aqueous solutions of iron (III) at different chloride concentrations are shown in Figure 5.3.3. These spectra were determined using a UNICAM SP-800 UV spectrophotometer by scanning a band of wavelength. They are not very accurate and give just a qualitative representation of the different spectra. In all cases a peak is observed for each spectrum. As the chloride concentration increases there is a shift in the wavelength of the peak, indicating variation of the composition of the chlorocomplexes. The spectra are far too complicated and no attempt was made to determine the stability constants of the chlorocomplexes in these solutions. The accurate determination of the wavelength of the peak of each spectrum was carried out in the Pye UNICAM SP6-200 spectrophotometer used to measure the iron concentration as a function of time during the kinetic experiment. At each of these wavelengths Beer's law is obeyed. Linear calibration curves are obtained, provided the standards have the same chloride concentration. When the concentration was off the scale of the instrument, samples of the aqueous phase were taken and diluted with a chloride solution with the same concentration as the aqueous phase.

The aqueous phase could also be analysed by atomic absorption but the results were less accurate and less reproducible than the results obtained using the spectrophotometric method described above.

A typical result of a kinetic experiment is shown in Figures 5.3.4. and 5.3.5. The change in the organic iron (III) concentration with time was determined by different analytical methods. Continuous reading of the iron (III) content using the spectrophotometric method described above gave the most accurate and reproducible results. The change in the aqueous iron (III) concentration with time was determined by atomic

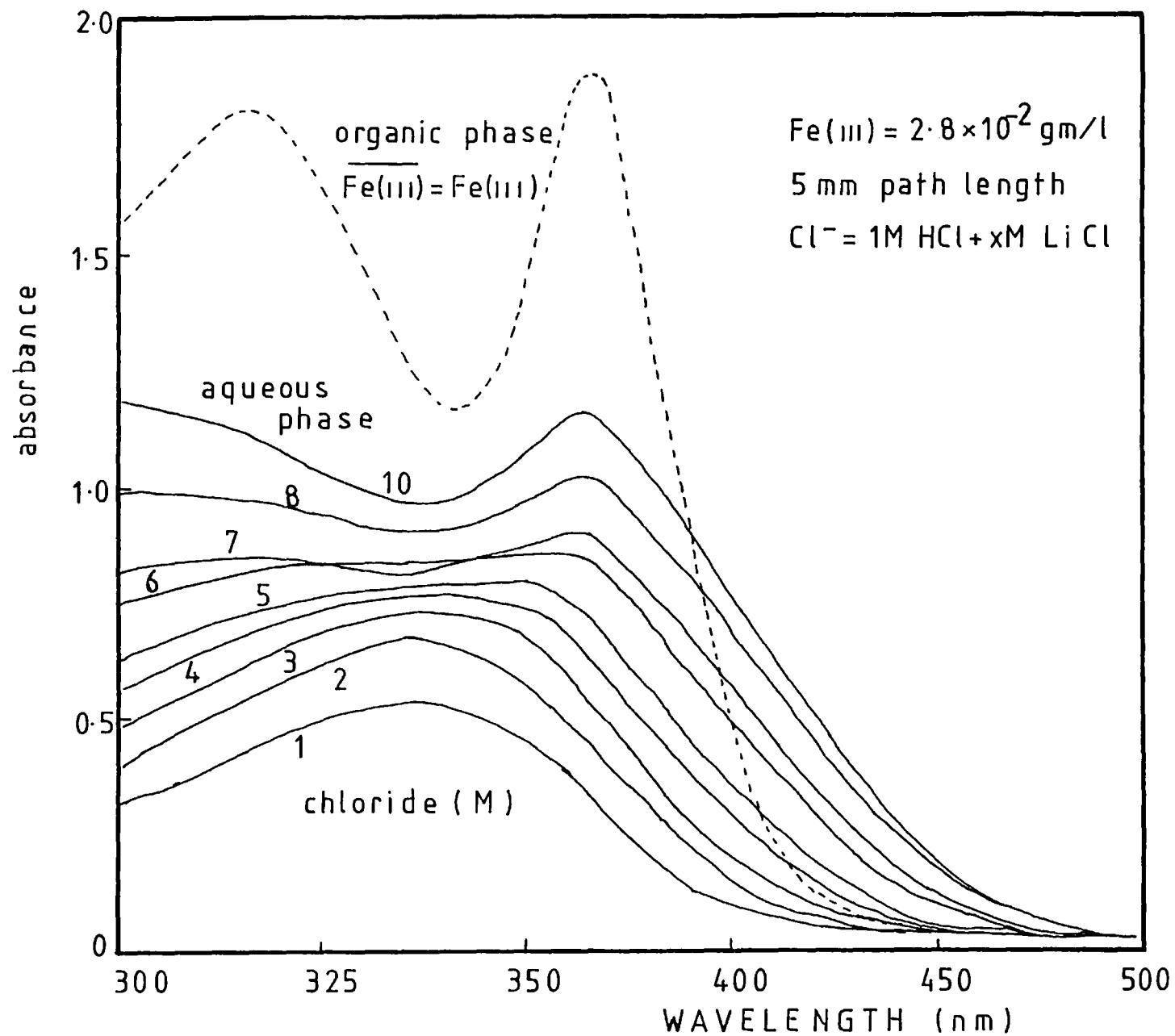


FIGURE 5.3.3. TYPICAL SPECTRA OF Fe(III) - HCl(LiCl) SYSTEM.

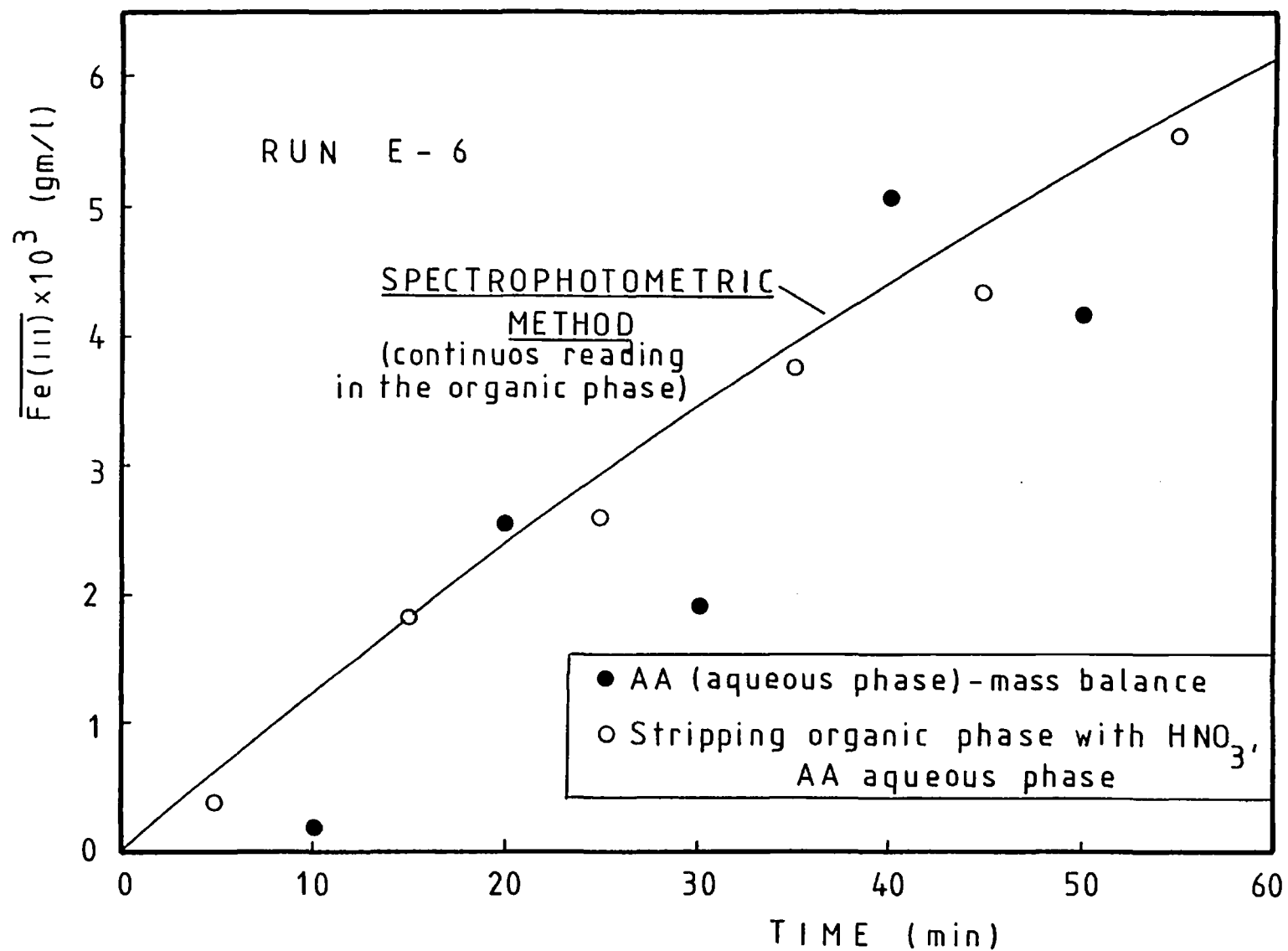


FIGURE 5.3.4. COMPARISON OF DIFFERENT METHODS USED TO DETERMINE THE Fe(III) CONTENT IN THE ORGANIC PHASE IN A TYPICAL EXTRACTION KINETICS EXPERIMENT.

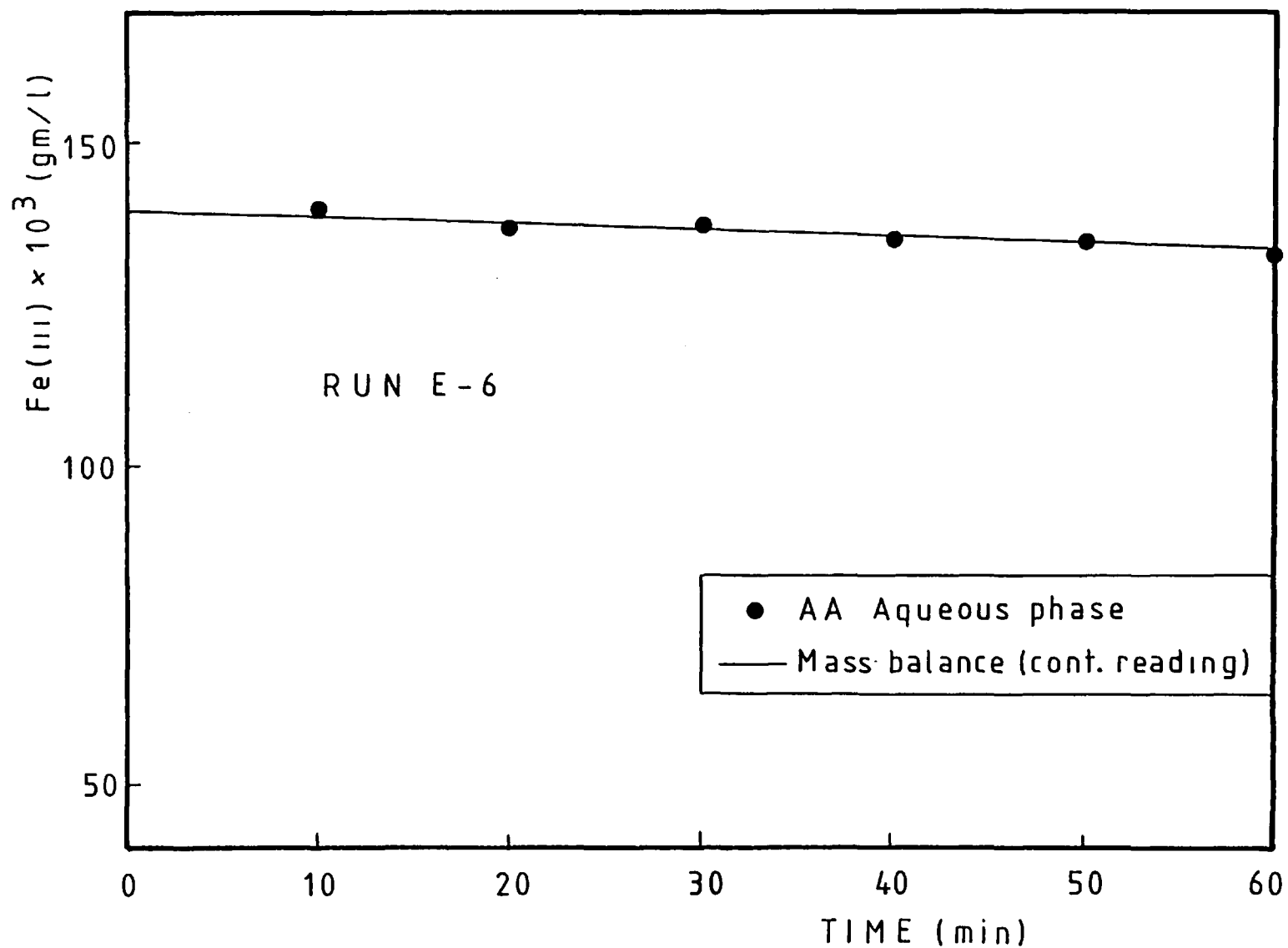


FIGURE 5.3.5. COMPARISON OF DIFFERENT METHODS USED TO DETERMINE THE Fe(III) CONTENT IN THE AQUEOUS PHASE IN A TYPICAL EXTRACTION KINETICS EXPERIMENT.

absorption and mass balance of the organic iron (III) concentration. The results show the inadequacy of analysing the aqueous phase in the extraction kinetics experiments, as relatively small errors in aqueous iron (III) concentration would give large errors in the organic iron (III) concentration, especially at the beginning of the experiment ($t \rightarrow 0$).

Table 5.3.1. shows how the results of a kinetic experiment were recorded.

5.4. β -COUNTING

The kinetics of chloride transfer was investigated using liquid scintillation counting of the beta emission of ^{36}Cl .

The equipment used was a two-channel liquid scintillation beta counter consisting of a E.M.I. Liquid Measuring Head 2022 - which contains the two photomultipliers tubes with the shutter, coupled with a Harwell 2000 Series Equipment - which contains an amplifier, an electronic unit with the discriminators, coincidence unit and high voltage supplies, and a scaler.

The advantage of using coincidence counting is due to the fact that measurements can be carried out at room temperature ($20-25^{\circ}\text{C}$), since noise pulses from the photomultipliers are largely rejected automatically.

The scintillation solution consisted of 8 gm of 2,5-diphenyloxazole (P.P.O.) and 0.36 gm of 1,4-bis-(2-(5-phenyloxazole))-benzene (P.O.P.O.P.) dissolved in 1 l. of sulfur-free toluene.

KINETICS of S-X						RUN E - 6			
SYSTEM: TOA(toluene) / Fe(III)-HCl - LiCl (water)									
Initial Concentrations			Counter - Rotating RPM			Spectrophotometer			
TOAHCl 0.01 M			Organic 250			$\lambda = 365 \text{ nm}$			
Fe (III) 0.00221 M			Aqueous 250			Abs Scale 0-1			
Cl ⁻ 1 M			T (°C) 25			Path Length 5 mm			
HCl 1 M			A (cm ²) 30			Recorder			
LiCl 0			V _{org} = V _{aq} 480 ml			mv. 10			
						Speed 600 mm/hr			
t	x 100 abs	x 1000 conc (gm/l)	t	x 100 abs	x 1000 conc (gm/l)	MAIN RESULTS: $c = c(t) = 0.128t - 0.0004 t^2$ $\frac{dc}{dt} = f(t) = 0.128 - 0.0008t$ CALIBRATION CURVE $c = 0.145 \text{ abs}^*$ $\text{abs}^* = \text{abs} \times 10^2$			
0	0	0	50	36.5	5.293				
5	4.3	0.624	55	39.2	5.684				
10	8.7	1.262	60	43	6.235				
15	12.7	1.842							
20	16.3	2.364							
25	20	2.900							
30	23.4	3.393							
35	27	3.915							
40	30.2	4.379							
45	33.7	4.887							
STANDARDS									
$\lambda = 365 \text{ nm}$									
abs x 100	0	19.5	39.0	58.0	77.0	97.0			
conc gm/lx10 ³	0	2.8	5.6	8.4	11.2	14.0			

TABLE 5.3.1. Typical results of a kinetic experiment.

The analyses were carried out using appropriate plastic vials (Koch-Light product) with a capacity up to 21 ml.

The organic reference solution was prepared in each experiment by equilibrating equal volumes of the organic phase (which contained known concentrations of TOAHCl in toluene) with the aqueous phase (which contained known concentrations of chloride and ^{36}Cl). The organic reference solution was this organic phase after phase separation.

It has been shown that the optimum operating conditions are obtained when the ratio R_S^2/R_B is maximum²²⁷, where R_S is the count rate from the sample alone and R_B is the background count. This is best achieved using a pulse height analyser (oscilloscope). Using this method conditions were optimized so that R_S^2/R_B was a maximum.

The organic solution contained some water, which is known to have a quenching effect on the β -counting. The addition of absolute alcohol usually helps to minimise or overcome this inconvenience. In order to investigate what proportion of scintillation solution/absolute alcohol would give the maximum relative efficiency, some of these proportions were tested. Approximate calculations (considering the ^{36}Cl activity in the aqueous phase and the volume and chloride concentrations of the phases) indicated that an appropriate sample volume of the organic phase would be 5 ml. The capacity of the vials was 21 ml. So a volume of up to 15 ml for the scintillation solution plus absolute alcohol could be used. The effect of this proportion on the counting rate of a typical organic sample is shown in Figure 5.4.1. The maximum counting rate was obtained when this proportion was 5 ml of scintillation solution/10 ml of absolute alcohol.

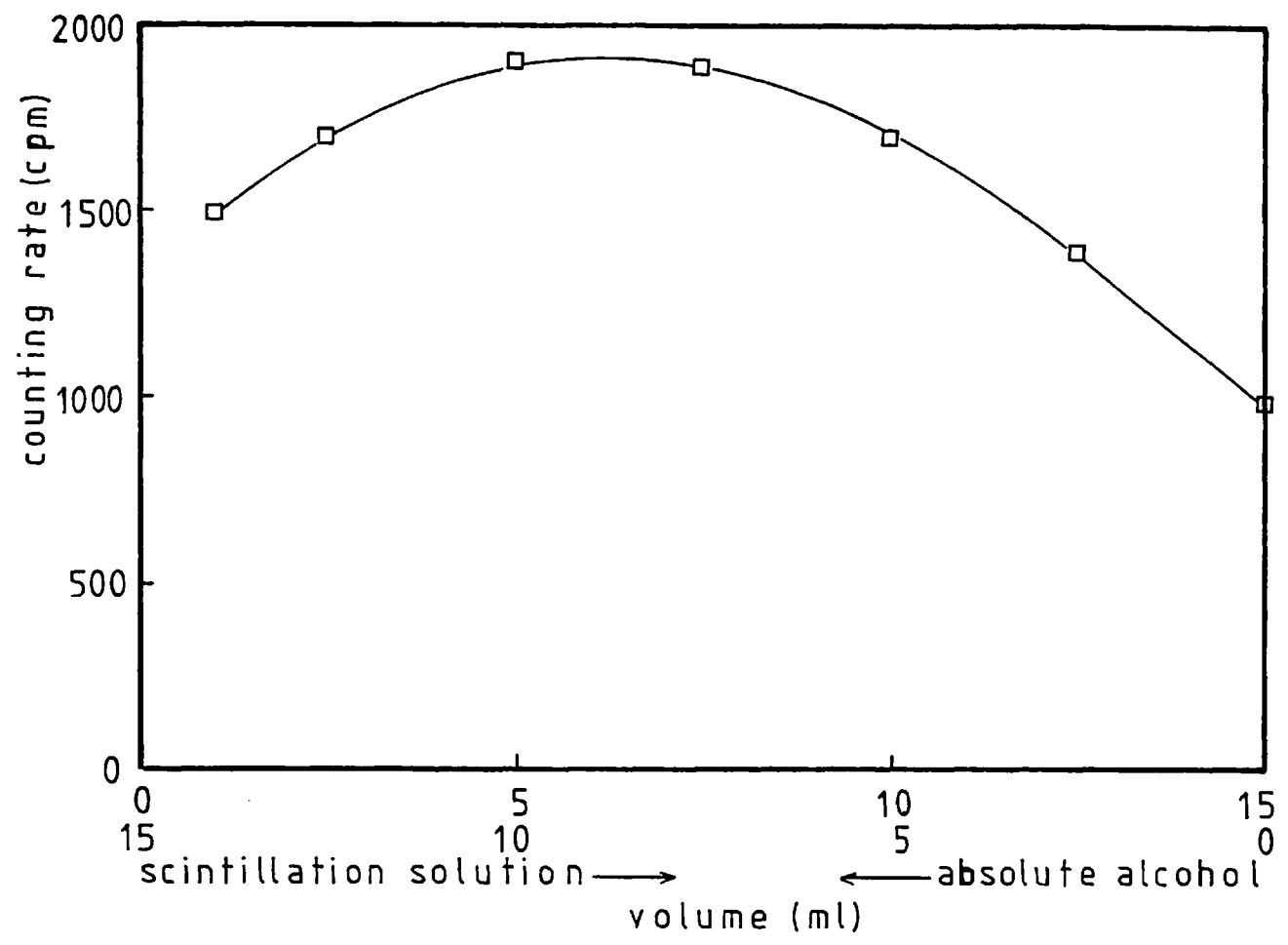


FIGURE 5.4.1. EFFECT OF THE PROPORTION OF SCINTILLATION SOLUTION/ABSOLUTE ALCOHOL ON THE β -COUNTING RATE.

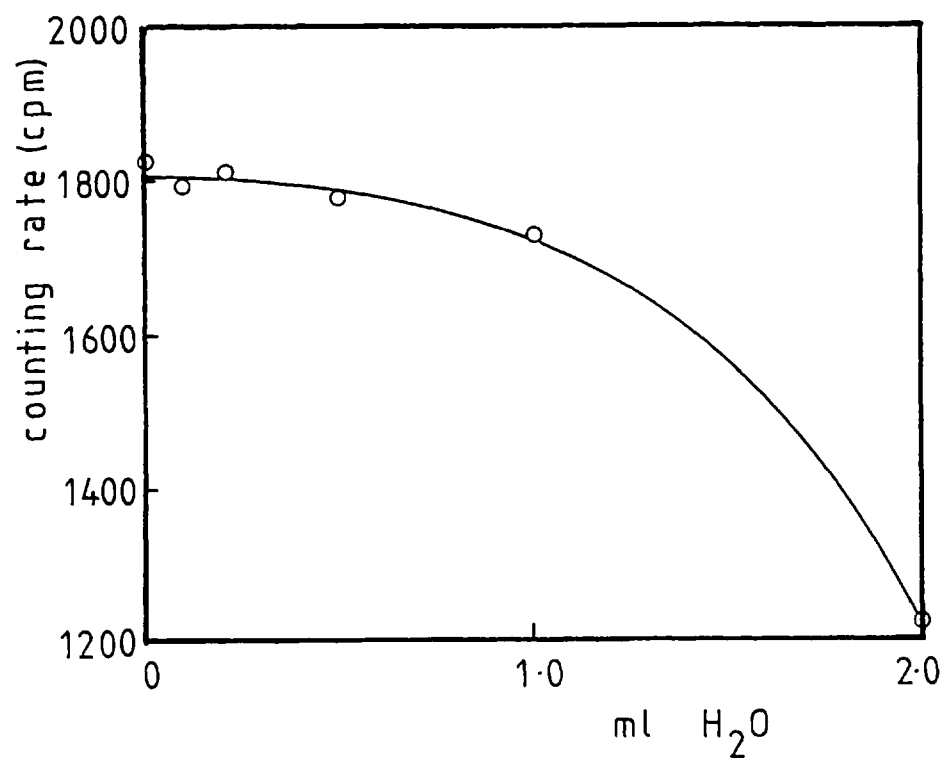


FIGURE 5.4.2. EFFECT OF WATER ON THE β -COUNTING RATE.

In order to investigate how much water could be "accommodated" by the counting solution, water was added to the samples. The results are shown in Figure 5.4.2. The presence of water up to 0.5 ml in the counting solutions had little effect on the counting rate.

When iron (III) chloride is extracted by TOAHCl a yellow complex is formed. To investigate the colour quenching effect, solutions of the organic phase with variable amounts of iron (III) at typical counting rates were prepared and analysed. It was found that iron (III)-TOAHCl complexes had a strong quenching effect. The results are presented in Figure 5.4.3. where the relative efficiency (Eff.) of the counting rate is defined as:

$$\text{Eff.} = \frac{\text{counting rate at Fe(III)} = \text{Fe(III)}}{\text{counting rate at Fe(III)} = 0} \times 100$$

The relative efficiency could be correlated to the concentration of iron (III) up to 0.2 gm/l through the equation:

$$\text{Eff.} = 100 - 175 (\text{Fe(III)}) \quad (5.4.1.)$$

$R_c^2 = 0.99$ and ST. DEV. = 0.0253 (22 d.f.) and Fe(III) concentration expressed in gm/l. Using this equation, the counting rate could be corrected for the colour quenching effect of Fe(III).

The counting solutions were made as follows:

Aqueous background: 5 ml of scintillation solution, 10 ml of absolute alcohol, 0.5 ml of water.

Aqueous reference: 5 ml of scintillation solution, 10 ml of absolute alcohol, 0.5 ml of aqueous phase before extraction.

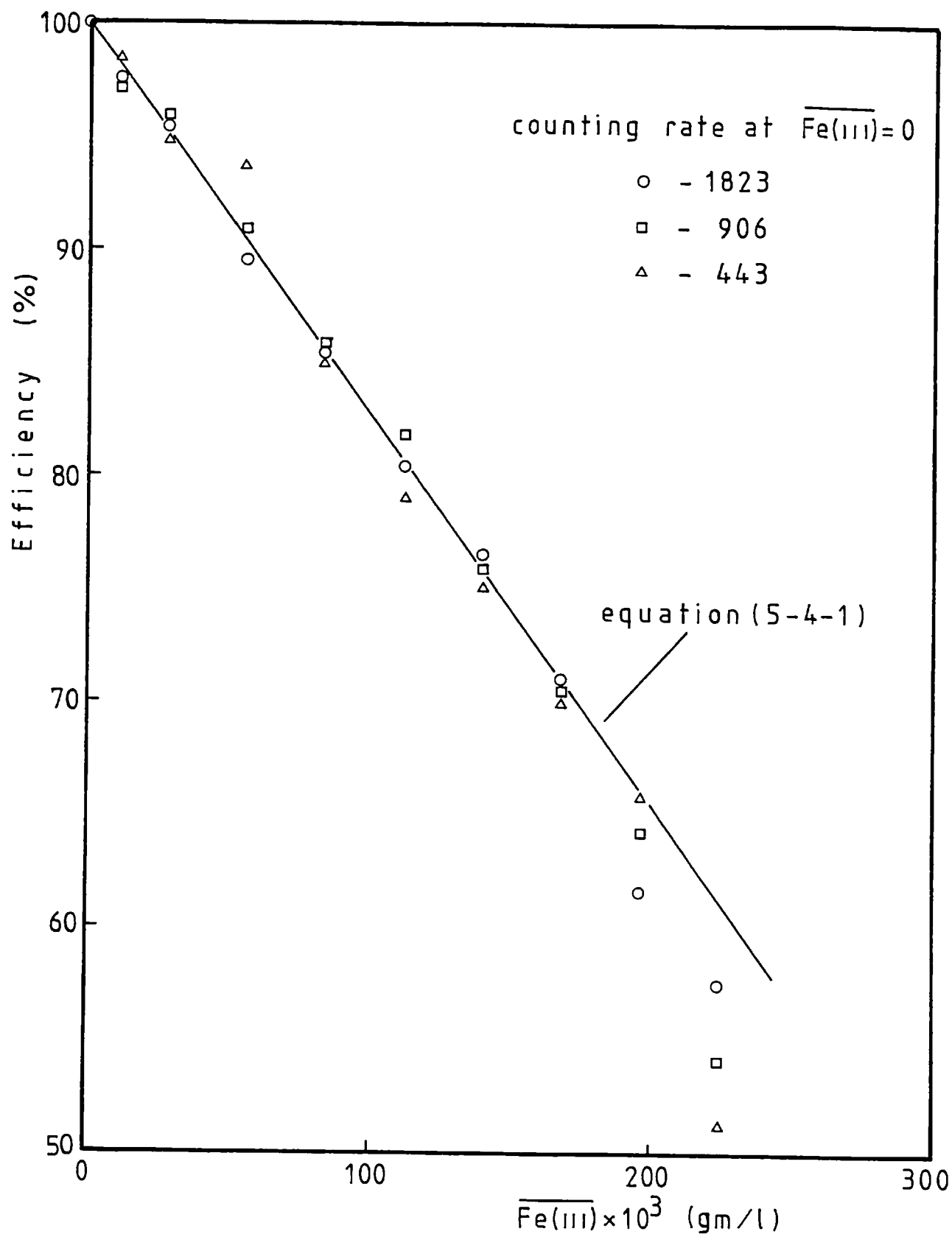


FIGURE 5.4.3. THE EFFECT OF Fe(III) CONCENTRATION ON THE EFFICIENCY OF THE COUNT RATE.

Aqueous samples: 5 ml of scintillation solution, 10 ml of absolute alcohol, 0.5 ml of aqueous phase.

Organic background: 5 ml of scintillation solution, 10 ml of absolute alcohol, 5 ml of organic phase before extraction.

Organic reference: 5 ml of scintillation solution, 10 ml of absolute alcohol, 5 ml of organic reference solution.

Organic samples: 5 ml of scintillation solution, 10 ml of absolute alcohol, 5 ml of organic phase.

The concentration of TOAHCl was always the same in all organic counting solution (background, reference and samples) in the same experiment, although it was found to have negligible effect on the count rate in the range of concentrations studied (up to 0.1 M TOAHCl).

Typical count rates obtained for the various samples were as follows:

Aqueous and organic backgrounds: 30-100 c.p.m.

Aqueous reference: 10000-50000 c.p.m.

Aqueous samples: 10000-50000 c.p.m.

Organic reference: 4000-6000 c.p.m.

Organic samples: 200-2000 c.p.m.

Counting was carried out until a net count of at least 2500 was obtained, to give 95.6% chance of the percentage error being less than $\pm 4\%$. In most cases, the net count was about 10000 (estimated error $< \pm 2\%$).

5.4.1. Statistical analysis of β -counting

Disintegration of radioactive materials is a random process, so the measurements of the counting rate will give only an approximation to the true value. If many observations over identical periods are made of the

same source, the counting rate obtained will follow a normal distribution, the mean of which is the best estimate.

In order to check whether the counting equipment was behaving properly, a statistical analysis was carried out. An organic sample was placed in the measuring head unit and 100 counting rates were measured, each of one minute duration. The observations were taken in a continuous series without long interruptions, and the experimental conditions were kept undisturbed throughout. The counting rates, uncorrected for background, dead-time, etc., were used in the calculations. The results are presented in Table 5.4.1.

If the data belong to a normal population the standard deviation (ST. DEV.) and the square root of the mean ($\bar{X}$) should be equal.

It was found that

$$\text{ST. DEV.} = 178$$

$$\sqrt{\bar{X}} = \sqrt{16015} = 126$$

In this case, they are not equal and the question arises whether the difference is significant (due to any fault in the counting equipment) or merely due to the finite number of observations.

A histogram of the results is presented in Figure 5.4.4. Apparently it looks like a histogram of a normal population. A better way to decide whether a sample of data might have come from a normal population is to plot the data on normal probability paper. This plot will be approximately a straight line if the data come from a normal population. If the plot curves substantially,

C1 (1-25)	C2 (26-50)	C3 (51-75)	C4 (76-100)
16167	15992	16055	15944
16373	16055	15864	16033
16145	16095	15984	16150
16150	15981	15883	15919
15967	15904	15958	15687
15958	16078	16028	15977
16082	15763	16029	15905
15815	15987	16050	15843
16037	16197	16014	15885
15769	15903	15824	16116
16291	16063	15849	16129
16064	16174	15899	16289
16047	15969	15740	16236
16019	15609	16054	16295
16062	15923	16017	16184
15984	15915	16036	16630
15744	16130	16166	16059
16997	15941	15827	16013
16054	16107	15763	15903
16154	15972	16249	15888
16001	16041	15873	15944
16122	15887	15830	15919
15959	15822	15961	15913
16111	16150	15928	16174
15969	15918	15888	16041

where C1 are observations 1 to 25
C2 are observations 26 to 50
C3 are observations 51 to 75
C4 are observations 76 to 100

TABLE 5.4.1. Counting rate (c.p.m.) of ^{36}Cl .

counting rate (cpm)	MIDDLE OF INTERVAL	NUMBER OF OBSERVATIONS
15500.	1	*
15700.	3	***
15900.	9	*****
15900.	22	*****
16000.	28	*****
16100.	19	*****
16200.	12	*****
16300.	3	***
16400.	1	*
16500.	0	
16500.	1	*
16700.	0	
16800.	0	
16900.	1	*

FIGURE 5.4.4. Histogram of β -counting results

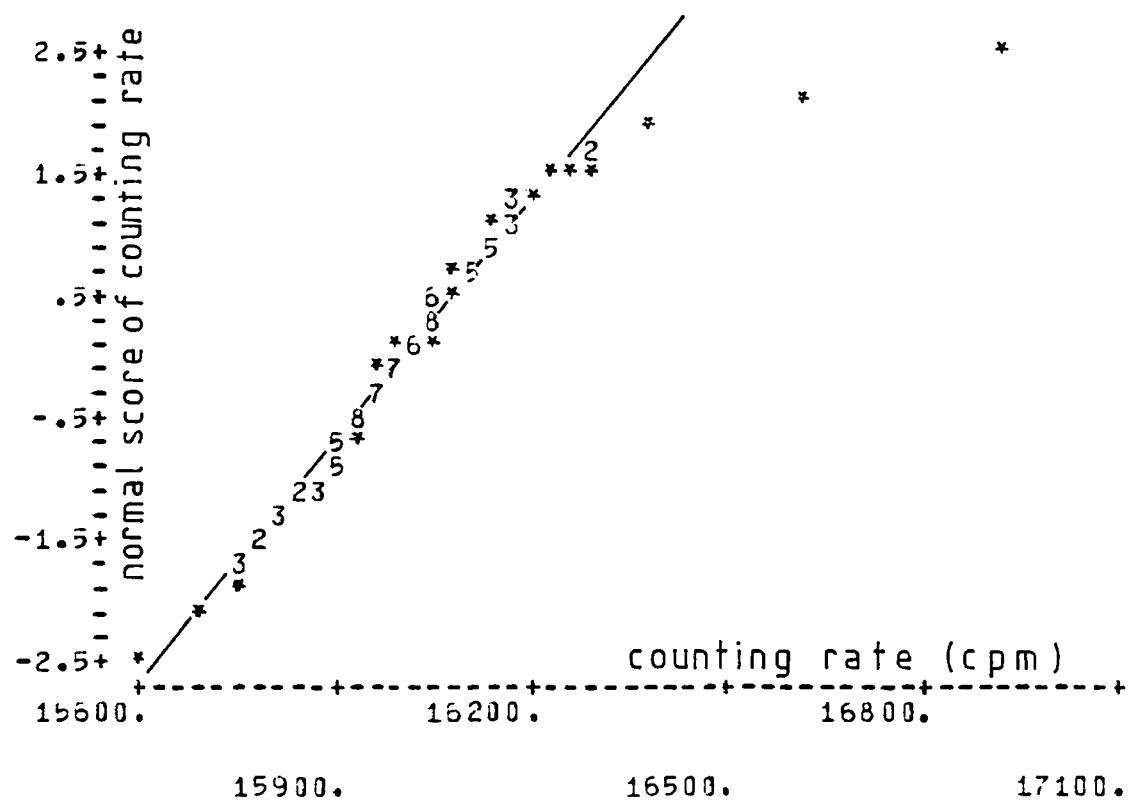


FIGURE 5.4.5. Plot of normal scores of β -counting results against counting rate.

then it is likely the data do not come from a normal population. A normal probability plot was carried out using a computer library package called MINITAB²²⁸. A plot of normal scores of the data is presented in Figure 5.4.5. This plot shows that most of the data are in a straight line, although there is some curvature. But is it curved enough to doubt the normality of the data? The "straightness" of the probability plot can be measured by the correlation coefficient of the points in the plot. This is a very powerful test for normality²²⁹. A very high correlation is consistent with normality. A table is given in Reference 229 so that the hypothesis of normality can be ascertained.

The linear correlation coefficient (R_c) between normal scores of counting rates and counting rates was found to be $R_c = 0.982$, indicating a probability of about 95% that the data came from a normal population. Hence, the discrepancy between the observed results and theoretical expectation cannot be regarded as significant and the difference obtained between the standard deviation and the square root of the mean is not unreasonable. The non-normal observations could have their origin in spasmodic fluctuations in the counting equipment, probably due to some fault in the operation of the scintillation assembly.

In order to investigate the stability of the counting equipment the results in Table 5.4.1. were split up in six data sets and then compared with a data set containing all the results, as follows:

- C1 - observations 1 to 25
- C2 - observations 26 to 50
- C3 - observations 51 to 75
- C4 - observations 76 to 100
- C5 - observations 1 to 50

-- ADVANCEWAY ON DATA IN C1,C2,C3,C4,C5,C6,C7

		LEVEL						
		C1	C2	C3	C4	C5	C6	C7
16800.	-		1			1		1
	+				1		1	1
	-							
	-							
16200.	+	2			2	2	2	4
	-	4	3		4	7	6	13
	-	8	7	2	5	15	11	26
	-	8	10	6	9	18	16	34
	-	1	2	7	3	3	11	14
	-	2	1	8	1	3	3	6
15600.	+		1	2		1		1

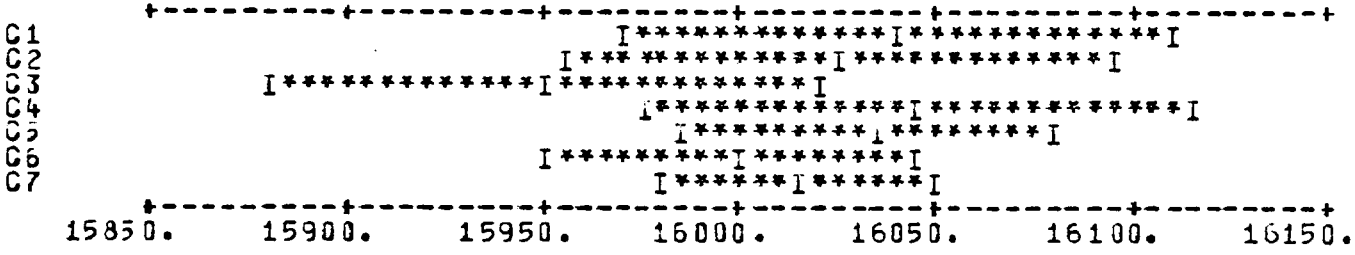
ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	6	173363.	28894.	.92
ERROR	293	9249396.	31568.	
TOTAL	299	9422759.		

LEVEL	N	MEAN	ST. DEV.
C1	25	16042.	142.
C2	25	16023.	230.
C3	25	15951.	123.
C4	25	16044.	192.
C5	50	16033.	189.
C6	50	15998.	166.
C7	100	16015.	178.

POOLED ST. DEV. = 178.

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)



where C1 = count rate 1 to 25
C2 = " " 26 to 50
C3 = " " 51 to 75
C4 = " " 76 to 100
C5 = " " 1 to 50
C6 = " " 51 to 100
C7 = " " 1 to 100

TABLE 5.4.2. Analysis of variance of β -counting rates.

C6 - observations 51 to 100

C7 - observations 1 to 100

The scintillation solutions are sensitive to light so that it is necessary to acclimatise them in the dark of the sample chamber in the measuring head unit for some time before the counting starts. If the given time was not enough, the non-normal results would be expected to appear in the first set of data, probably at the beginning of it. Analysis of the data in Table 5.4.1. shows this was not the case.

Plots of normal scores of data set C1 to C7 were carried out and the hypothesis of normality tested for each data set. The results were similar for all data sets indicating that any of them would be a reasonable representation of the same normal population and the non-normal observations would happen at random.

Analysis of variance of data set C1 to C7 were carried out. The results are presented in Table 5.4.2. At 95% level of confidence no significant difference was found amongst the data sets indicating that there was no "time" effect in the counting rate and no reason to suspect of the stability of the equipment.

5.5. COMPUTATION OF MASS TRANSFER RATES

MINITAB²²⁸ was used to fit an equation to the data of organic (or aqueous) iron (III) concentration against time observed in each experiment. Several polynomials were considered in each case. In all cases the polynomial

$$\frac{\overline{\text{Fe}}}{t} = a_1 + a_2 t \quad (5.5.1.)$$

CORRELATION	$\overrightarrow{R}_{t=0}$ (gm / l. min) $\times 10^3$	T-ratio (a_1 /ST.DEV.)	R_c^2 (%)
$C = a_0 + a_1 t$	0.102	55.77	99.6
$= a_0 + a_1 t + a_2 t^2$	0.123	56.86	100
$= a_0 + a_1 t + a_2 t^2 + a_3 t^3$	0.132	32.50	100
$= a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4$	0.129	18.66	100
$= a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5$	0.129	16.56	100
$= a_1 t$	0.108	80.24	-
$= a_1 t + a_2 t^2$	0.125	100.84	-
$= a_1 t + a_2 t^2 + a_3 t^3$	0.132	55.20	-
$\frac{C}{t} = a_1 + a_2 t$	0.128	<u>141.26</u>	99.9

TABLE 5.5.1. Fitting polynomials to a typical kinetic experiment (Run E-6)

gave values more consistent and statistically more significant for the parameter a_1 , which is related to the mass transfer rate:

$$a_1 = \left[\frac{d(\overline{Fe})}{dt} \right]_{t \rightarrow 0} \quad (5.5.2.)$$

This polynomial could be used to represent the kinetic results up to 50% of maximum extraction capacity. The advantage of using this type of polynomial is due to the fact that an infinite weight is given to the point $t = 0$, so that high precision is obtained when calculating the initial mass transfer rate, as well as avoiding computational errors when fitting a polynomial without the constant. Although the correlation coefficient (R_c) is very high in all cases, the goodness of the fitting can be better ascertained by the T-ratio (coefficient/standard deviation). This will give the uncertainty of the coefficient. The higher the T-ratio, the higher the degree of confidence in the value of the parameter. Plots of fitted value against experimental value, residuals against experimental values and normal scores of residuals against residuals confirmed the adequacy of this polynomial to represent the concentration-time profiles.

Appendix C shows an extract from a typical computer output for the curve fitting programme (MINITAB).

The log-linear plot method of calculating mass transfer rate is well known to be insensitive¹⁰² and could mask the results, leading to misleading conclusions. This method has been widely used in kinetic studies and could well be a source of error.

In the study of the various parameters, comparisons were made in terms of the specific initial extraction rate.

This was taken to be the rate of change of the bulk concentration per unit surface area per unit phase volume:

$$\overline{R} = [R]_{t \rightarrow 0} = \frac{V_a}{A} \left[\frac{d(\text{Fe})}{dt} \right]_{t \rightarrow 0} = \frac{V_o}{A} \left[\frac{d(\overline{\text{Fe}})}{dt} \right]_{t \rightarrow 0} \quad (5.5.3.)$$

The value of the rate of change of concentration at time $t \rightarrow 0$, $\left[\frac{d(\overline{\text{Fe}})}{dt} \right]_{t \rightarrow 0}$, was obtained from equation (5.5.1.), parameter a_1 . As a high degree of accuracy was obtained when measuring concentrations close to time zero and a high degree of accuracy was also obtained when calculating the initial mass transfer rates, a high degree of reliability of conclusions based on values of initial rates can be assumed.

CHAPTER VI

RESULTS AND DISCUSSION

6.1. INVESTIGATION OF CELL CHARACTERISTICS

The effect of changing the hydrodynamics of the stirred cell has been investigated qualitatively by means of a dye tracer and quantitatively by transferring labelled radioactive chlorine (^{36}Cl) across the TOAHCl (toluene) - aqueous chloride solutions (HCl, LiCl) interface. This work was carried out to investigate the operating characteristics and hydrodynamic behaviour of the cell. It has been pointed out⁷⁴ that in order to distinguish mass transfer control of the extraction rate from chemical control, it is necessary to have studied a mass transfer controlled system in the apparatus.

The isotopic transfer of ^{36}Cl was chosen because it would not affect the interfacial properties, as well as having bulk properties as close as possible to the system studied in this work. It is apparently the ideal system to compare the hydrodynamic behaviour of the cell under mass transfer control with the one under investigation, where chemical control might occur under certain conditions. The initial mass transfer rate for the isotopic transfer would be expected to be comparable to the rate of self-diffusion of chloride, which is clearly a pure mass transfer process.

The hydrodynamic stability of the interface should depend upon the ratio of the gravitational forces to the interfacial tension forces. This ratio of forces is expressed by the ratio of the dimensionless groups, Weber number (We) to Froude number (Fr), which gives

$$\frac{We}{Fr} = \frac{\Delta \rho g L^2}{\sigma} \quad (6.1.1.)$$

where $\Delta \rho$ is the density difference between the two phases, σ the interfacial tension and L a linear dimension.

The critical stirring speed (N_c), for a given cell, for transition from a smooth interface to a rippled interface should thus be a function of We/Fr , i.e.,

$$N_c \propto (We/Fr)^n$$

Olander²³⁰ found that such a relationship applied to his cell with $n = 0.25$. Systems sensitive to changes in the hydrodynamics in the interfacial area would be those with low We/Fr ratios or those with small density differences and high interfacial tension.

The benzene-water system is known to have a stable interface over a reasonable range of stirring speeds. This was confirmed in Austin's pure mass transfer studies.¹⁰² By defining the width of the annulus as the linear dimension, it was found for the benzene-water system in Austin's cell, $We/Fr = 8.75$. Systems with a value of We/Fr greater than 8.75 should exhibit a stable interface over a wider range of stirring speeds than does benzene and water. The value for the toluene-water system was calculated to be about 24. The addition of the surface active TOAHCl extractant to the toluene would be expected to decrease the interfacial tension and increase We/Fr and thus the tendency of the interface to slip rather than ripple. The presence of ionic solutes in the aqueous phase should have the opposite effect, but the affinity of the extractant for the metal ions may reduce this tendency in some way. The overall result is still probably a net decrease in interfacial tension, at least up to a certain aqueous chloride concentration. The

effective We/Fr is therefore probably greater than the calculated value for the pure diluents and the resistance of the interface to deformation greater than in the benzene-water system.

6.1.1. Dye Experiments

Water, saturated with toluene at 25°C, was poured carefully into the cell until the surface was at the centre of the annulus. The upper chamber was then filled with the toluene phase. The stirrers were contra-rotated at 50 rpm. The dye was injected slowly near the wall of the cell into each of the phases in turn. The mixing of the dye into the bulk of the fluid was observed, as well as the stability of the interface. This was repeated at increasing stirring speeds until it could be said that the mixing in the bulk of the fluid was "instantaneous" and that there were no dead spaces in the cell. It was found that a stable interface, for which the bulk conditions were well mixed, was produced for a wide range of stirring speeds (150-350 rpm).

Talc particles were spread at the interface and it was observed that at low stirring speeds the interface was completely stagnant. As the speed was increased random movements appeared and persisted over a wide range of speeds and it was not until a speed of approximately 380 rpm that ripples appeared at the interface.

Some experiments were carried out without the vertical baffles. It was observed that under most stirring conditions the interface revolved. The mixing at low stirring speeds was also inadequate, so that the assumption of constant composition was invalid for most stirring conditions. Unbaffled mixers are known to exhibit poor mixing in the vertical plane whereas baffled cells have been shown to provide good uniformity of concentration in the vertical and horizontal directions.

6.1.2. Phase Homogeneity

An experiment was carried out at 150 rpm to check the mixing conditions. The aqueous phase consisted of 0.0025 M Fe (III) chloride in 1 M HCl and the organic phase was 0.01 M TOAHCl in toluene. The course of the extraction was recorded on a chart recorder using the spectrophotometric method described in section 5.3. Continuous sampling was made at several positions within the organic phase. The concentration-time profile showed a smooth curve indicating that mixing was uniform at that stirring speed. Other experiments at lower stirring speeds showed that mixing was not very good. This could also be verified by significant change in the slope of the plot extraction rate versus stirring speed. At stirring speeds between 200 and 350 rpm a plateau was attained. Above 350 rpm the interface was disturbed by waves and a sharp change in the slope of the plot extraction rate versus stirring speed indicated a significant change in the hydrodynamic conditions at the interface. All these findings confirmed the dye experiments, indicating that sample concentration was independent of sampling location, so that the bulk phase could be considered homogeneous with stirring speeds at least down to 150 rpm.

6.1.3. Isotopic transfer

6.1.3.1. Experimental procedure

The aqueous phase consisted of HCl-LiCl solutions (1 M HCl + x M LiCl) and the organic phase of TOAHCl in toluene. These solutions were equilibrated. After the separation of the phases, radioactive chloride (^{36}Cl as HCl) was added to the aqueous phase and the two equilibrated phases were immersed in the water bath in stoppered glass flasks with the heater-pump adjusted to the

required temperature. After the temperature reached equilibrium, the aqueous and organic phases were transferred to the cell as described in section 5.2 and the run started. Samples of the organic phase were taken at 0, 5, 10, 15, 20, 25, 30, 40, 50 and 60 minutes and analysed for the radioactive chloride content using β -counting, as described in section 5.4. The chloride transferred was assumed to be proportional to the activity of the labelled tracer in the organic phase. The experimental results are presented in Appendix C, Tables C.1 to C.4. The results were statistically analysed and only the most relevant parameters are reported. The best fitting of the data was obtained using a second degree polynomial of the form

$$\frac{C}{t} = a_1 + a_2 t$$

where C is the chloride concentration (g mol/l), t is time (min) and a_1 and a_2 are constants. The advantage of using this type of polynomial has been shown in Section 5.5. The value of the initial mass transfer rate (R) is the value of the parameter a_1 . The experimental reproducibility of the initial mass transfer rate was within $\pm 2\%$. At 95% level of confidence, the initial mass transfer rate gave a variation of 1-7% of the central value, depending on the accuracy of the β -counting, so that $\pm 5\%$ of the central value of the initial mass transfer rate would reflect the experimental error and lack of fit for most results.

6.1.3.2. Mass transfer coefficient calculation.

The overall mass transfer coefficient with respect to the organic phase (K) was the parameter used to study the effect of the different variables on the mass transfer rate of chloride. This was calculated using the differential method⁹⁶. The following equation was used:

$$K = \frac{V_o}{A} \cdot \frac{d(\overline{Cl^*})}{dt} \left[\frac{1}{(\overline{Cl}) - (\overline{Cl^*})} \right] \quad (6.1.2.)$$

where V_o is the volume of the organic phase, A is the interfacial area, $\frac{d(\overline{Cl^*})}{dt}$ is the mass transfer rate, $\overline{Cl}$ is the organic chloride concentration and $\overline{Cl^*}$ is the concentration of transferred chloride. At high driving force $(\overline{Cl} - \overline{Cl^*})$, K values are practically constant and these values were used to analyse the results. Under these conditions $\overline{Cl^*}$ can be neglected. The overall mass transfer coefficient, then, has the same value of the normalised specific initial mass transfer rate $\overline{R}_o$:

$$K = \frac{V_o}{A} \cdot \left[\frac{d\overline{Cl^*}}{dt} \right]_{t \rightarrow 0} \cdot \frac{1}{\overline{Cl}} = \frac{\overline{R}}{\overline{Cl}} = \overline{R}_o \quad (6.1.3.)$$

6.1.3.3. Discussion of results

All the results showed that the overall mass transfer coefficient is reasonably independent of driving force at the start of the experiment but that it eventually starts to decrease as the driving force decreases, probably due to the lack of fit of the equation used to represent the data.

An extract from Tables C.1 to C.4 is presented in Table 6.1.3.1. showing the experimental conditions and K values. The experiments were carried out at random. The run number is just for an easy identification of the experimental conditions and does not reflect the actual order of the experiments.

a) Effect of stirring speed

The effect of stirring speed was investigated and it was found (Figure 6.1.3.1.) that the overall mass transfer coefficient increased with increasing stirring

TABLE 6.1.3.1. Experimental conditions and K values

Run	TOAHCl (M)	Cl ⁻ (M)	T (°C)	Stirring speed (rpm)	Kx10 ³ (cm/sec)
MT-1	0.025	1	25	150	1.920
MT-2	"	"	"	200	2,336
MT-3	"	"	"	250	2.697
MT-4	"	"	"	"	2.734
MT-5	"	"	"	300	3.392
MT-6	"	"	"	350	4.117
MT-7	"	"	15	250	2.645
MT-8	"	"	35	"	2.763
MT-9	"	3	25	"	2.507
MT-10	"	5	"	"	2.261
MT-11	"	7	"	"	1.749
MT-12	0.010	1	"	"	2.747
MT-13	0.050	"	"	"	2.613
MT-14	0.100	"	"	"	2.859

Additional experimental conditions:

$\text{rpm}_{\text{aq}} = \text{rpm}_{\text{org}}$, contra-rotating stirrers

Interfacial area = 30 cm²

Phase volume: O = A = 480 ml

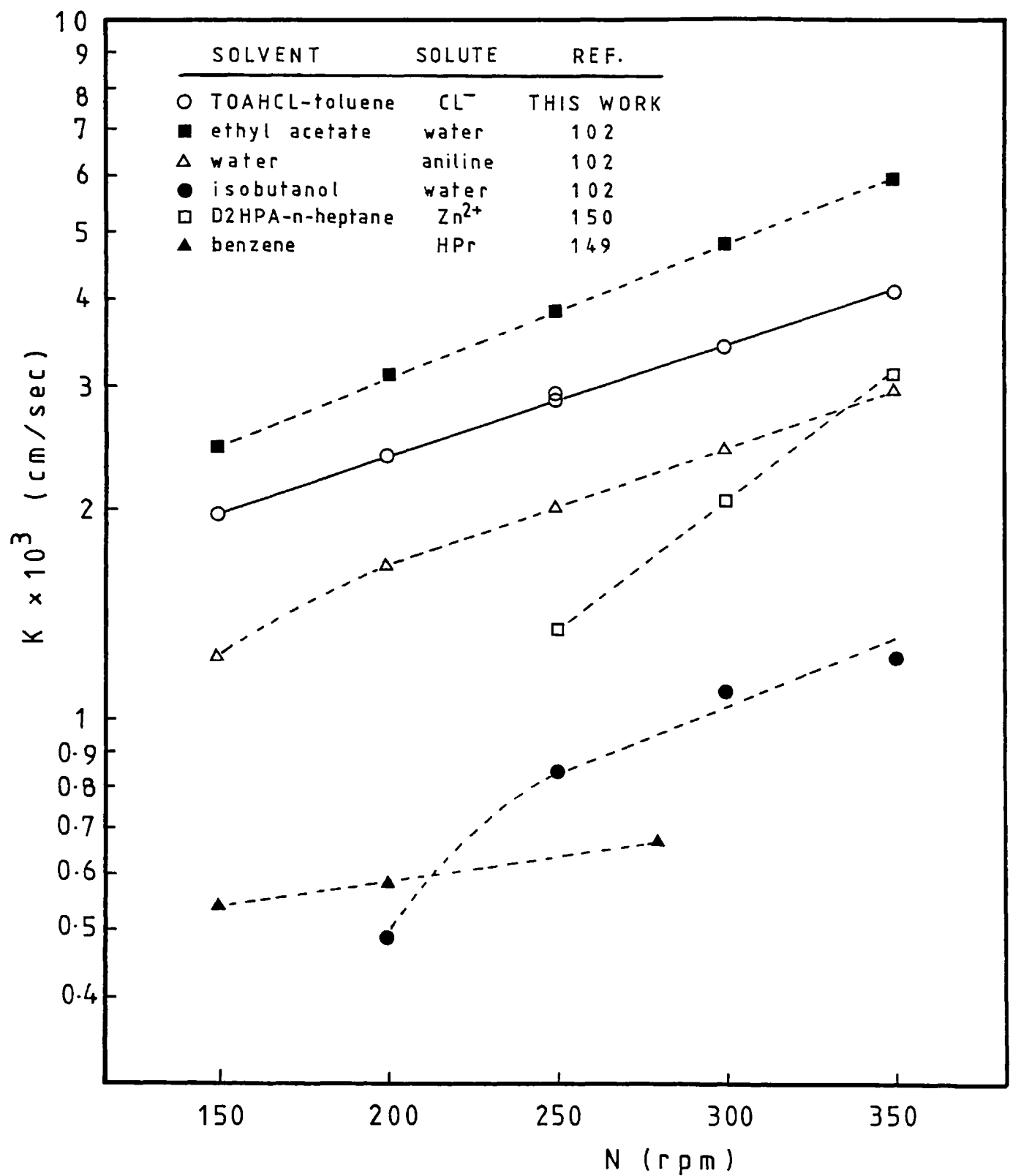


FIGURE 6.1.3.1. EFFECT OF STIRRING SPEED ON MASS TRANSFER COEFFICIENT.

speed. This would be expected for a mass transfer controlled process, where an increase in stirring speed would increase the rate at which fresh bulk solute is brought to the interface, resulting in an increase in the overall mass transfer coefficient.

In Figure 6.1.3.1. the results are compared with analogous experiments for other systems available in the literature. The slope of the curves reflect the mixing conditions in the cells, whereas the vertical position of the different curves indicates the effect of the diffusion coefficient of the transferred species on the mass transfer rate. It can be seen that the agreement between this work and Austin's results,¹⁰² both in the magnitude of K values and in the shapes of the curves is good. This is not surprising due to the similarity in the design of both cells. No reasonable explanation was found for Molnar's results,¹⁴⁹ as the design of the cell and the diffusion coefficient of the investigated system are comparable to Austin's, so that the results should be similar but they are not. Ajawin's results¹⁵⁰ are of the same order of magnitude of the K values of this work, but the steeper slope indicates a stronger dependence of K on the mixing conditions.

The results obtained in this work were correlated by the equation

$$\log K = -2.97 + 0.00166 (N) \quad (6.1.4.)$$

or

$$K = 1.072 \times 10^{-3} \times 10^{\frac{N}{602}} \quad (6.1.5.)$$

Equation (6.1.4.) is in agreement with the form of the equation given by Austin (Table 2.3.1.) for a renewed interface. A problem with Austin's correlation is that the dependence of K on the variation of the physical properties (i.e., density, viscosity, etc.)

cannot be predicted, and also the correlation is very sensitive to small changes in the diffusion coefficient. Because no reliable diffusivity data are available for the system investigated in this work, no attempt was made to use Austin's correlation.

b) Effect of temperature

The effect of temperature on chloride transfer is shown in Figure 6.1.3.2. The increase of temperature increased very little the overall mass transfer coefficients. A value of the apparent activation energy was calculated giving 1.7 kJ/mol. This value is very low when compared with the activation energy of a typical mass transfer controlled process. It is questionable whether the concept of activation energy is applicable to a heterogeneous system such as this one. The transfer mechanism may involve a number of steps. The effect of the temperature on the transfer may be a complex function of the effects on each of the individual rate constants and the measured effect may not indicate the true activation energy. It is possible also that this low value could be due to the absence of chemical interactions, so that the system is almost ideally mass transfer controlled (in the ideal mass transfer controlled process the activation energy should be zero).

c) Effect of aqueous chloride concentration

The effect of aqueous chloride concentration is shown in Figure 6.1.3.3. The increase of chloride concentration produced a considerable decrease in the overall mass transfer coefficients. As shown in Figure 3.7.2., the viscosity of the aqueous phase increases considerably with the increase of chloride concentration. It is known that mixing conditions are proportional in some way to the Reynolds number. As the stirring speed remained the same in this set of experiments, poorer mixing resulted with the increase of viscosity as a

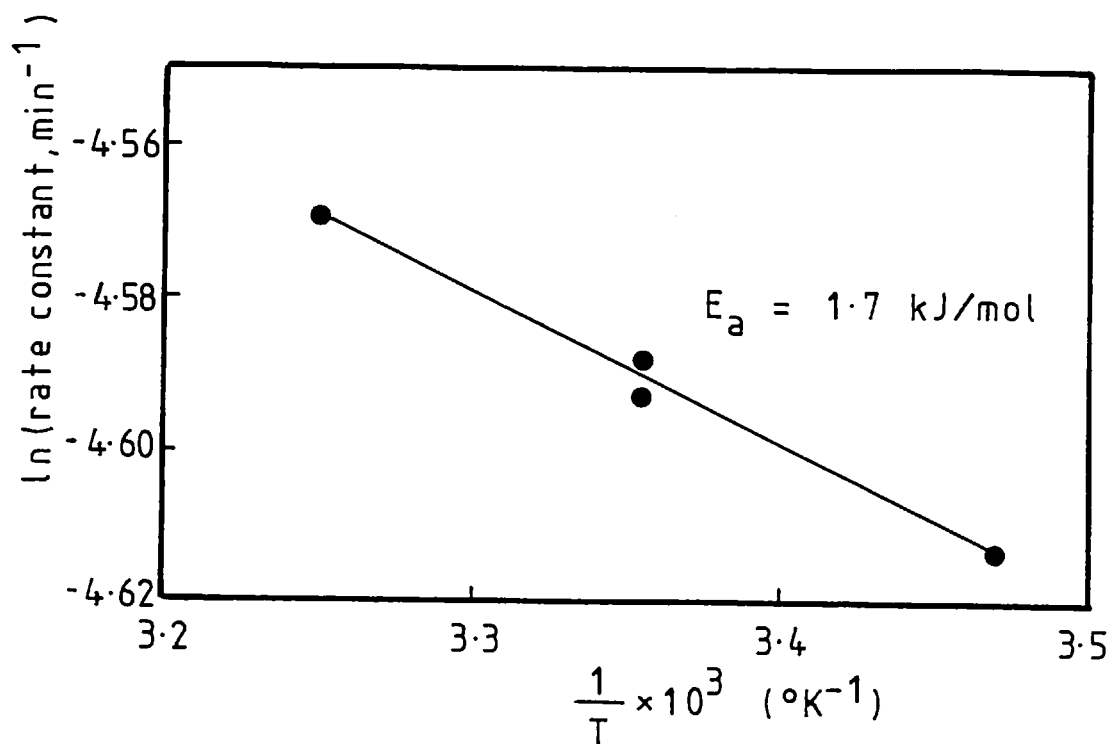


FIGURE 6.1.3.2. EFFECT OF TEMPERATURE ON MASS TRANSFER.

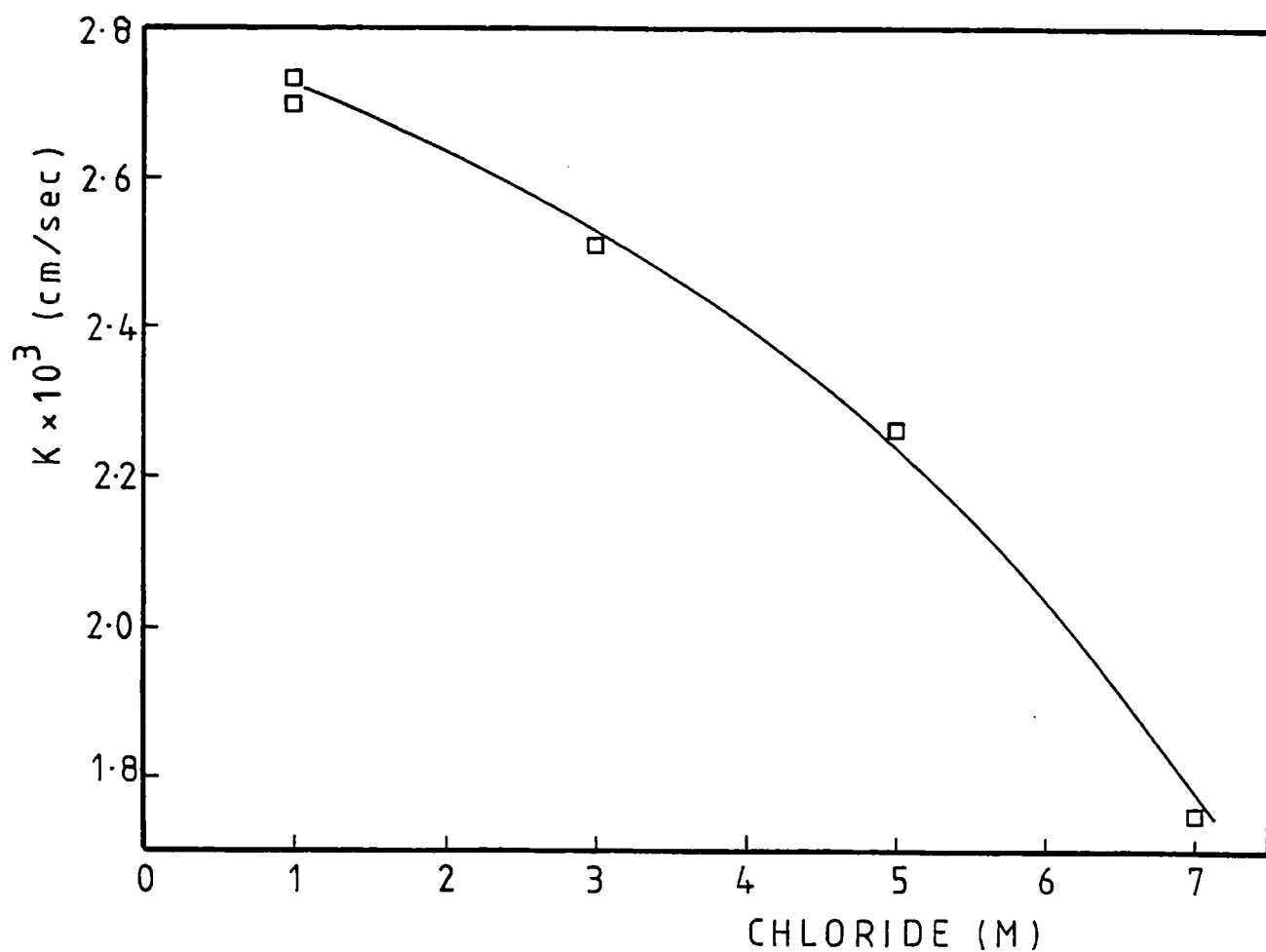


FIGURE 6.1.3.3. EFFECT OF AQUEOUS CHLORIDE CONCENTRATION ON THE MASS TRANSFER COEFFICIENT.

consequence of the increase of chloride concentration. Another fact that may account for a considerable proportion of this reduction in the overall mass transfer coefficient is the decrease in the value of the diffusion coefficient. It is known that increases in viscosity decrease the value of the diffusion coefficient. Hence, poorer mixing conditions and decreases in the diffusion coefficient could explain the significant decrease in K values.

d) Effect of TOAHCl concentration

The dependence of the initial mass transfer rate is first order with respect to the bulk TOAHCl concentration, whereas the overall mass transfer coefficient is independent of TOAHCl concentration, as expected from equation (6.1.2.). These findings confirm the adequacy of the equation used for the calculation of the overall mass transfer coefficients.

6.2. IRON(III) - TOAHCl EXTRACTION

The main objective of this work is a systematic study of the kinetics of the extraction of iron (III) from chloride solutions by TOAHCl in toluene. This was carried out in a Lewis type stirred cell by evaluating the initial specific mass transfer rate from the concentration-time profiles under a variety of conditions. Firstly, experiments were carried out to select a range of conditions where a chemical reaction was the rate controlling step. Under these conditions, the effect of different concentration parameters were investigated. Other parameters, such as the nature of the diluent or the interfacial properties, would give additional information, but these were not examined in the present work.

6.2.1. Experimental procedure

The aqueous phase consisted of iron (III) chloride in HCl-LiCl solutions and the organic phase TOAHCl in toluene for the extraction experiments, whereas for the stripping experiments the aqueous phase consisted of HCl-LiCl solutions and the organic phase TOAHFeCl₄ in TOAHCl-toluene solutions. These solutions were pre-equilibrated (without Fe (III)-chloride or TOAHFeCl₄). After the separation of the phases, Fe (III)-chloride or TOAHFeCl₄ was added to the aqueous or organic phase, depending whether it was an extraction or stripping experiment, and the two phases were immersed in the water bath in stoppered glass flasks with the heater-pump adjusted to the required temperature. After the temperature reached equilibrium, the aqueous and organic phases were transferred to the cell, as described in Section 5.2 and the run started. The course of the reaction was recorded on a chart recorder using the spectrophotometric method described in Section 5.3. The experimental results are presented in Appendix C. The results were statistically analysed and only the most relevant parameters are reported. The evaluated rate parameter from the concentration-time profiles was the initial specific mass transfer rate as defined in Section 5.5.

6.2.2. Experimental conditions

In order to gain familiarity with the operating characteristics of the equipment and to develop the experimental technique, about 50 experiments were carried out under a variety of conditions, all at room temperature (20-25°C) using practical TOAHCl prepared from technical grade TOA (Newton Maine product). These results were erratic, as well as not being comparable with the following runs, and this was thought to be due to the presence of

impurities in the extractant (as the material used was rather impure), or because the experimental conditions were not fully standardised, or most probably both. No data are reported for these experiments.

It is known that in this type of work, purified materials should be used in order to reduce or eliminate the effects of unknown chemical components on the extraction mechanism and kinetics. Attempts to purify the Newton Maine product by re-crystallization in petroleum ether were unsuccessful and the final product (solid TOAHCl) was a yellowish wax, with a low melting point ($63-65^{\circ}\text{C}$), although a large number (over 20) of recrystallization cycles were used. The use of this recrystallised material did not improve the reproducibility of the results and further use of it was abandoned.

The experimental behaviour of practical TOAHCl (prepared from TOA Fluka), purified TOAHCl (from TOA Fluka), pure TOAHCl (Eastman-Kodak product) and purified TLAHCl (purified as described in reference 139) is presented in Table 6.2.1. It was found that none of these experiments, under the same conditions, produced results (concentration-time profiles) which were significantly different from each other, indicating similar chemical behaviour. In some cases, the extractants were regenerated by stripping the iron and HCl with 0.1 M NaOH, followed by equilibration with 1 M HCl. The experiment was repeated with the regenerated material. It was found that in some cases, significantly lower values of the initial mass transfer rates were obtained, probably due to some contamination of the extractant during the regeneration process. The great sensitivity of stirred cell kinetic experiments to very small quantities of contaminants at the interface, which may be introduced in a laboratory not specifically set up for the experiments, is emphasized in cells with higher V/A ratios, such as the one used in the present

TABLE 6.2.1. Effect of extractant purity on initial mass transfer rates.

Conditions: Temp = 25°C, Interfacial area = 30 cm²
 Phase volume A = O = 480 ml
 Contra-rotating stirrers O = 250 rpm
 A at constant Re = 2680

Extractant	Extractant concentration (M x 10 ²)	Fe(III) (Mx10 ³)	Cl ⁻ (M)	R x 10 ³ $\frac{\text{gm}}{\text{l} \times \text{min}}$
Practical TOAHCl (Fluka)	1.0	2.5	1	0.147
"	"	"	"	0.149
Purified TOAHCl (Fluka)	"	"	"	0.151
"	"	"	"	0.148
Pure TOAHCl (Eastman-Kodak)	"	"	"	0.146
"	"	"	"	0.149
Purified TLA	"	"	"	0.146
"	"	"	"	0.153
Practical TOAHCl (Fluka)	"	1.0	4	0.812
"	"	"	"	0.859
Purified TOAHCl (Fluka)	"	"	"	0.826
Practical TOAHCl (Fluka)	"	"	7	1.053
"	"	"	"	0.991
Purified TOAHCl (Fluka)	"	"	"	0.974
Pure TOAHCl (Eastman Kodak)	"	"	"	1.038

study ($V/A = 16$). In order to minimise any source of contamination, only fresh solutions and the same glassware were used throughout the experimental work. Each piece of glassware was used for a specific job and cleaned only with the pure diluent (distilled water or toluene).

If impurities play some role at the interface, then small amounts may be enough to produce considerable effects. The as-received TOA (Fluka product) contained some impurities, as shown by gas chromatography analysis (Section 5.1), but these had no noticeable effects on the initial mass transfer rates and so the question arises about their nature. It is unlikely that they were eliminated during the preparation of practical TOAHCl, as several recrystallization cycles were needed to produce pure solid TOAHCl. Most probably they are other amines (as indicated by the infra-red spectra, Section 5.1) and behave like pure TOA, or alternatively they are not surface active enough to compete with TOAHCl for interfacial sites and so do not hamper the extraction.

The kinetic experiments were carried out in blocks (group of experiments). Stock solutions of the reagents were prepared at convenient concentrations, so that the aqueous and organic phases could be prepared by suitable dilution of the stock solutions. These stock solutions were prepared in quantities large enough to last until the block of experiments was completed. These solutions were analysed using the analytical methods described in Section 5.1. and kept in dark stoppered flasks in the dark, in order to minimise any photochemical decomposition. Another reason for using bulk stock solutions was to minimise possible differences in solution compositions, so that the errors involved would be only the errors associated with the dilution of the stock solutions.

The ageing effect of the stock solutions was investigated. It was found that these solutions would keep unaltered for several months. Under the same conditions, experiments using fresh extractant solution and solutions aged 7, 30, 90 and 180 days produced the same initial mass transfer rate within the expected experimental error.

Different blocks of experiments were performed. In the first block, a series of experiments was carried out to establish the effect of stirring speed on the initial mass transfer rate and the extent, if any, of a plateau region where the reaction rate was independent of stirring rate. The other blocks of experiments involved the study of the effect of variation of TOAHCl and Fe(III) concentrations, interfacial area and temperature on the extraction rate at 1 M, 4 M and 7M aqueous Cl^- concentration, and the effects of the same variables on the stripping rate. The effect of aqueous chloride concentration on extraction and stripping rate was also investigated. Finally, the determination of the ratio Cl/Fe in the transferred Fe(III) - chloride species was carried out at different aqueous Cl^- concentrations, using labelled radioactive ^{36}Cl . These results are presented in detail in the following sections.

In each block, the experiments were performed at random. The run number (Appendix C) does not indicate the order in which the runs were carried out and they are used just for an easy identification of the experimental conditions. Some experiments were rejected because of experimental problems. Some other runs produced some suspect results that were also rejected. These rejected experiments are not reported. The analysis of the residuals from the curve fitting program used to calculate the initial mass transfer rate was the criterion used to reject an experiment. If the residuals were not

reasonably randomly distributed, the plot of normal scores of the residuals against residuals was not regular and the correlation coefficient was used as a test for normality, as shown in Section 5.4. If there was a probability of less than 90% that the residuals were normally distributed, the experiment was rejected. The inadequacy of the equation used to fit the data was ruled out, as the fit was good in most of the cases. Non normal distribution of residuals was observed in only a few runs and the unidentified source of error could have been the misbehaviour of some part of the equipment or some contamination at the interface. Most probably the problem was due to contamination as all rejected runs showed initial mass transfer rates far less than expected. Although extra care was always taken to avoid any possible contamination, the working conditions were never ideal, as the laboratory was not specifically set up for this type of work.

Some replication of the experiments was carried out. The replicates gave an indication of the reproducibility. The results are shown in Table 6.2.2. It can be seen from the data that the reproducibility in general decreases with the increase of the initial mass transfer rate. The reproducibility is considered good for this type of work and indicates the adequacy of the experimental and analytical methods and the statistical method used to analyse the results. From these observations it was concluded that a range of $\pm 5\%$ reflected the accuracy of the experimental technique employed under the worst conditions. The magnitude of the experimental error is much less than that usually obtained in other stirred cell kinetic studies and this emphasizes the advantage of continuous, accurate monitoring of the concentration of metal species in the phase to which the metal species is being transferred.

TABLE 6.2.2. Experimental reproducibility

Replicate runs	TOAHCl (Mx10 ²)	Fe(III) (Mx10 ³)	Cl ⁻ (M)	R x 10 ³ (gm/l.min)	
				average	± %
E-2, E-3	1.0	1.0	1	0.0584	1.9
E-6, E-7	1.0	2.21	1	0.131	2.0
E-8, E-9	1.0	2.5	1	0.149	0.6
E-17, E-18	2.5	2.5	1	0.271	1.5
E-30, E-31	1.0	1.0	4	0.836	2.8
E-45, E-46	1.0	1.0	7	1.022	3.1
S-5, S-6	1.0	1.74	1	0.526	1.2

6.2.3. Effect of stirring speed

The initial mass transfer rate was studied over a range of stirring speeds from 100 rpm to 600 rpm with contra- or co-rotating stirrers, with or without baffles and at different aqueous chloride concentrations. Speeds below 100 rpm were not used as there was evidence that the stirring was not strong enough to keep the phases suitably homogeneous.

The results are shown graphically in Figures 6.2.3.1 to 6.2.3.5 and numerical values are given in Appendix C. As this series of results were of a more qualitative nature, it was decided that there was no need for a high degree of accuracy when calculating the initial mass

transfer rates. Thus, the slopes of the concentration-time profiles were calculated graphically and then converted to initial specific mass transfer rates in suitable units. In some cases, more than one run was carried out in one single experiment, by changing the stirring speed. The error introduced by this procedure was found to be not significant, as the concentrations were measured in the linear range of the concentration-time profiles.

The first set of experiments consisted of the investigation of the effect of the direction of the stirrers and the effect of baffles. The results are shown graphically in Figure 6.2.3.1. Firstly, the cell was operated fully baffled with contra-rotating stirrers. As the stirring speed was increased, there was little change in the appearance of the interface, which was subjected to random movements, but there was no systematic motion. However, at speeds above 350 rpm, waves appeared at the interface and at 500 rpm, the interface was disrupted and mixing of the phases started to occur. As expected from the idealized description of the response of the extraction rate in a chemical extraction system to changes in stirring speed in a stirred cell, presented in Section 2-2-3, it was found that a plateau region occurred between 200 and 350 rpm. It was assumed that, in the plateau region chemical reaction was controlling the extraction rate. In order to exclude the possibility of mass transfer control, these results were compared with the results presented in Section 6.1.3. for the isotopic transfer, where a linear relationship between $\log K$ versus stirring speed was found. Thus if the iron extraction rate was controlled by a mass transfer process, it should behave similarly and a plateau region would not be observed. The results show clearly a plateau which indicates that the control was by chemical reaction. It is possible that the "plateau" is not a true horizontal line and more rigorously the plateau region should be defined as "the range

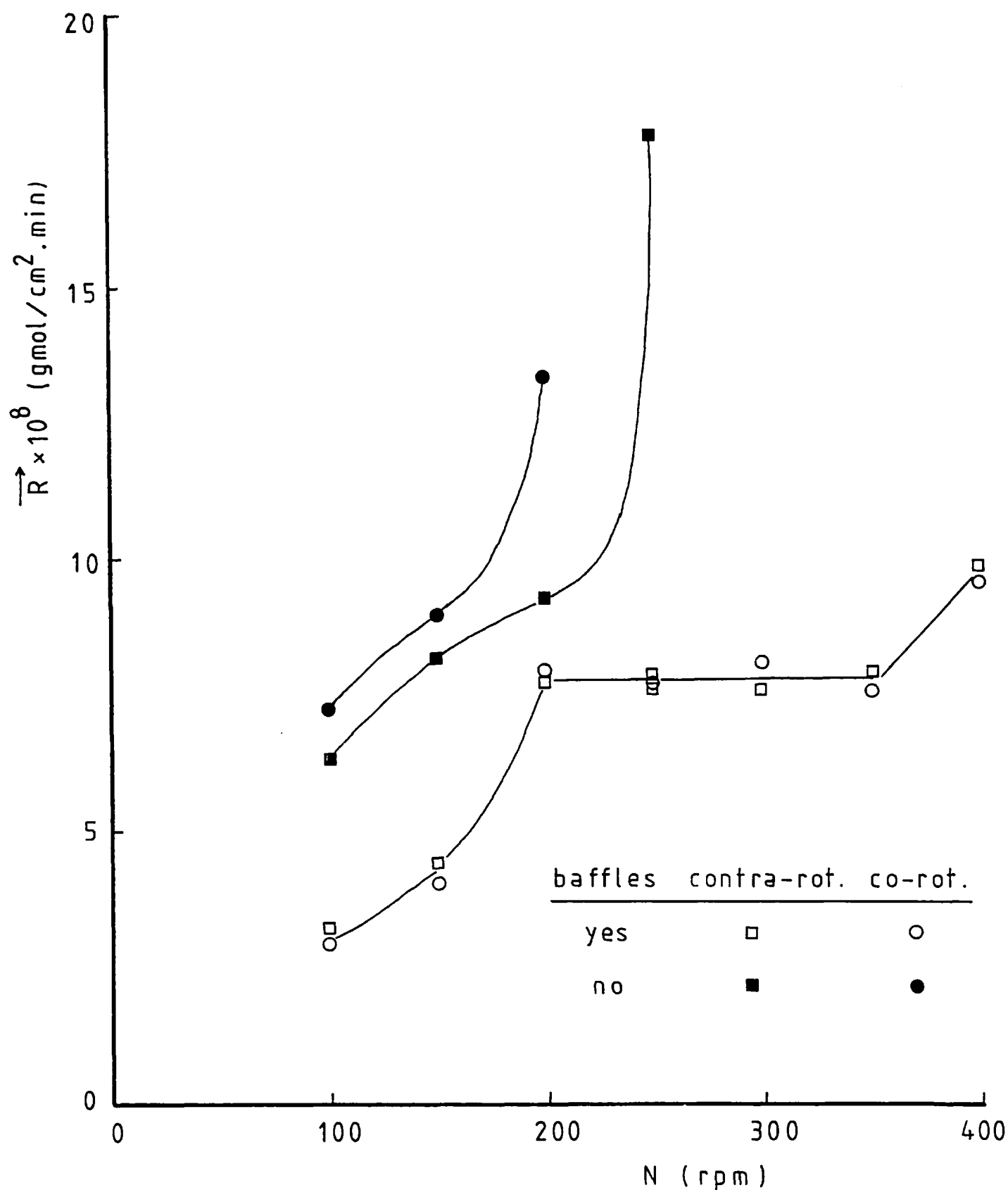


FIGURE 6.2.3.1. EFFECT OF BAFFLES, DIRECTION OF STIRRERS AND STIRRING SPEED ON EXTRACTION RATE. CONDITIONS: Fe(III) = 0.0025 M, TOAHCl = 0.025 M, HCl = 1 M, 25°C, Int. area = 30 cm², Phase volume A = O = 480 ml.

of stirring speeds where there the rate of change of extraction rate with stirring speed approximates to zero so that the contribution made by mass transfer processes to the overall rate is small or negligible." The shape of the curve below 200 rpm is rather unusual and contrary to what would be expected for the dependence of reaction rate with stirring speed, as the curve is concave. One possible reason for this could be that under these conditions the actual or useful volume (V^*) of the phase is a fraction of the total volume (V) used to calculate the initial specific mass transfer rate. This would indicate that in this range of conditions, the cell contains dead spaces and the phases are not completely homogeneous, as a consequence of the cell being heavily baffled (probably over-baffled). The geometry and design of the baffles were based on the studies of Austin¹⁰², Grosjean¹⁰³ and Molnar¹⁴⁹. These works found that the baffles were essential in order to obtain a reasonably quiescent interface. This unusual characteristic of the stirred cell should not, however, affect extraction studies under conditions of chemical control, as the hydrodynamic effects have no or negligible influence on the mass transfer rates. Under similar conditions, the cell was operated with co-rotating stirrers. The results were very close to the results for contra-rotating stirrers presented above and the same conclusions would apply. These results confirm that the cell was fully baffled and, although no significant difference was found between contra- or co-rotating stirrers, it was decided to work with contra-rotating stirrers, as in principle they should provide more efficient stirring conditions at the interface. The operation of the cell with no baffles, either contra- or co-rotating did not give good results, as the interface rotated under most stirring speeds and was never "near" quiescent. These results show the inadequacy of the unbaffled cells used by some investigators, as it is unlikely that a quiescent interface will be obtained under

these conditions. Until a standard design for the stirred cell is available, where the influence of the geometric factors have been optimized, it is likely that the stirred cell will be over-baffled - and thus unsuitable for pure mass transfer studies, or if unbaffled - unsuitable for kinetic studies.

The observation that the rates did not change between 200 and 350 rpm indicated that 250 rpm would be a safe and valid speed at which to perform the experiments and to be sure that the chemical reaction was predominantly responsible for the extraction rate.

The effect of stirring conditions is shown in Figure 6.2.3.2. The effect of the stirring speed of the aqueous phase, keeping the stirring speed of the organic phase at 250 rpm, on the mass transfer rate, and vice-versa, keeping the stirring speed of the aqueous phase at 250 rpm and having variable stirring speed in the organic, is compared with the previous case, where both were equal and varied simultaneously. From these results it can be concluded that there is some transfer of momentum from one phase to another as indicated by the different curves in Figure 6.2.3.2., and provided the stirring speed of the aqueous phase is in the plateau region, the stirring speed of the organic phase has little effect. The resistance to the transfer appears to be located almost entirely in the aqueous phase. This dependence may give some insight on how and where the reaction occurs and it can be speculated how the TOAHCl and iron (III) chlorides may interact to affect it. The geometry of TOAHCl molecule at the interface is not exactly known. It is likely that the hydrophilic end protrudes into the aqueous phase, while the hydrophobic end remains anchored in the organic phase. Metal ions are not surface active as shown by their tendency to increase interfacial or surface tension. Therefore, it

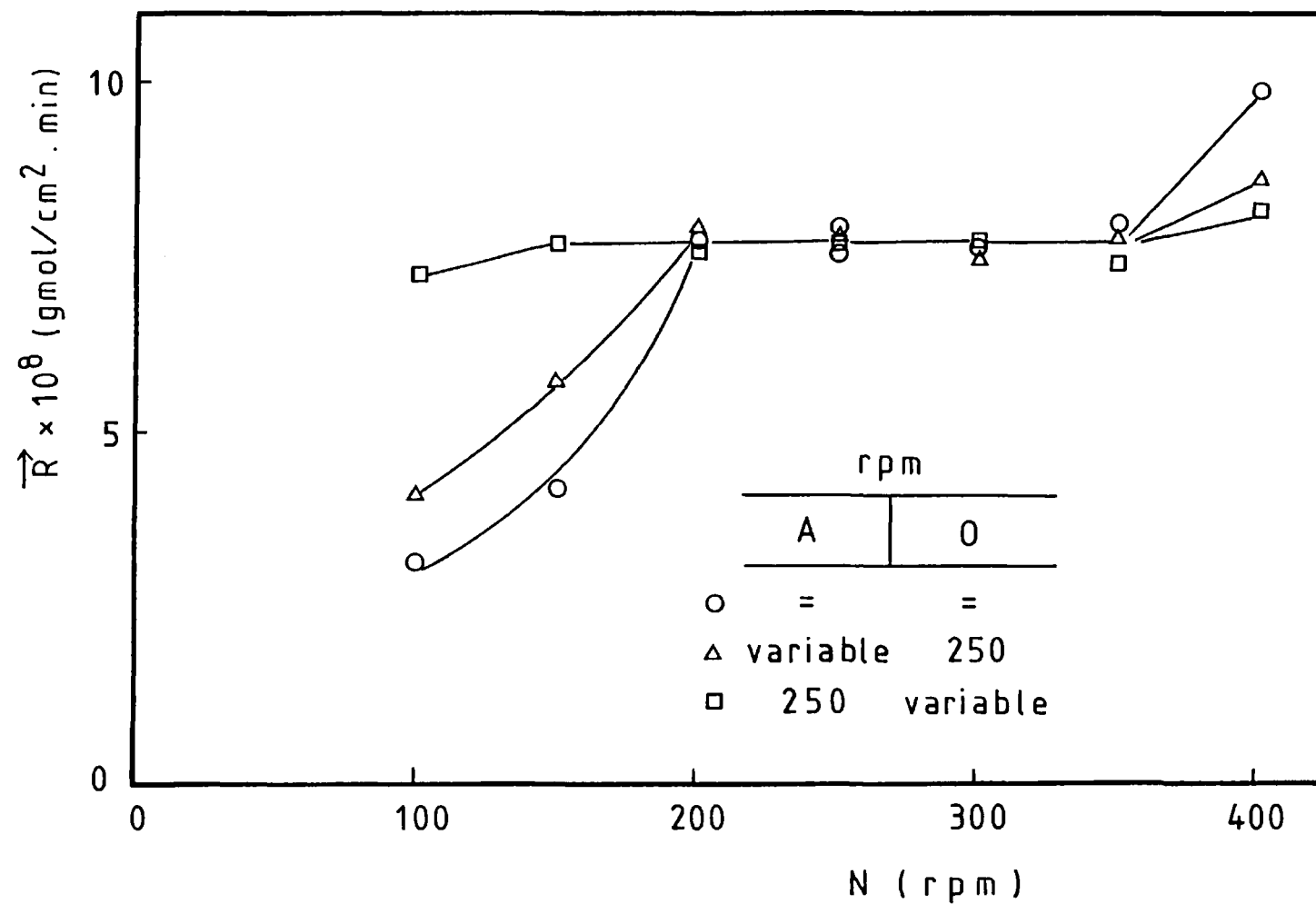


FIGURE 6.2.3.2. EFFECT OF STIRRING SPEED ON EXTRACTION RATE. CONDITIONS: Fe(III) = 0.0025 M, TOAHCl = 0.025 M, HCl = 1 M, 25°C, Int. area = 30 cm², Phase volume A = O = 480 ml, contra-rotating stirrers.

would be easier for them to react with TOAHCl molecules protruding into the aqueous phase, rather than having to adsorb at the interface, possibly requiring prior dehydration, before any reaction takes place. If this happens, it seems reasonable to assume that the reaction takes place at the aqueous side near the interface. It is unlikely that the reaction occurs homogeneously in the aqueous phase due to the low solubility of TOAHCl in water.

The effect of stirring speed on the rate of stripping is shown in Figure 6.2.3.3. The experimental conditions were similar to those described above. As expected, a plateau region between 200 and 350 rpm was found, which confirms that at 1 M aqueous chloride concentration and at these concentration levels of Fe(III) and TOAHCl chemical reaction was the rate controlling step.

It is possible that the plateau will shift or disappear entirely as the experimental conditions are changed (i.e., reagent concentrations, physical properties, etc.) and the extraction process will no longer be entirely chemically controlled. To investigate this, experiments at various stirring speeds were carried out at high TOAHCl and Fe (III) concentrations at 1 M chloride and also under similar conditions as described before but using 4, 7 and 9 M chloride concentrations. The stirring speed of the organic phase was kept at 250 rpm, while the stirring speed of the aqueous phase was varied. The results are shown in Figure 6.2.3.4. No plateau was found at 1 M Cl^- when high concentrations of TOAHCl and Fe were used. The rate increased with stirring speed until the interface was disrupted. Because the reaction was fast, in order to achieve chemical control it would be necessary to use stirring conditions incompatible with the "strength" of the interface. At 4 and 7 M Cl^- , it was found that the plateau region shifted

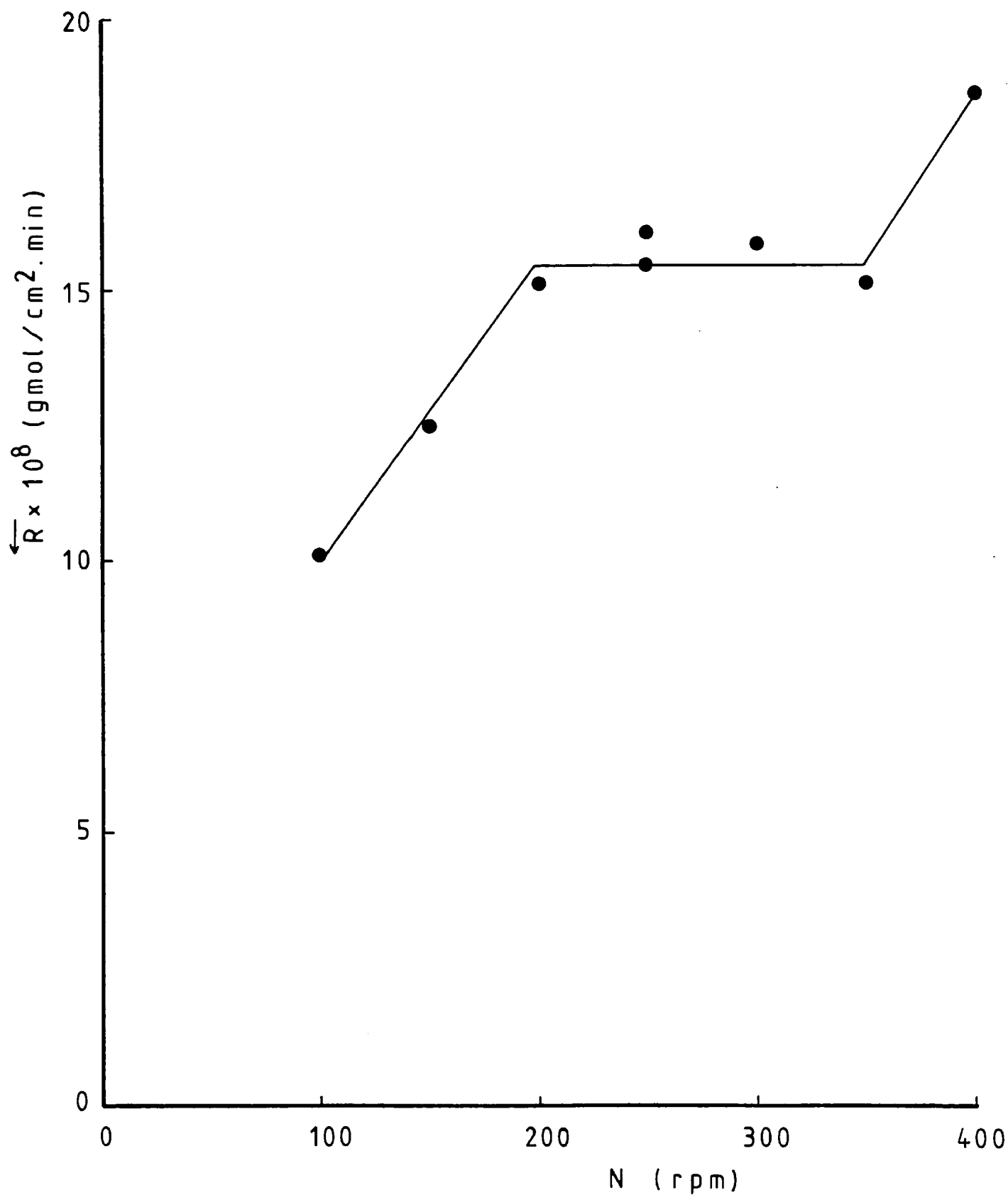


FIGURE 6.2.3.3. EFFECT OF STIRRING SPEED ON STRIPPING RATE.
CONDITIONS: Fe = 0.00174 M, TOAHCl = 0.01 M, HCl = 1 M,
Int. area = 30 cm², Phase volume A = O = 500 ml, contra-
rotating stirrers A = O.

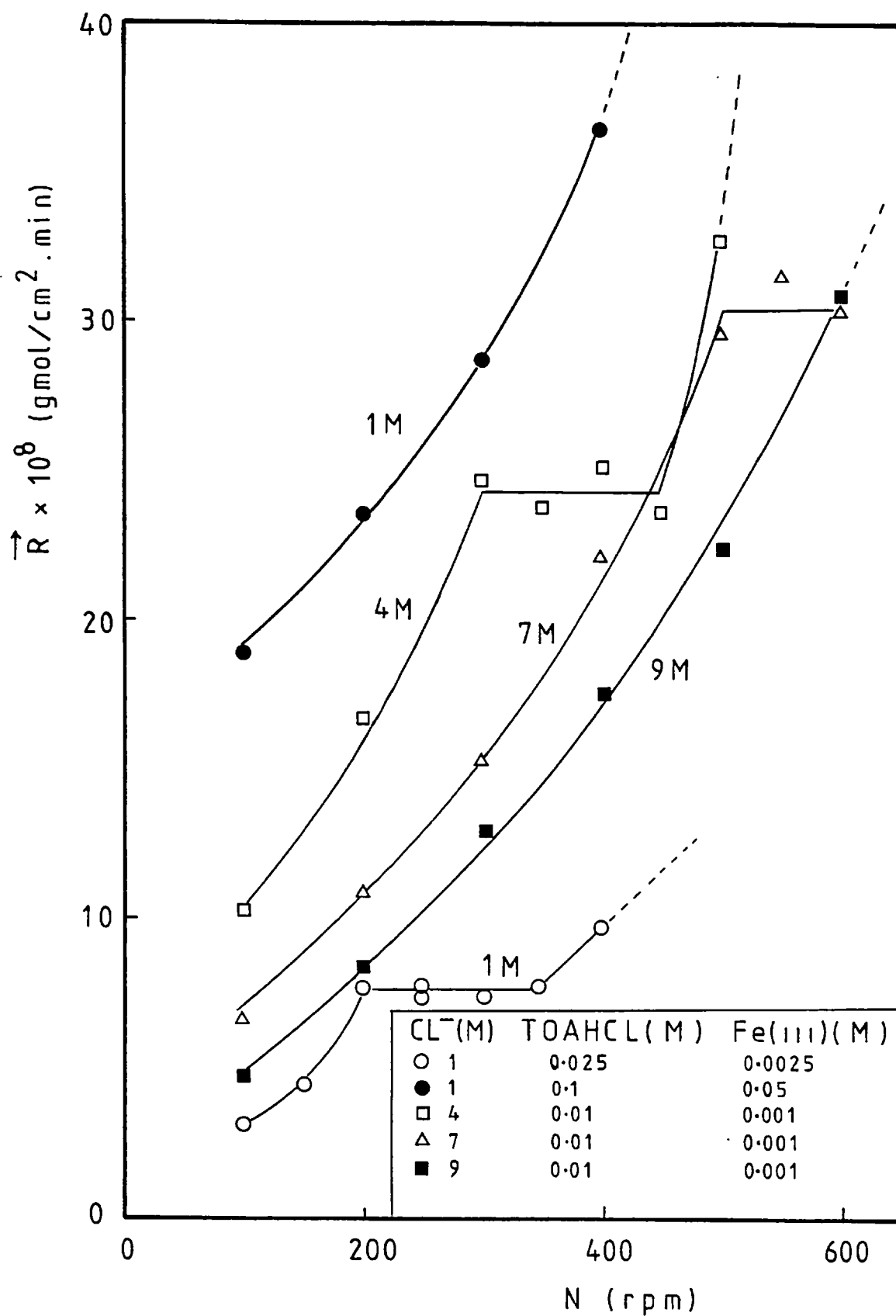


FIGURE 6.2.3.4. EFFECT OF AQUEOUS CHLORIDE CONCENTRATION AND STIRRING SPEED ON EXTRACTION RATE.

considerably. No plateau was observed at 9 M Cl^- . The viscosity of the aqueous phase increases considerably with the chloride concentration, and this will affect the mass transfer rate by affecting the mixing conditions and the diffusivity of the transferred species. In the plateau region, diffusivity should have no or negligible effect as the reaction is chemically controlled. The shift and length of the plateau region may also be related in some way to the interfacial tension. As discussed in Section 6.1, the stability of the interface is a function of the interfacial tension, amongst other factors. The presence of large concentrations of ionic solutes in the aqueous phase will increase the interfacial tension and decrease the stability of the interface. The lack of any available information on the variation of interfacial tension at high aqueous chloride concentrations precluded further analysis of the results.

A criterion of hydrodynamic similarity must be introduced. The obvious choice would be the mixing power dissipated, but this could not be calculated with accuracy as the stirred cell is not a reactor of standard geometry. The Reynolds number, although not ideal, may provide a reasonable indication of the mixing conditions. If this assumption is correct, for solutions with different viscosities the plateau should start at a constant Reynolds number ($\text{Re} = NL^2/\nu$, where N = stirring speed (rps), L = tip-to-tip stirrer length (cm) and ν = viscosity (Stokes)). The length of the plateau should be related to the "strength" of the interface and this should be related to the interfacial tension. A plot of Reynolds number at the start and at the end of the plateau region versus aqueous chloride concentration is presented in Figure 6.2.3.5. The results confirm the postulate described above. It may be seen that plateau region decreases as the concentration of chloride and hence the viscosity of the aqueous phase increases (and probably the interfacial tension

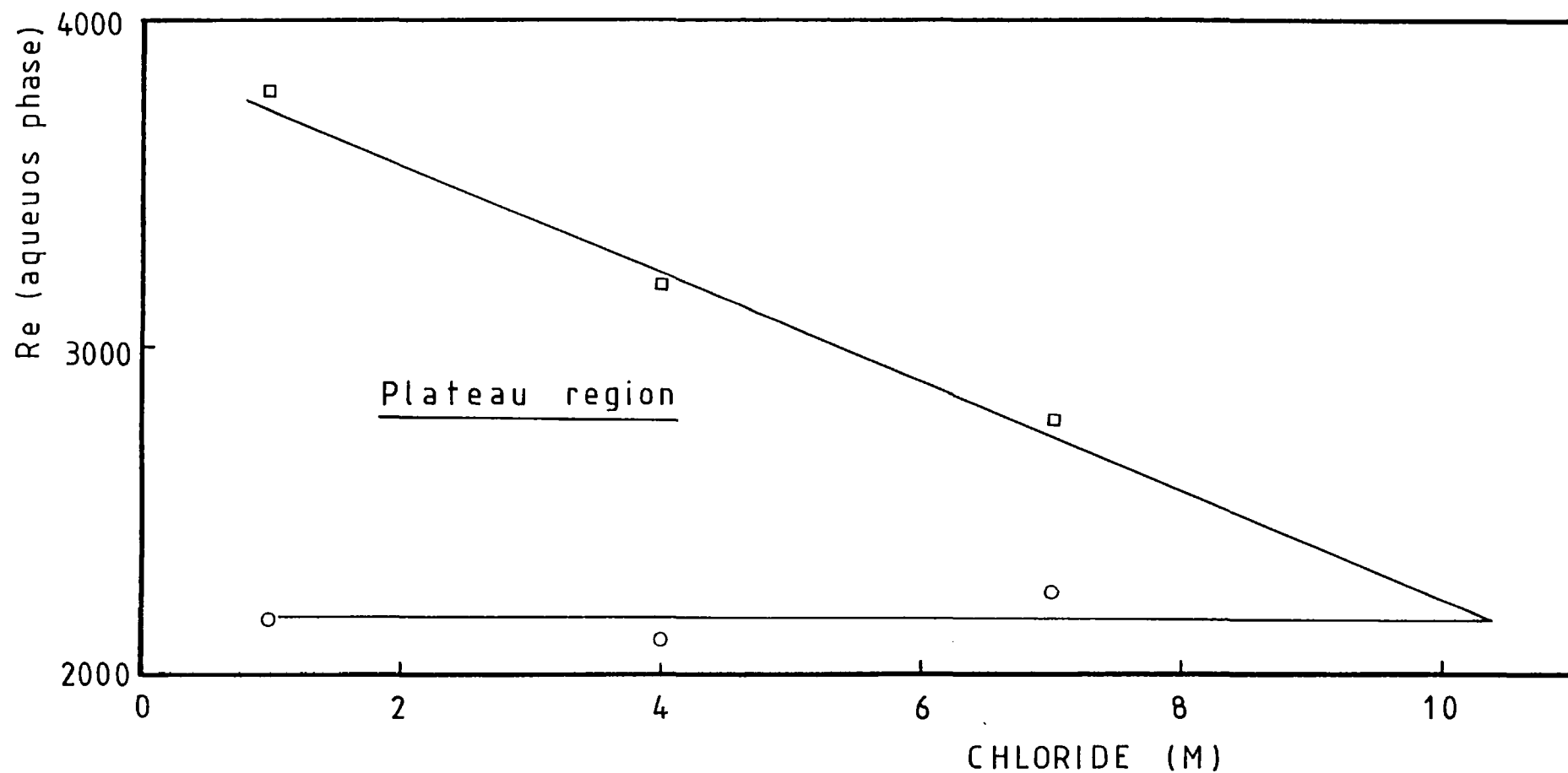


FIGURE 6.2.3.5. EFFECT OF AQUEOUS CHLORIDE CONCENTRATION AND STIRRING CONDITIONS (REYNOLDS NUMBER) ON THE PLATEAU REGION.

increases as well). The results suggest that above 10 M chloride there will be no plateau. On the 8 to 10 M region the plateau will be difficult to detect, if it exists at all. It was thus concluded that up to 7 M chloride under the chemical conditions investigated the Reynolds number could be used as reasonable criterion of hydrodynamic similarity, since at constant Reynolds numbers, similar mixing conditions would be expected. There will also be a range of conditions where a plateau cannot be attained in the stirred cell. This range of conditions includes high reagent concentrations and high aqueous chloride concentrations. Based on these findings it was then decided to carry out further experiments at a constant Reynolds number equal to 2680, equivalent to 250 rpm at 1 M Cl^- , which was known to be a safe and valid stirring speed where the mixing conditions were within the plateau region.

6.2.4. Effect of Interfacial area

In order to establish the location of the chemical reaction controlling the mass transfer, rate experiments were carried out at different specific interfacial areas (V/A) under chemical conditions typical of the range studied. The results are presented in Figures 6.2.4.1 to 6.2.4.3 in two forms. The mass transfer and specific mass transfer rates are plotted as a function of specific interfacial area. The results show that the mass transfer rate (dC/dt) is a linear function of the specific interfacial area, while the specific mass transfer rate ($(V/A)(dC/dt)$) is independent of the specific interfacial area. The fact that in the first case the straight line passes through the origin demonstrates that the geometrical area calculated from the dimensions of the annulus is identical with the area available for contact between the phases.

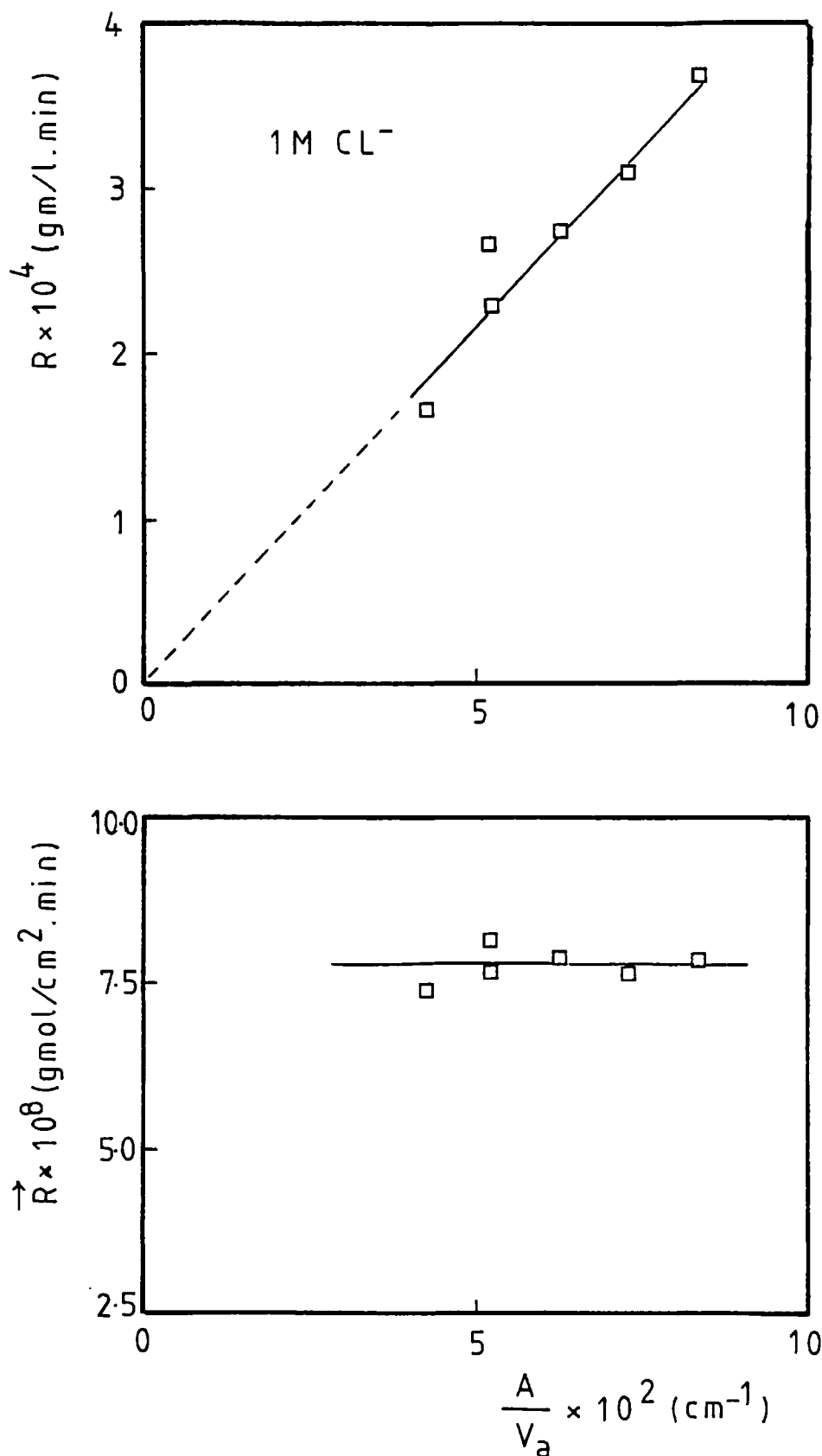


FIGURE 6.2.4.1. EFFECT OF INTERFACIAL AREA PER UNIT PHASE VOLUME ON EXTRACTION RATE. CONDITIONS: TOAHCl = 0.025 M, Fe = 0.0025 M, HCl = 1 M, 25°C, Phase volume A = O = 480 ml, contra-rotating stirring A = O = 250 rpm.

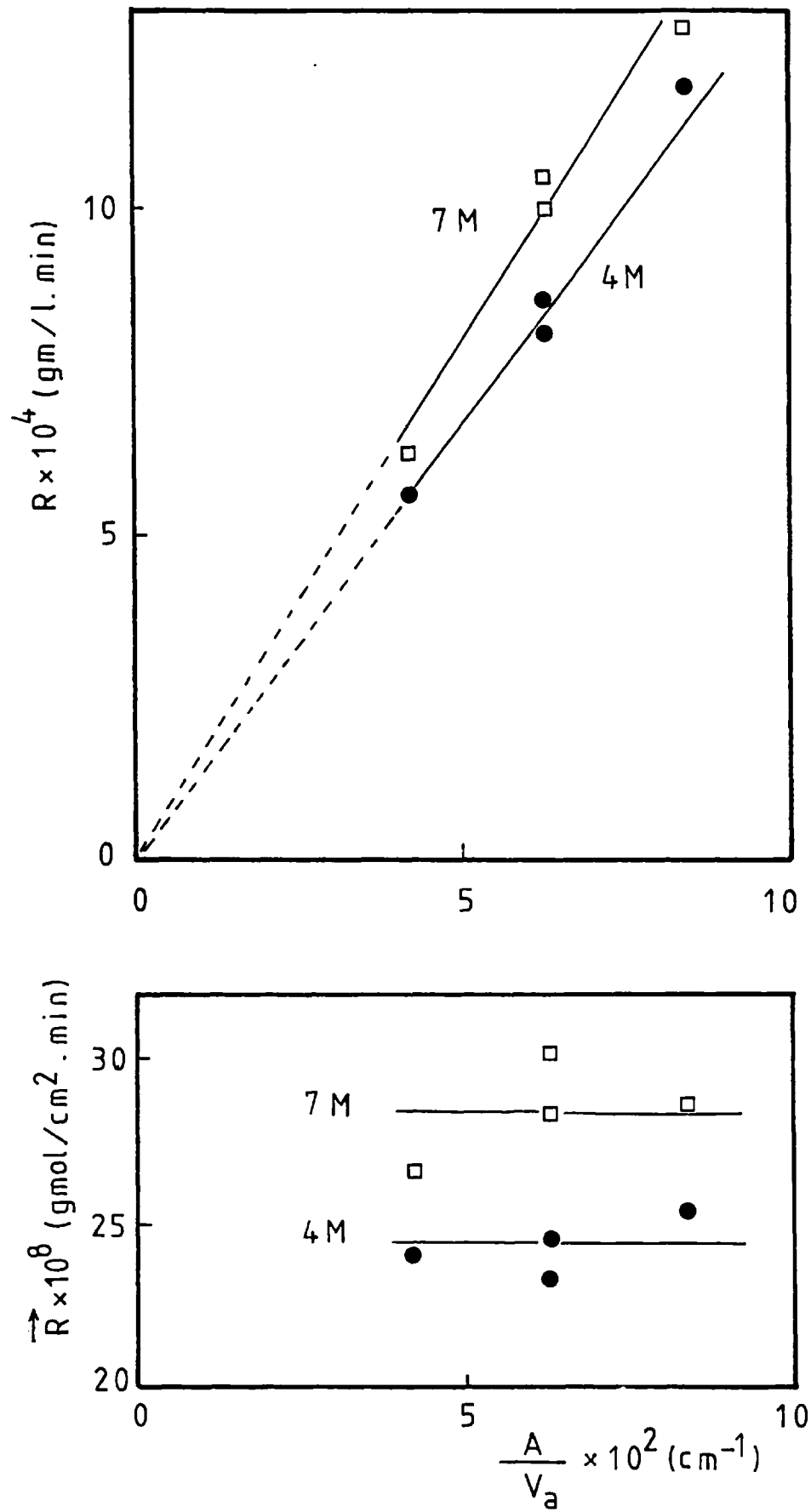


FIGURE 6.2.4.2. EFFECT OF INTERFACIAL AREA PER UNIT PHASE VOLUME ON EXTRACTION RATE. CONDITIONS: TOAHCl = 0.010 M, Fe = 0.0010 M, 25°C, phase volume A = O = 480 ml, contra-rotating stirring A = O = 250 rpm.

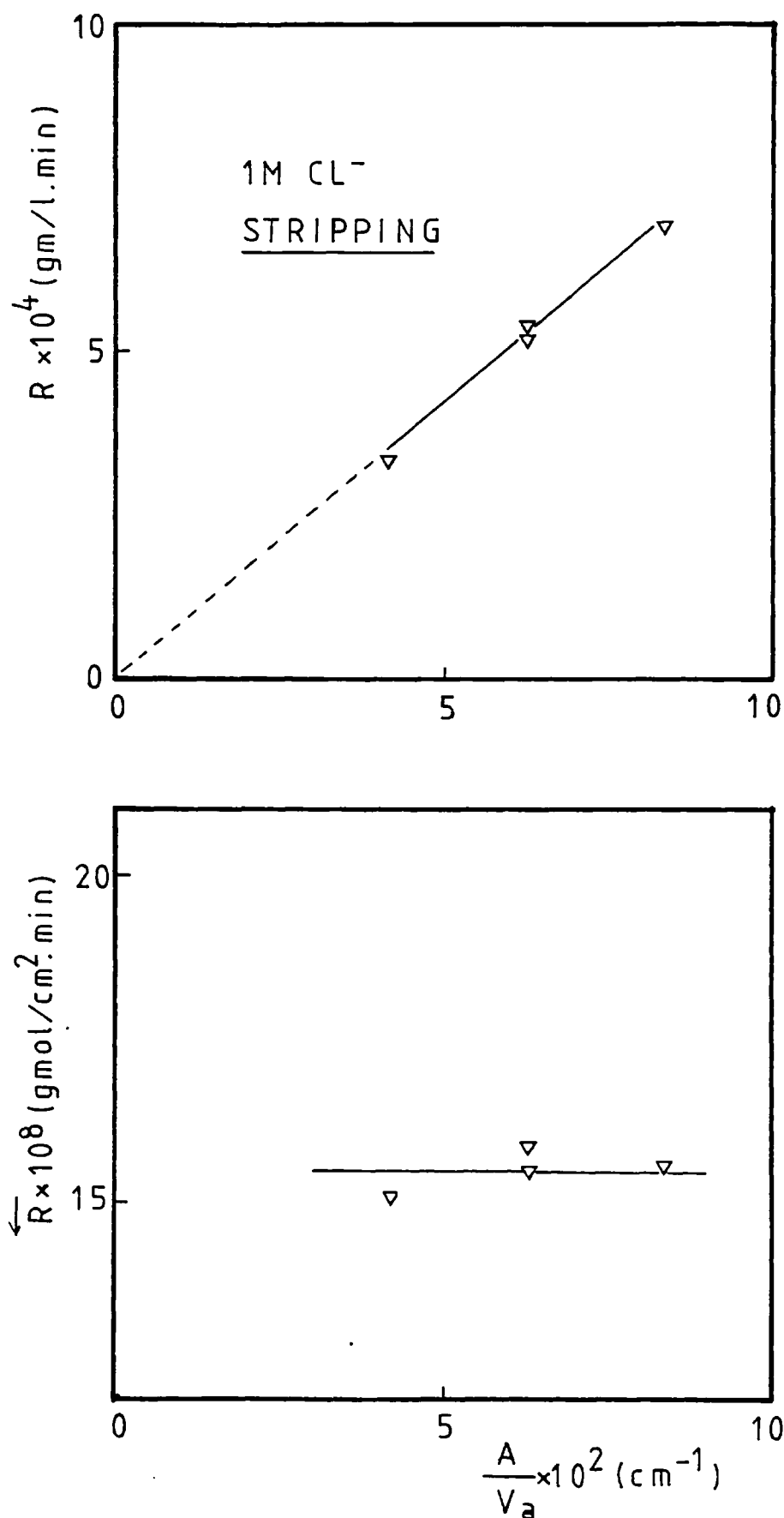


FIGURE 6.2.4.3. EFFECT OF INTERFACIAL AREA PER UNIT PHASE VOLUME ON STRIPPING RATE. CONDITIONS: Fe = 0.00174 M, TOAHCl = 0.01 M, 25°C, HCl = 1 M, phase volume A = O = 500 ml, contra-rotating stirring A = O = 250 rpm.

The combined effect of phase volume and interfacial area on the mass transfer rate was not investigated, as this would have required substantial modifications to the geometry of cell and this was thought to be unnecessary. Danesi et al.^{131,139} showed the independence of mass transfer rate on phase volume and the independence of specific mass transfer rates on the specific interfacial area for the extraction of some metal ions by TLAHCl and by dinonylnaphtalenesulfonic acid. Similar results were obtained by Ajawin¹⁵⁰ on the extraction of zinc by HDEHP.

The rate of interfacial reactions is always proportional to the amount of interfacial area available. This is true for reactions catalysed by solid surfaces as well as for reactions taking place at the interface between immiscible liquid phases. Homogeneous reactions taking place in the bulk liquid show no such dependence. Only an interfacial slow reaction explains satisfactorily the experimental results. The results cannot be attributed to a fast reaction since the process is chemically controlled. It is thus concluded that the mass transfer rate is controlled by a slow chemical reaction taking place at or near the interface.

6.2.5. The dependence of the specific mass transfer on the concentration parameters

Experiments were carried out to investigate the dependence of the extraction and stripping rates on TOAHCl and Fe concentrations at different aqueous chloride concentrations. A schematic representation of the investigated system is presented in Figure 6.2.5.0. In Figure 6.2.5.1. is shown the effect of Fe concentration on the extraction rate at 1 M chloride. The range of Fe concentrations investigated varied between 5×10^{-4} and 5×10^{-3} M, whereas the TOAHCl

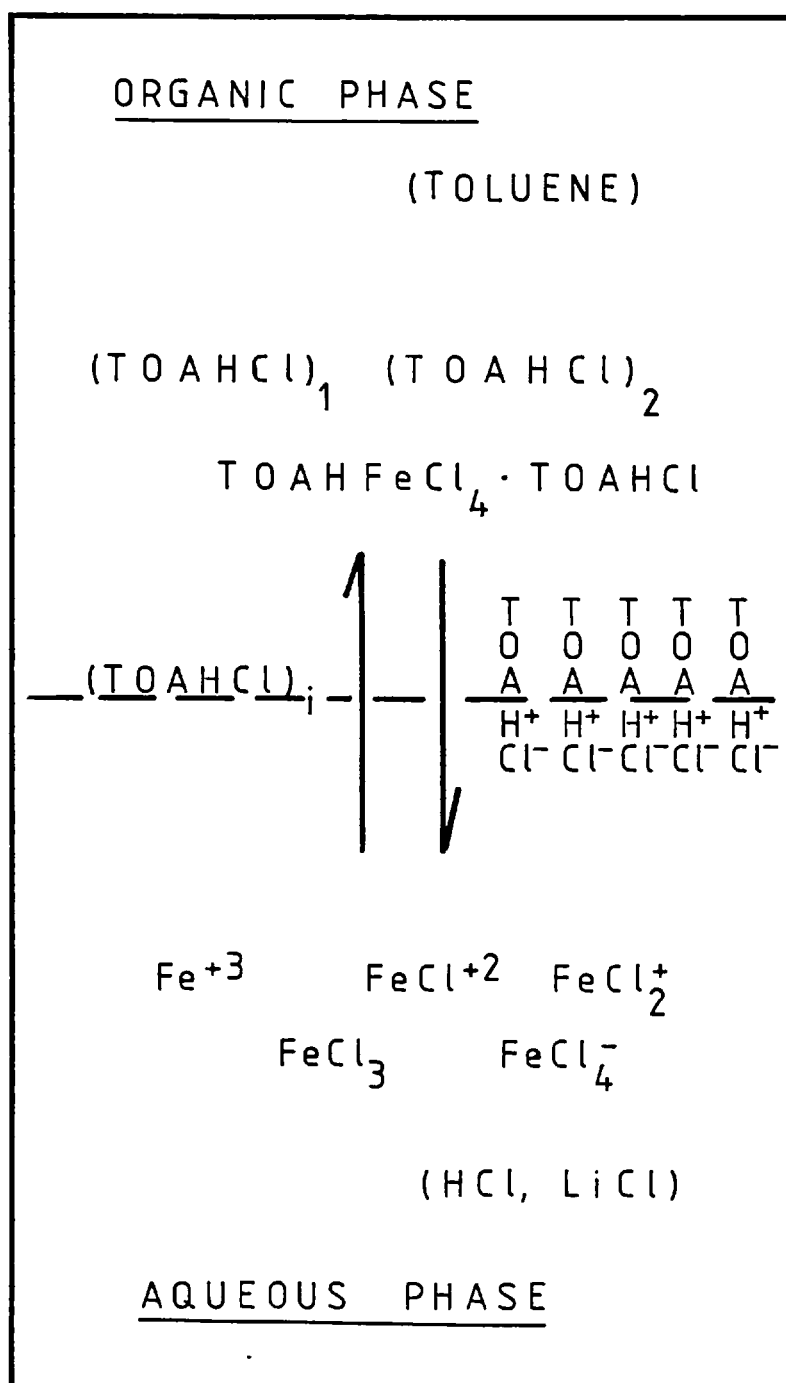


FIGURE 6.2.5.0. SCHEMATIC REPRESENTATION OF THE INVESTIGATED SYSTEM.

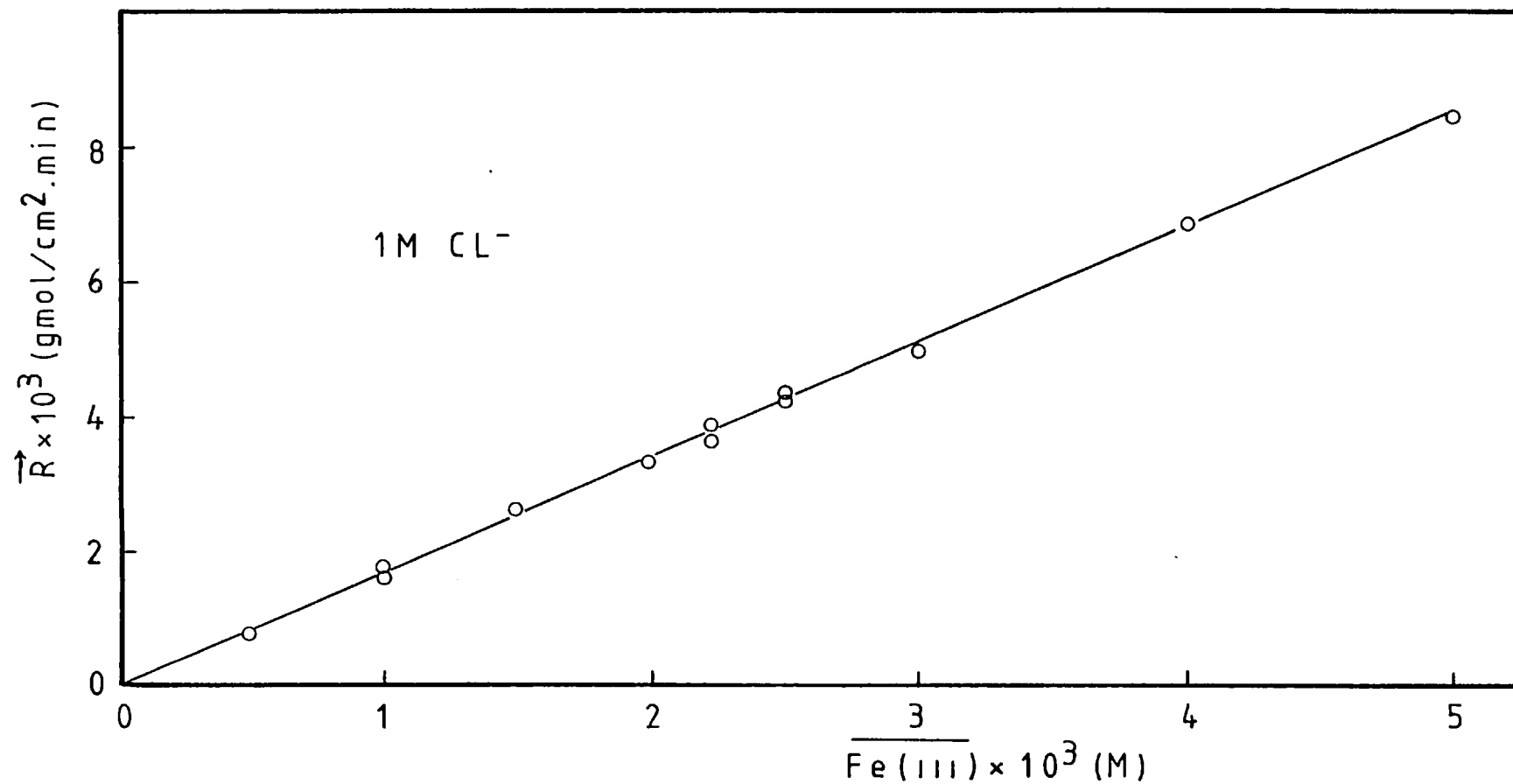


FIGURE 6.2.5.1. EFFECT OF AQUEOUS Fe(III) CONCENTRATION ON EXTRACTION RATE.
 CONDITIONS: TOAHCl = 0.01 M, HCl = 1 M, 25°C, Interfacial area = 30 cm², Phase
 volume A = O = 480 ml, contra-rotating stirrers A = O = 250 rpm.

concentration was kept constant at 0.01 M. The stirring speed was kept at 250 rpm in both phases, which was found to be in a safe and valid region of the plateau, in order to ensure that chemical control was mainly responsible for the extraction rate. Under these conditions, a linear dependence between extraction rate and Fe concentrations is observed, which indicates that the extraction rate is first order with respect to the Fe concentration.

In Figure 6.2.5.2. is presented the effect of Fe concentration on the extraction rate, at 4 and 7 M aqueous chloride concentration. The range of Fe concentrations investigated varied between 5×10^{-4} and 2.5×10^{-3} M and the TOAHCl concentration was kept constant at 0.01 M. The stirring speed in the organic phase was kept at 250 rpm in both cases, while the stirring speed in the aqueous phase was kept at 375 rpm at 4 M Cl^- and 550 rpm at 7 M Cl^- . These aqueous stirring conditions gave, in each case, a Reynolds number of about 2680, which was known to be in the plateau region. As at 1 M Cl^- , a linear dependence between extraction rate and Fe concentration is observed at the higher chloride concentrations, which indicates that the extraction rate is first order with respect to the Fe concentration. The slopes of the plots of extraction rate versus total Fe concentration increase with the aqueous chloride concentration, which indicates that in this range of conditions (1 to 7 M Cl^-) the concentration of the active Fe chlorocomplexes increase with increases in the aqueous chloride concentration.

The effect of the organic Fe concentration at 1 M on the stripping rate is shown in Figure 6.2.5.3. The range of Fe concentrations investigated varied between 1.74×10^{-4} and 1.74×10^{-3} M and the TOAHCl concentration was kept constant at 0.01 M. The solvated TOAHCl in the Fe-TOAHCl complex was not considered when estimating the free TOAHCl concentration, as it should be bonded in some

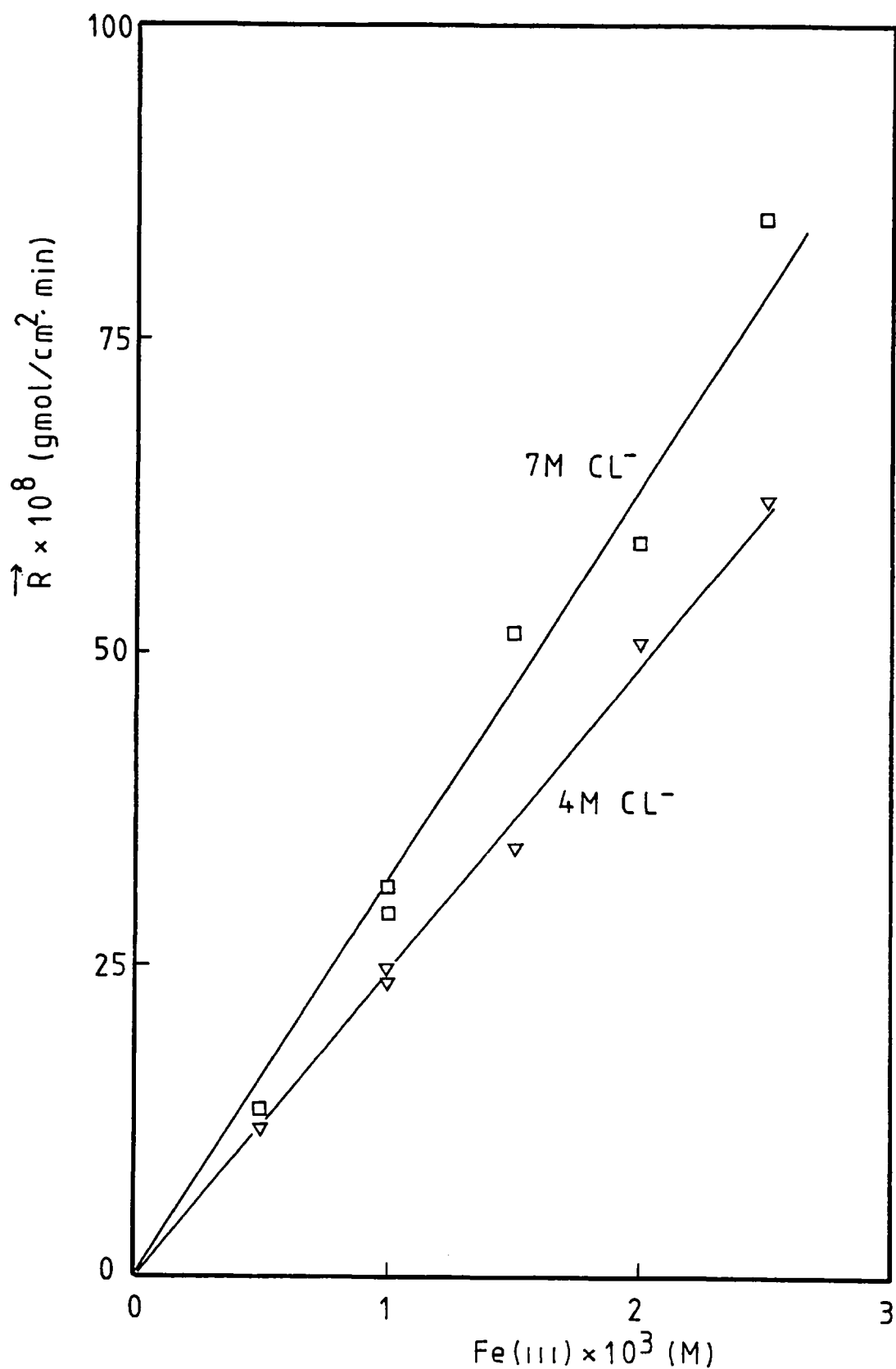


FIGURE 6.2.5.2. EFFECT OF Fe(III) CONCENTRATION ON EXTRACTION RATE. CONDITIONS: TOAHCl = 0.01 M, Cl⁻ = 4 or 7 M, 25°C, Interfacial area = 30 cm², Phase volume A = O = 480 ml, contra-rotating stirrers O = 250 rpm, A = 375 rpm at 4 M Cl or 550 rpm at 7 M.

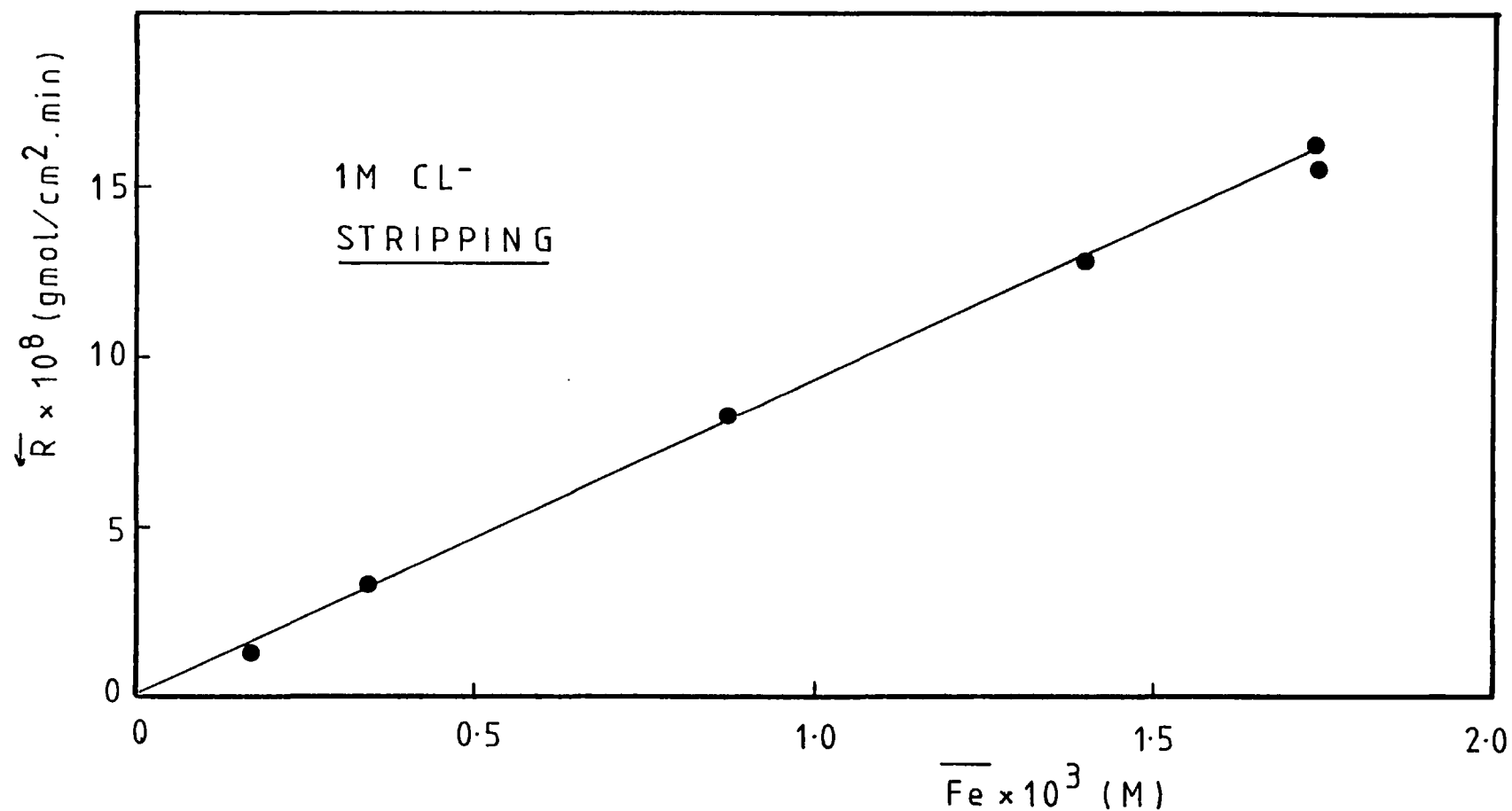


FIGURE 6.2.5.3. EFFECT OF ORGANIC Fe(III) CONCENTRATION ON STRIPPING RATE.
 CONDITIONS: TOAHCl = 0.01 M, HCl = 1 M, 25°C, Interfacial area = 30 cm²,
 Phase volume A = O = 500 ml, contra-rotating stirring A = O = 250 rpm.

way and so can be considered as part of the Fe-TOAHCl complex molecule. The stirring speed was kept at 250 rpm in both phases. Under these conditions, a linear dependence between stripping rate and organic Fe concentration is observed, which indicates that the stripping rate is first order with respect to Fe concentration.

The effect of TOAHCl concentration on the extraction rate at 1 M Cl^- is shown in Figure 6.2.5.4. The range of TOAHCl concentrations investigated varied between 0.002 and 0.1 M and the Fe concentration was kept constant at 2.5×10^{-3} M. The stirring speed was kept at 250 rpm in both phases. Under these conditions a parabolic relationship between extraction rate and total TOAHCl concentration is observed. At high TOAHCl concentrations the extraction rates tend to a plateau, although this was not reached under the investigated conditions. Monomer and dimer TOAHCl concentrations were calculated, as shown in Appendix B-1, using the determined and estimated dimerisation constants (K_2). Figure 6.2.5.5. shows the concentration of monomer and dimer TOAHCl as a function of total TOAHCl concentration. In a log-log plot a linear relationship is observed. Calculated monomer and dimer concentration derived from all K_2 values presented in Appendix B-1 are shown in Figure 6.2.5.5. The $K_2 = 45$ value was estimated based on the determined K_2 value at 37°C and the enthalpy value for the system TLAHCl-Toluene given in reference 224. It was assumed that the same enthalpy value would apply to the TOAHCl-toluene system, due to the chemical similarity of both systems. Thus, $K_2 = 45$ should be a reasonable estimate of the dimerisation constant of the present system at 25°C . Using the monomer and dimer concentrations calculated by assuming $K_2 = 45$, the extraction rates were plotted against monomer and dimer TOAHCl concentrations and the resulting plot is shown in Figure 6.2.5.4. It can be seen that, under these conditions, a linear dependence between extraction rate and monomer TOAHCl is observed, whereas the

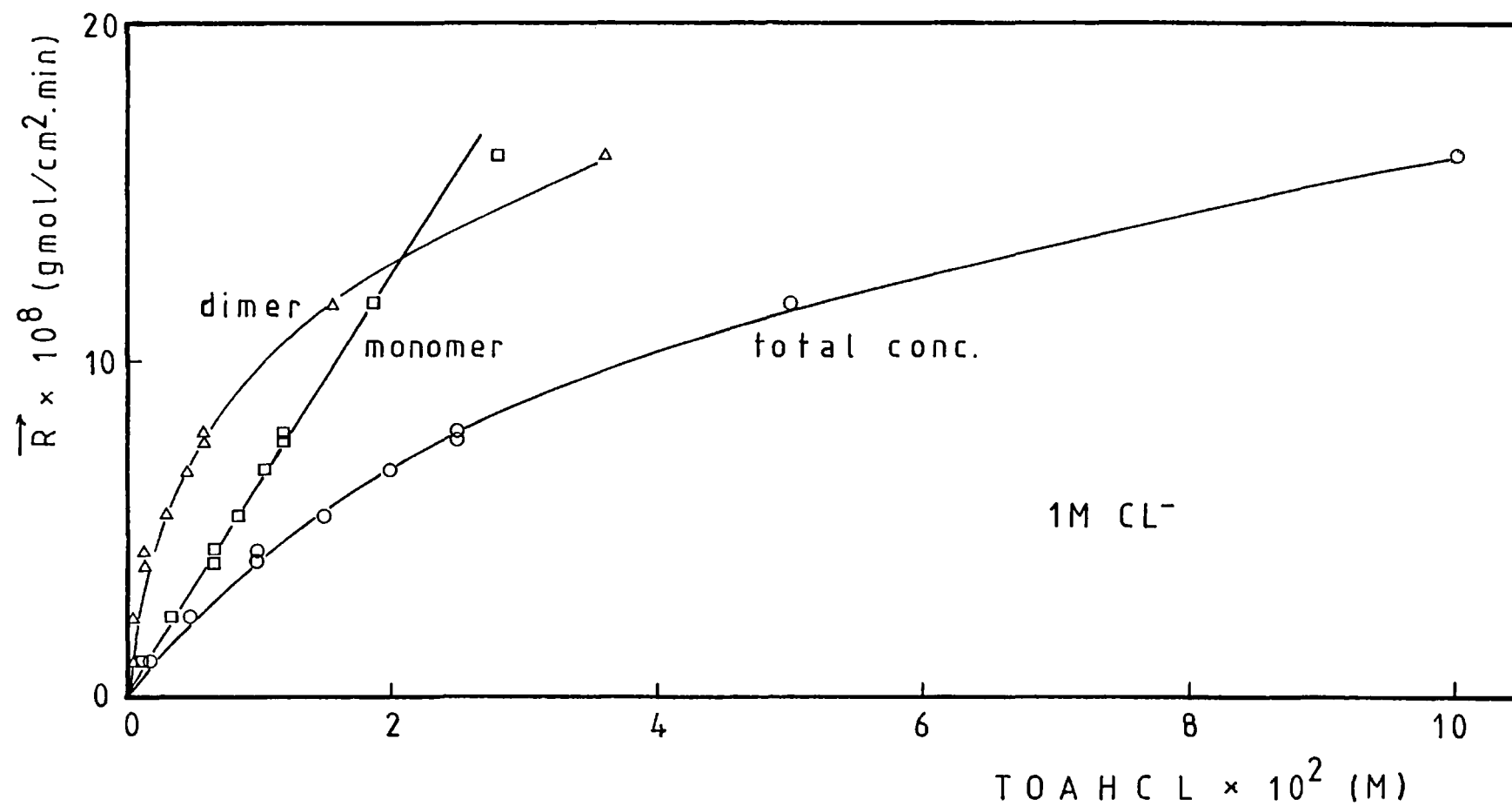


FIGURE 6.2.5.4. EFFECT OF TOAHCl CONCENTRATION ON EXTRACTION RATE.
 CONDITIONS: Fe(III) = 0.0025 M, Temp = 25°C, HCl = 1 M, Interfacial area = 30 cm²,
 Phase volume A = O = 480 ml, contra-rotating stirrers A = O = 250 rpm.

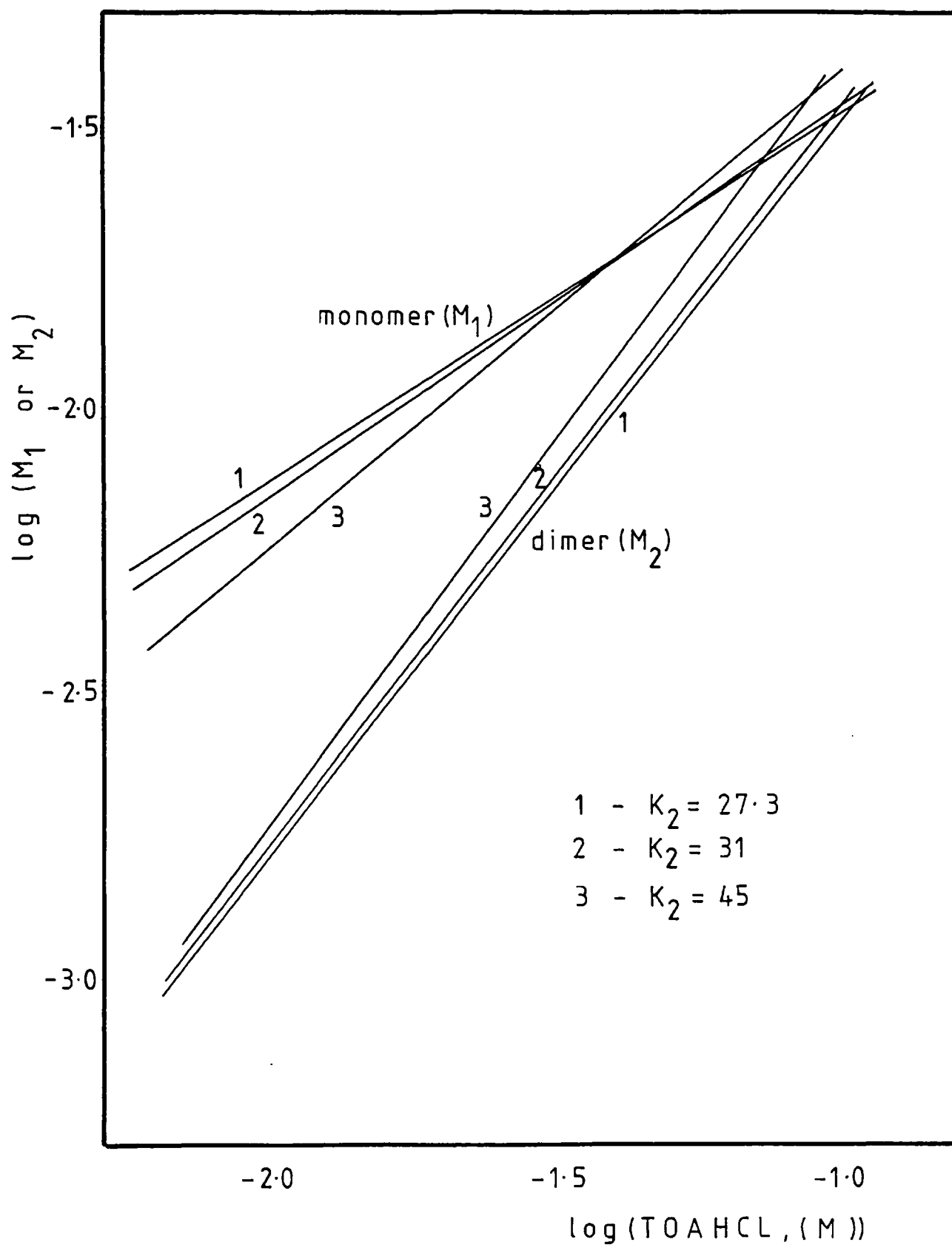


FIGURE 6.2.5.5. VARIATION OF THE CONCENTRATION OF MONOMERS AND DIMERS AS A FUNCTION OF THE DIMERISATION CONSTANT (K_2).

relationship between extraction rate and dimer TOAHCl is a parabolic one. This indicates that the extraction rate is first order with respect to the monomer TOAHCl. The plots of extraction rate against monomer TOAHCl concentrations calculated using the other K_2 values did not show linear relationships. Thus, if the extraction rate is indeed first order with respect to the monomer TOAHCl, the assumptions leading to $K_2 = 45$ were valid and correct. In the previous section (6.2.4.) it was shown that the extraction rate was controlled by an interfacial reaction at or near the interface. Interfacial studies^{135,137} using TLAHCl in toluene with some chloride solutions and similar systems have shown that only monomeric amine species are adsorbed at the interface.

The dependence of extraction rate on TOAHCl concentration at 4 and 7 M Cl^- was also investigated and the results are shown in Figures 6.2.5.6. and 6.2.5.7. The range of TOAHCl concentrations investigated varied between 0.005 and 0.025 M and Fe concentration was kept constant at 10^{-3} M in both cases. The stirring speed in the organic phase was kept at 250 rpm in both cases, while the stirring speed in the aqueous phase was kept at 375 rpm at 4 M Cl^- and 550 rpm at 7 M Cl^- . Using the monomer and dimer TOAHCl concentrations calculated, the extraction rates were plotted against the total (M), monomer (M_1) and dimer (M_2) TOAHCl concentrations in Figures 6.2.5.6. and 6.2.5.7. It can be seen that, under these conditions, a linear dependence between extraction rate and monomer TOAHCl is observed at both aqueous chloride concentrations, whereas the relationships between extraction rate and total and dimer TOAHCl are parabolic. These results again indicate that the extraction rate is first order with respect to the monomer TOAHCl concentration, confirming the same dependence observed, at 1 M Cl^- . The slopes of the plot of extraction rate versus monomer TOAHCl increase with the aqueous chloride concentration, as in the case of the Fe

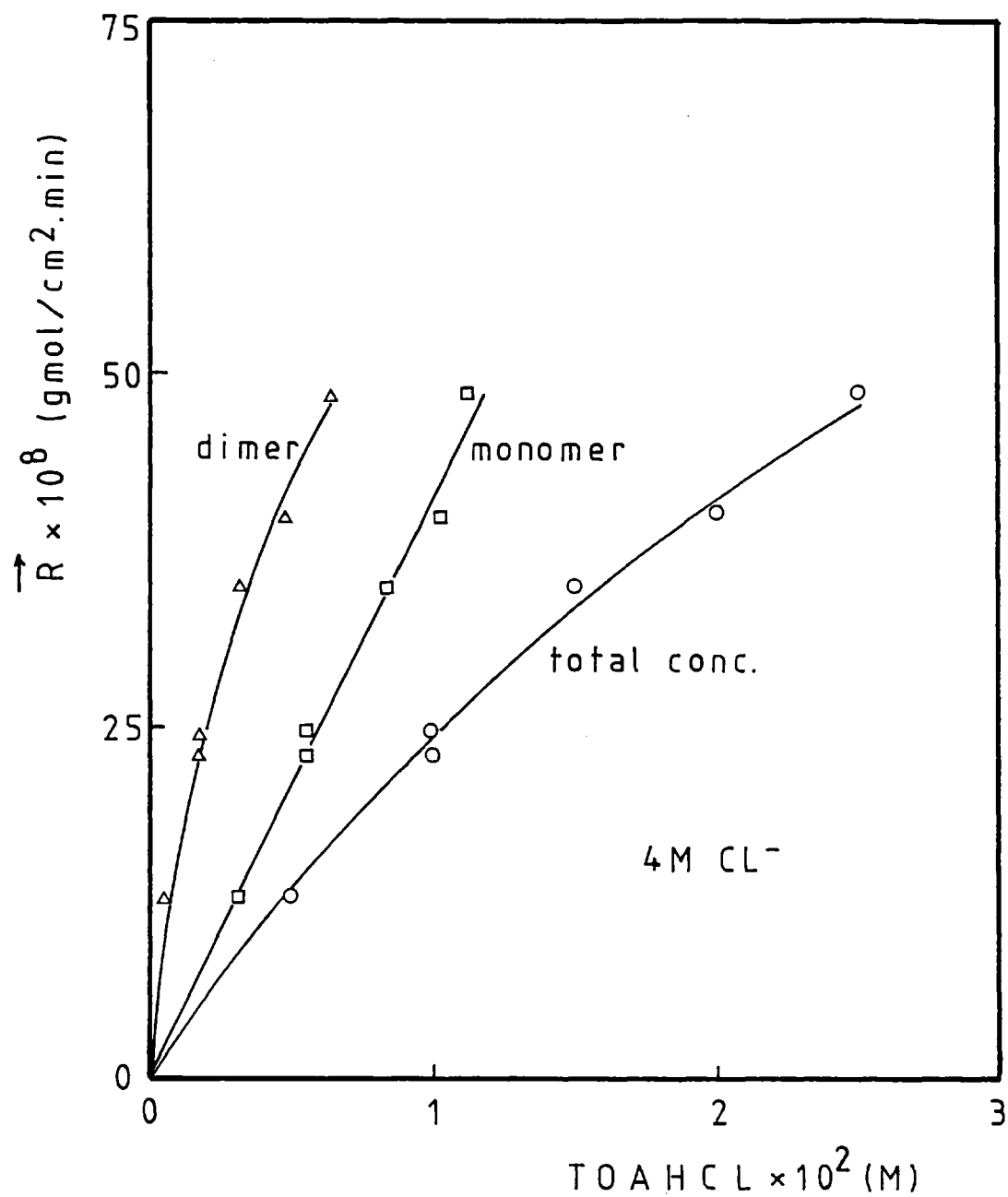


FIGURE 6.2.5.6. EFFECT OF TOAHCl ON EXTRACTION RATE.
 CONDITIONS: Fe(III) = 0.0010 M, Cl⁻ = 4 M, 25°C,
 Interfacial area = 30 cm², Phase volume A = O = 480 ml,
 contra-rotating stirrers, O = 250 rpm, A = 375 rpm.

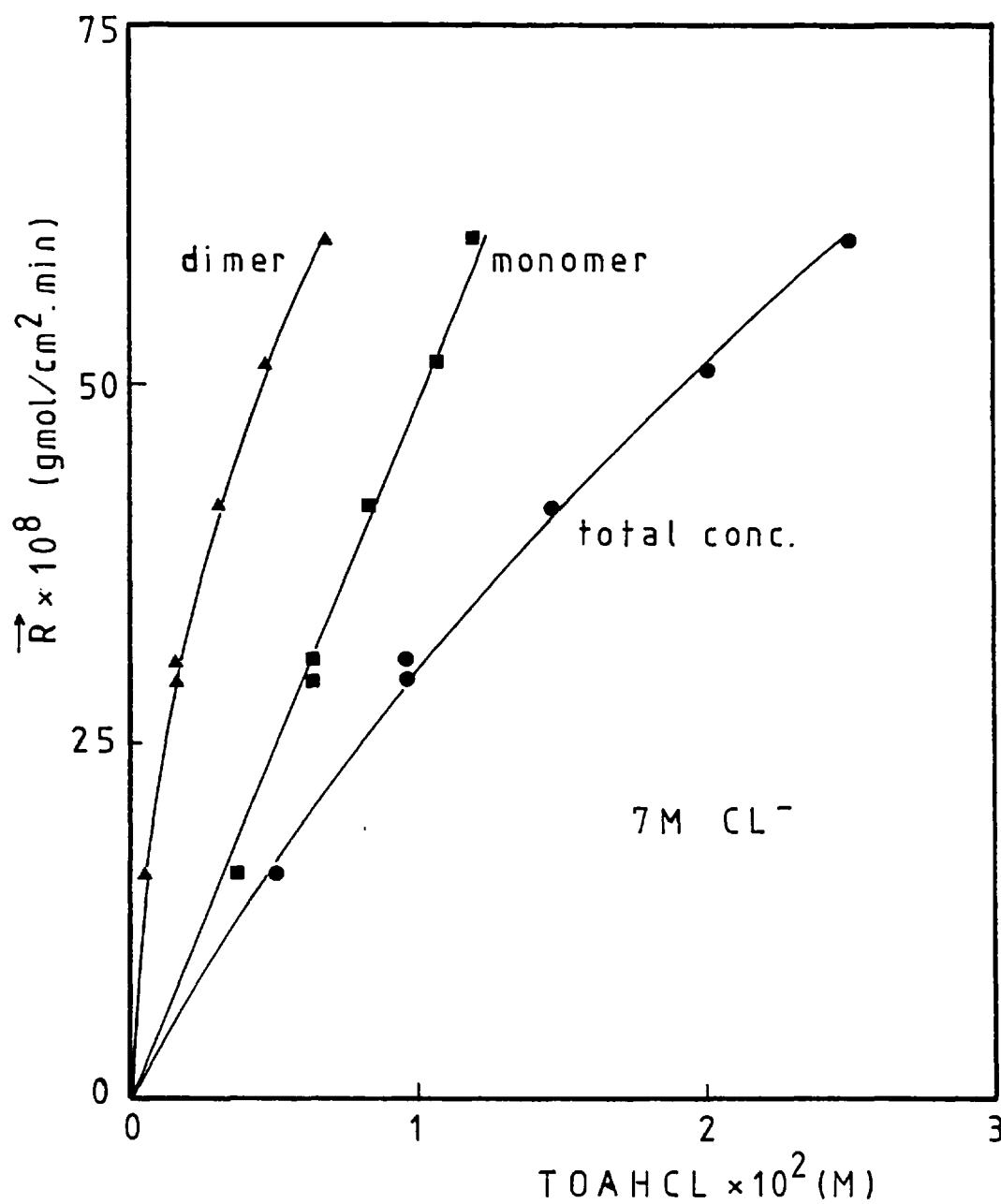


FIGURE 6.2.5.7. EFFECT OF TOAHCl ON EXTRACTION RATE.
 CONDITIONS: $\text{Fe(III)} = 0.0010 \text{ M}$, $\text{Cl}^- = 7 \text{ M}$, 25°C ,
 Interfacial area = 30 cm^2 , Phase volume A = O = 480 ml ,
 contra-rotating stirrers, O = 250 rpm , A = 550 rpm .

dependence, which confirms that in this range of conditions the concentration of the active Fe chlorocomplexes increase with increases in the aqueous chloride concentration.

The effect of TOAHCl concentration on the stripping rate at 1 M Cl^- is shown in Figure 6.2.5.8. The range of concentrations investigated varied between 0.01 and 0.1 M and the organic Fe concentration was kept constant at $1.74 \times 10^{-3} \text{ M}$. The stirring speed was kept at 250 rpm in both phases. Under these conditions, an increase in the TOAHCl concentration results in a decrease in the stripping rate, which suggests an inverse dependence between stripping rate and TOAHCl concentration. Using the total, monomer and dimer TOAHCl concentration calculated, the stripping rates were plotted against the reciprocals of total (M), monomer (M_1) and dimer (M_2) TOAHCl concentrations. This plot is presented in Figure 6.2.5.9. It can be seen that, under these conditions, a linear dependence between extraction rate and the reciprocal dimer TOAHCl concentration is observed, although a reasonable linear fit between stripping rate and monomer or total TOAHCl is also possible, which indicates the need of a more thorough investigation in order to confirm the most likely dependence. Visual observation of Figure 6.2.5.9. indicates that an inverse first order dependence of stripping rate with respect to the dimer TOAHCl concentration is the most likely possibility. This observation may indicate that the Fe-TOAHCl complex in the organic phase is associated with the dimer form of TOAHCl as suggested by the slope analysis of the distribution measurements under equilibrium conditions and Raman spectroscopy studies¹⁹⁹.

The dependence of the extraction rate on the aqueous chloride concentration was investigated and the results are shown in Figure 6.2.5.10. The range of chloride concentrations investigated varied between 1 and 9 M Cl^- , whereas the TOAHCl and total Fe concentrations were kept

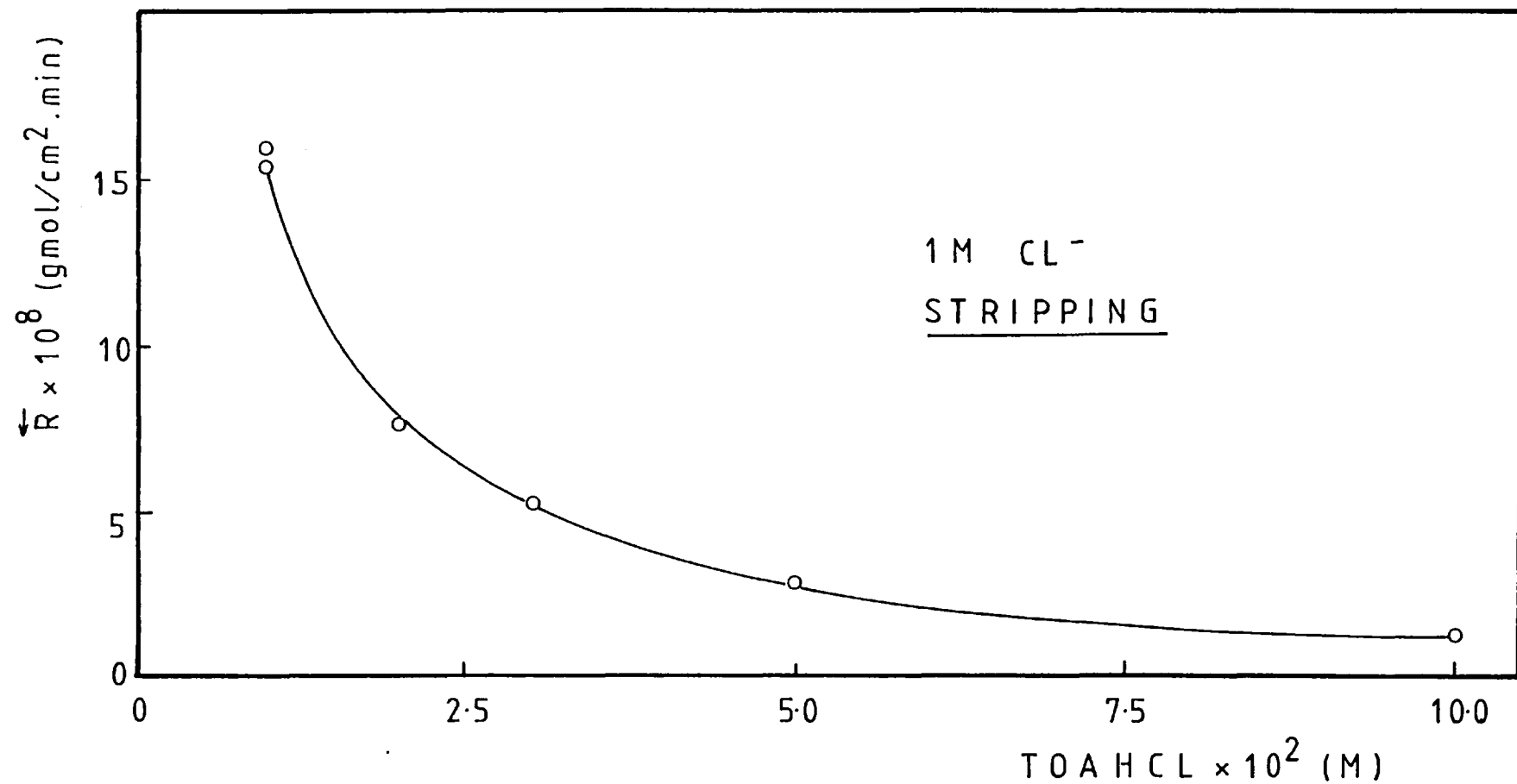


FIGURE 6.2.5.8. EFFECT OF TOAHCl on STIRRING RATE. CONDITIONS: Fe = 0.00174 M, HCl = 1 M, 25°C, Interfacial area = 30 cm², Phase volume A = O = 500 ml, contra-rotating stirrers A = O = 250 rpm.

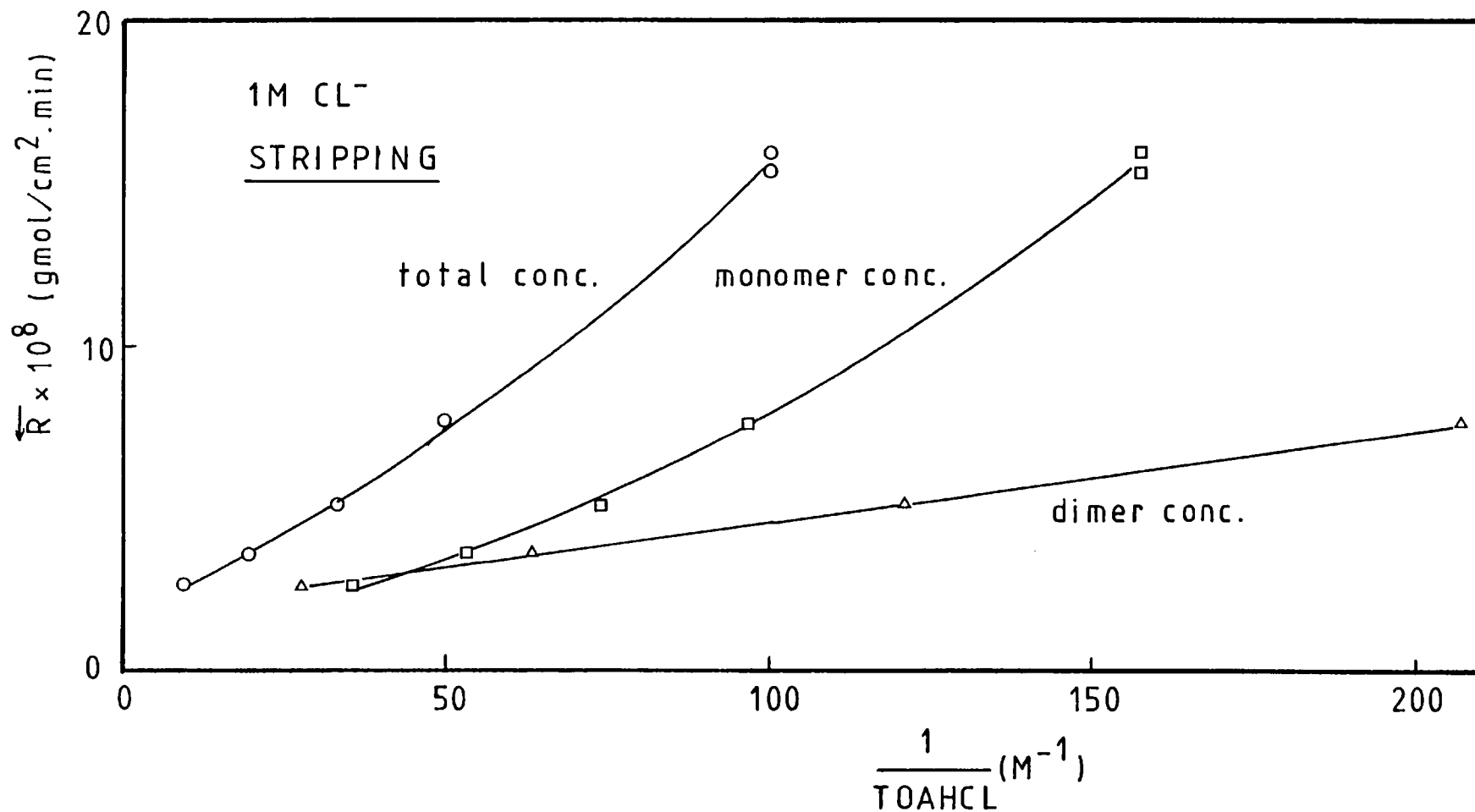


FIGURE 6.2.5.9. EFFECT OF TOAHCl on STRIPPING RATE. CONDITIONS: Fe = 0.00174 M, HCl = 1 M, 25°C, Interfacial area = 30 cm², Phase volume A = O = 500 ml, contra-rotating stirrers, A = O = 250 rpm.

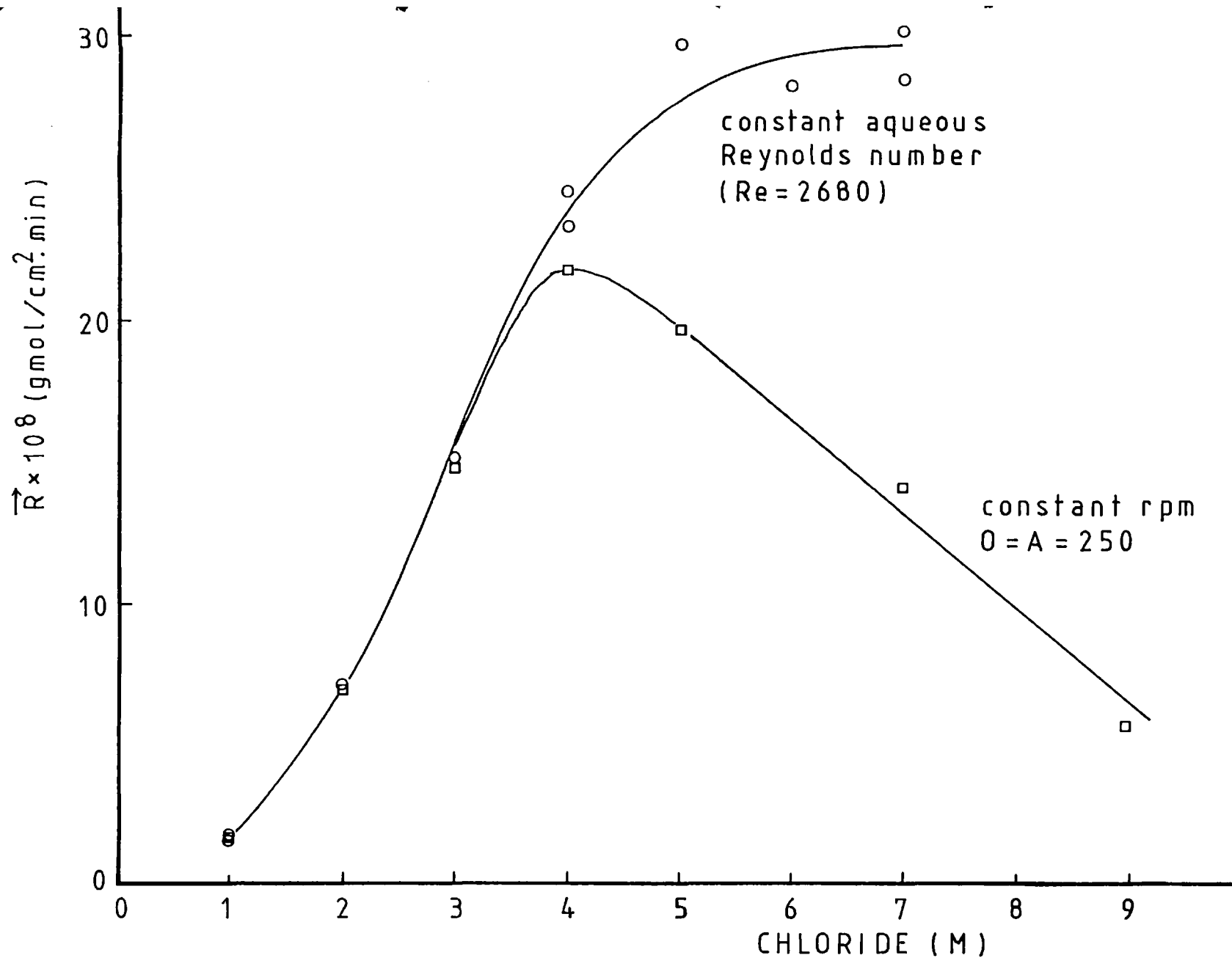


FIGURE 6.2.5.10. EFFECT OF AQUEOUS CHLORIDE CONCENTRATION ON INITIAL MASS TRANSFER RATE. CONDITIONS: $TOAHCl = 0.01\text{ M}$, $Fe(III) = 0.001\text{ M}$, Interfacial area = 30 cm^2 , Phase volume $A = O = 480\text{ ml}$, 25°C .

constant at 0.01 and 0.001 M respectively. At first, the experiments were carried out at a constant stirring speed of 250 rpm in both phases. It was observed that the extraction rate increased with increases in the aqueous chloride concentration up to 4 M and then started to decrease steadily. However, since the viscosity of the aqueous phase increases with increased aqueous chloride concentration, hydrodynamic similarity of the mixing conditions was not maintained, and also the stirring conditions were not in the plateau region throughout this series of experiments. Thus, some experiments were carried out under conditions of chemical control and others under mixed or mass transfer control. This could lead to misleading conclusions as in the work presented by Chiarizia and Danesi^{131,133}. A second series of experiments was then carried out under similar chemical conditions but with the aqueous Re kept constant at $Re = 2680$, by varying the aqueous stirring speed. Aqueous chloride concentrations over 7 M were not used as no plateau was found under these conditions, so that chemical control could not be attained. The results are shown in Figure 6.2.5.10. It can be seen that under conditions of hydrodynamic similarity of the mixing conditions in the aqueous phase, the effect of chloride concentration was significantly different. The extraction rate increased with the increase of the chloride concentration up to 5 M Cl^- and then, apparently, a plateau was reached. The relationship between the extraction rate and aqueous chloride concentration is a complex one. It may reduce to a simple dependence if the concentrations of the active Fe chlorocomplex(es) is (are) considered, but as shown in Section 3.6. the calculation of the distribution of the chlorocomplexes as a function of aqueous chloride concentration is far from simple, as no reliable data are available for the stability constants. This problem will be analysed in more detail in the following section.

The effect of aqueous chloride concentration on the initial stripping rate is shown in Figure 6.2.5.11. The range of chloride concentrations investigated varied between 1 and 4 M, whereas TOAHCl and organic Fe concentrations were kept constant at 0.01 and 1.74×10^{-3} M respectively. The stirring speed in the organic phase was kept at 250 rpm, while the stirring conditions in the aqueous phase were kept at $Re = 2860$ in order to give hydrodynamic similarity of the mixing conditions. Under these conditions, the stripping rate was found to be independent of aqueous chloride concentration. The results indicate also that, if the stripping rate is indeed independent of the Cl^- concentration, then the criterion of hydrodynamic similarity used throughout this investigation is a reasonable one.

Examining the dependence of the extraction and stripping rates on the aqueous chloride concentration, it can be concluded that the reactions involved in the process do not take place in a plane interface, but in a zone near the interface, as indicated by the different relationships obtained between extraction and stripping rates and aqueous chloride concentration. These chloride dependencies combined with other results indicate also that the slow step for the extraction rate is located in the aqueous phase near the interface, whereas the slow step for the initial stripping rate is located in the organic phase near the interface or at the interface.

The classical chemical mechanism postulated¹⁷⁰ for the amine system is one involving sequential reactions between metal ions and the extractant taking place at or near the interface. The mechanism involves adsorption of the extractant onto the interface, partial ionization of the hydrophilic end of the extractant in the aqueous phase near the interface, followed by reaction between the extractant and metal ions and termination of the process

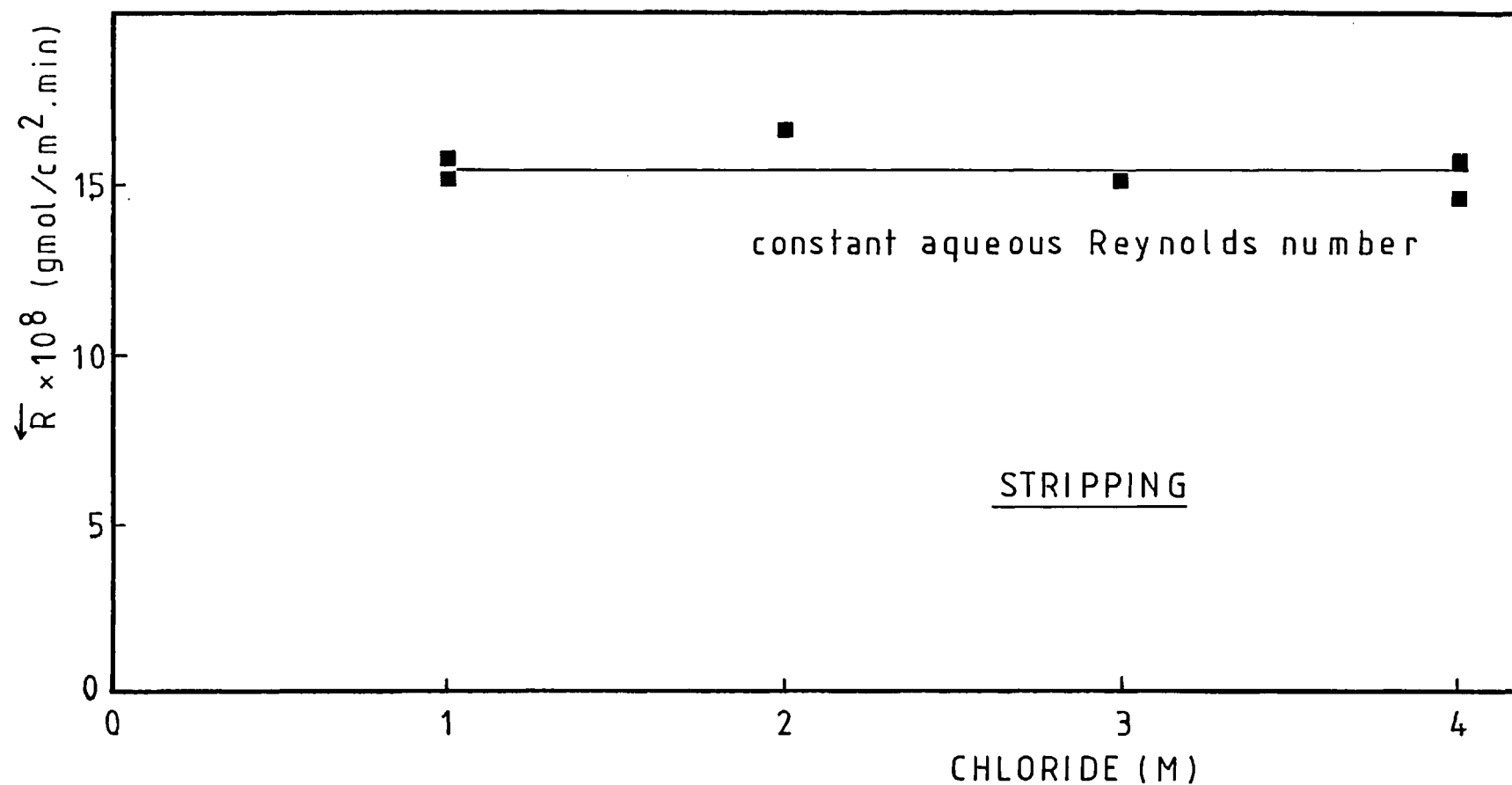


FIGURE 6.2.5.11. EFFECT OF AQUEOUS CHLORIDE CONCENTRATION ON INITIAL MASS TRANSFER RATE (STRIPPING). CONDITIONS: $\text{Fe} = 1.74 \times 10^{-3} \text{ M}$, $\text{TOAHCl} = 0.01 \text{ M}$, 25°C , Interfacial area = 30 cm^2 , Phase volume A = O = 500 ml, contra-rotating stirring, constant aqueous Reynolds number ($\text{Re} = 2680$), $\text{O} = 250 \text{ rpm}$.

by transferring back the metal-extractant complex to the organic phase. An alternative mechanism assuming that metal ions invade the organic phase is ruled out because transfer of hydrated metal ions into a water immiscible oil phase is not energetically favoured.

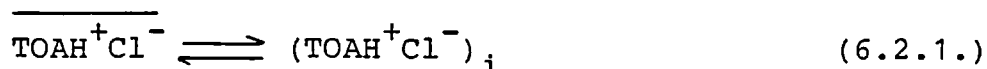
The preliminary analysis of the results indicate that under the investigated conditions the extraction and stripping rates are first order with respect to the Fe concentration and the extraction rate is first order with respect to TOAHCl monomer concentration, whereas the stripping rate is, probably, inverse first order with respect to TOAHCl dimer concentration. The extraction rate is of complex order with respect to the aqueous chloride concentration, but it may reduce to a simple dependence with respect to the active Fe chlorocomplex(es) concentration. The stripping rate is independent of the aqueous chloride concentration.

For a system where the mass transfer rate is controlled by an interfacial chemical reaction, the objective of kinetic experiments is to study the dependence of the mass transfer rate on concentration variables and thereby attempt to derive a model of the chemical mechanism. A rate equation can be written relating the mass transfer rate to concentration variables. The form of the equation will depend on the single, or combination of, elementary reaction steps that have been taken to represent the overall reaction scheme. The stoichiometric equation for the overall reaction will generally give no information about the steps in the chemical mechanism. In order to test whether the derived rate equation can be used to describe the experimental rate results and, thus, to confirm or reject the proposed mechanism, the appropriate rate constants must be evaluated. Two methods may be used to do this²³². The assumed rate equation can be integrated to give bulk concentrations as a function of time and the

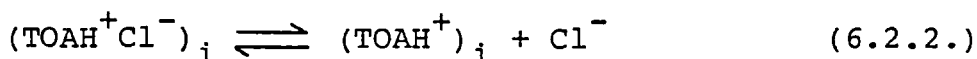
experimental results can be used to see if they fit the integrated form (integral method). Alternatively, the slopes of the concentration-time profiles are obtained and tested directly against the assumed rate equation (differential method). The integral method tends to lead to integral orders irrespective of the true mechanism. Where rates do not depend on concentrations raised to integral powers, the differential method will reveal the correct non-integral orders. The problem with the differential method lies in the difficulty of accurately measuring the slopes of the concentration-time profiles, but it is more reliable and gives more information than the integration method. In some cases, the rate equation cannot be integrated so the differential method must be used. Another method (slope analysis) has been used by a number of investigators⁴⁵⁻⁴⁷ in solvent extraction kinetic studies. The basic assumptions in this method are that the overall reaction rate is represented by a rate expression derived from the overall chemical reaction and that the interfacial concentrations can be replaced by bulk concentrations. The assumed rate equation is integrated and the resulting equation tested for the different concentrations investigated. This method is a combination of the integral and differential methods. The slope analysis method involves the log-log plots of the slope of semi-log plots, so that some real trends may be entirely masked by the insensitivity of the log plots. As shown in Section 5.5., the experimental conditions used in this investigation gave accurate values of the initial mass transfer rates, which indicates that the use of the differential method should give more reliable conclusions.

As shown in Section 3.5, the extraction mechanism may involve addition, anion exchange or several simultaneous reactions of addition and anion exchange. Firstly, the bulk extractant must be transferred to and

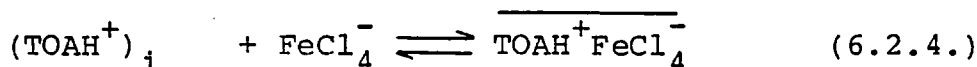
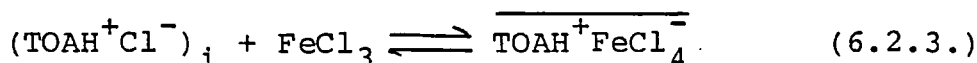
adsorbed at the interface, as follows



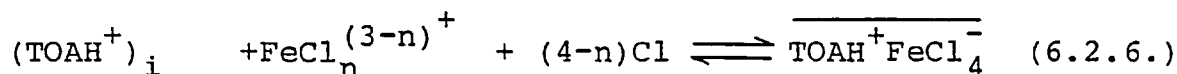
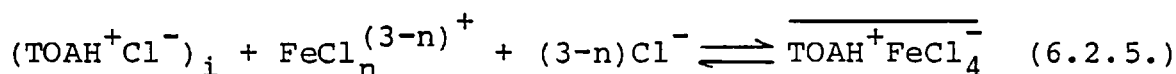
where the subscript ()_i refers to interfacial species. The extractant contains a hydrophilic group which should protrude into the aqueous phase and may dissociate



Then, the chemical reaction between the iron chlorocomplex and the extractant must take place at or near the interface, followed by the transfer of the metal complex to the bulk organic phase. The following reactions are possible:



It is also conceivable that cationic species may be extracted as shown by the following generalised equations:

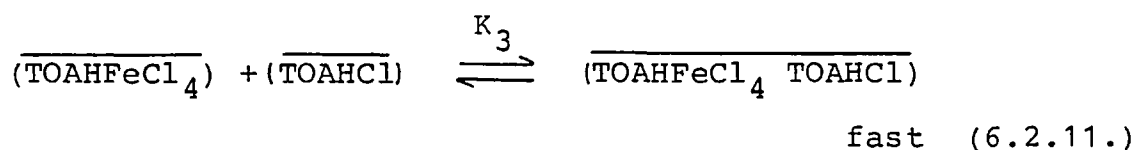
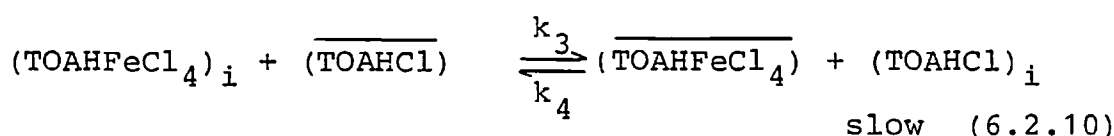
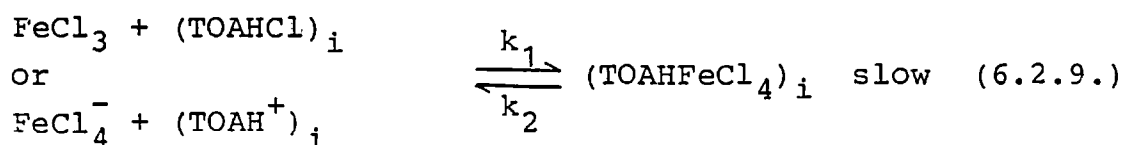
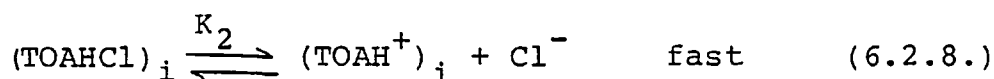


where $n = 0, 1$ or 2 (Fe^{3+} , FeCl^{2+} or FeCl_2^+). The stripping reactions would be vice-versa. However, reactions (6.2.5.) and (6.2.6.) should reduce to neutral or anionic transfer at some stage of the mechanism, if not, these would require a third, fourth or fifth order reaction, which is most unlikely. So, the most probable mechanism should involve neutral and (or) anionic transfer.

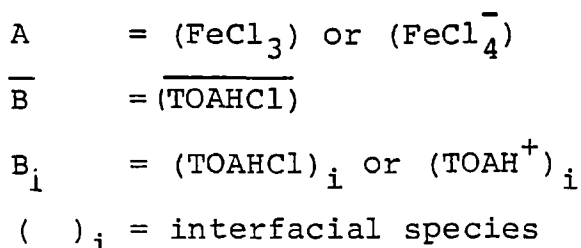
An attempt was made to elucidate the reaction mechanism in the light of the experimental results. The

chemical reaction process at the interface is a complex one which will involve a number of elementary reaction steps. The relative rates of these steps are important and they all contribute to the overall rate. However, the slowest step, or series of sequential steps will be rate controlling. It is therefore assumed that any step before the rate controlling ones will be much faster and so essentially at equilibrium, while steps after the rate controlling ones are assumed to go rapidly to completion and will be also in equilibrium.

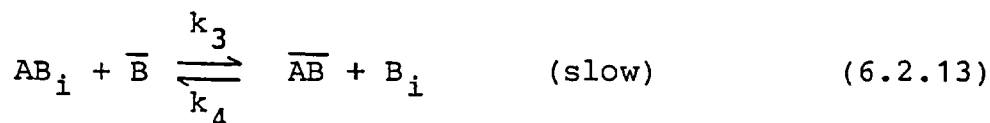
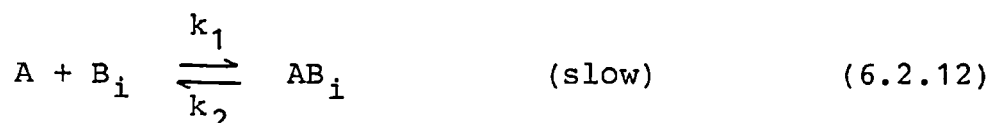
The proposed reaction mechanism can be represented by the following elementary steps:



and for the sake of simplicity



and equations (6.2.9) to (6.2.11) are re-written as



The extractant contains a hydrophilic group which renders it surface active. It should therefore be adsorbed rapidly at the interface. Adsorption and desorption are both very rapid processes and are generally limited only by the rate at which the species can diffuse to or from the interface. It has already been shown that a mass transfer process was not controlling the rate in the plateau region where this study was being carried out and so that equation (6.2.7.) could not be the slow step.

Danesi et al.¹³⁹ studied the kinetics of the system TLA (in toluene) - HCl (water). They showed that the dissociation of the amine hydrochloride at the interface, represented by the equation



is a fast step. The dissociation of the interfacial TOAHCl should be also a rapid process compared with the other reactions. Acid dissociations in aqueous media are very fast reactions with rate constants over 10^9 (litre/gmol. sec)²³². Even though the TOAHCl is restricted to the interface, the hydrophilic end of the molecule protruding into the aqueous phase would be expected to behave as if the dissociation were taking place homogeneously in the aqueous phase. Honaker and Freiser⁵⁹ proposed such a scheme for dithizone in the zinc dithizonate extraction.

For the reasons outlined above, equation (6.2.8.) should not be a slow step.

Equation (6.2.14) must be considered in order to fully characterize the reaction mechanism. The slope analysis of the distribution measurements ($\log D_{\text{Fe}}$ versus $\log \text{TOAHCl}$) at concentration levels typical of this work together with spectrophotometric¹⁹⁶⁻¹⁹⁸ and Raman spectroscopy¹⁹⁹ studies showed that at trace levels of iron in the organic phase the organic complex can be represented by $\text{TOAHFeCl}_4 \cdot \text{TOAHCl}$ (or AB.B) solvated with some TOAHCl . As the organic Fe concentration was monitored in the bulk organic, where this complex was predominant under the investigated conditions, equation (6.2.14) must be used in order to be consistent with the experimental results. As the rate controlling step has been shown to be an interfacial chemical reaction, equation (6.2.14) should not be the rate controlling one as only bulk concentrations are involved.

The hydration of the Fe chlorocomplexes is not considered in this mechanism for the reasons outlined in Section 3.6. Metal ions are not surface active. It would be easier for them to react with interfacial TOAHCl or TOAH^+ protruding into the aqueous phase, rather than having to adsorb at the interface. On the organic side it might be possible that the rate of adsorption or desorption of the Fe- TOAHCl complex, represented by equation (6.2.13) could be the rate controlling step. The difficulty of displacing the organic complex from the interface could be a slow step. Interfacial tension measurements should give some useful information about this possibility, but these were not available.

It would thus seem that the rate controlling steps are those represented by equations (6.2.12) and (6.2.13). Either one could be a rate controlling step, or both if they

have comparable rates. The relative velocities in equations (6.2.12) and (6.2.13) will depend on the existing chemical conditions.

A rate equation based on equations (6.2.12) and (6.2.13) can be derived. Forward and reverse reaction rates for both steps are taken into consideration. From equation (6.2.12) the following expression is obtained for the extraction rate:

$$\frac{V}{A} \frac{d(AB)_i}{dt} = k_1 (A) (B)_i - k_2 (AB)_i \quad (6.2.15)$$

Since equation (6.2.7.) is assumed in equilibrium, then

$$\frac{(TOAHCl)_i}{\overline{TOAHCl}} = \frac{B_i}{\overline{B}} = K_1 \quad (6.2.16)$$

under the investigated conditions $\overline{B} \gg A$ and at least at the beginning of the extraction, $\overline{B}$ will be constant and thus

$$B_i = K_1 (\overline{B}) = \text{constant} \quad (6.2.17)$$

$$\text{and } k_1 (B)_i = k_1^* \quad (6.2.18)$$

Substituting equation (6.2.18) into (6.2.15) gives

$$\frac{V}{A} \frac{d(AB)_i}{dt} = k_1^* (A) - k_2 (AB)_i \quad (6.2.19)$$

The active Fe chlorocomplex has been written as A ($FeCl_3$ or $FeCl_4^-$) without implying which chlorocomplex(es) is (are) reacting. However a direct proportionality always exists between the total aqueous iron concentration and the concentration of any Fe chlorocomplex at a constant chloride concentration. Since a linearity between extraction rate and total Fe concentration was observed in

all cases, k_1^* would represent the product of a reaction constant k_1^{**} and the fraction of the concentration of the active chlorocomplex (α_n) reacting with TOAHCl. There is also no "a priori" reason or need to assume that either only monomer or dimer TOAHCl, or both monomers and dimers will be the reacting species, although the results showed clearly that monomer TOAHCl was the active species involved in the initial extraction rate.

The extraction rate derived from equation (6.2.13) gives

$$\frac{V}{A} \frac{d(AB)_i}{dt} = k_3 (AB)_i (\overline{B}) - k_4 (\overline{AB}) (B)_i \quad (6.2.20)$$

using the same assumption to eliminate $(B)_i$ as in equation (6.2.17) gives

$$k_4 (B)_i = k_4^* \quad (6.2.21)$$

and equation (6.2.20) becomes

$$\frac{V}{A} \frac{d(AB)_i}{dt} = k_3 (AB)_i (\overline{B}) - k_4^* (\overline{AB}) \quad (6.2.22)$$

Using the steady state assumption with respect to the intermediate complex gives

$$k_1^* (A) - k_2 (AB)_i = k_3 (AB)_i (\overline{B}) - k_4^* (\overline{AB}) \quad (6.2.23)$$

then

$$(AB)_i = \frac{k_1^* (A) + k_4^* (\overline{AB})}{k_2 + k_3 (\overline{B})} \quad (6.2.24)$$

Substituting equation (6.2.24) into (6.2.22) gives

$$\frac{V}{A} \frac{d(AB)_i}{dt} = \frac{\frac{k_1^* k_3}{k_2} (A) (\overline{B}) - k_4^* (\overline{AB})}{1 + \frac{k_3}{k_2} (\overline{B})} \quad (6.2.25)$$

The rate of appearance of iron in the bulk organic phase would be the rate of appearance of the intermediate complex at the interface, as a consequence of the steady state assumption, so that

$$\frac{d(AB)_i}{dt} = \frac{d(\overline{AB})}{dt} \quad (6.2.26)$$

and equation (6.2.25) becomes

$$\frac{V}{A} \frac{d(\overline{AB})}{dt} = \frac{\frac{k_1^* k_3}{k_2} (A) (\overline{B}) - k_4^* (\overline{AB})}{1 + \frac{k_3}{k_2} (\overline{B})} \quad (6.2.27)$$

Since equation (6.2.14) is assumed in equilibrium, then

$$\frac{(\overline{AB.B})}{(\overline{AB}) (\overline{B})} = K_3 \quad (6.2.28)$$

and

$$(\overline{AB}) = \frac{(\overline{AB.B})}{K_3 (\overline{B})} \quad (6.2.29)$$

The concentration of the $\overline{AB}$ organic complexes should be very small, so that on a molar basis $(Fe) \simeq (AB.B)$.

Remembering that $k_1^* = k_1^{**} \alpha_n$, where α_n is the fraction of the active chlorocomplex, then

$$\frac{k_1^* k_3}{k_2} = \frac{k_1^{**} \alpha_n k_3}{k_2}$$

writing

$$\frac{k_1^{**} \alpha_n k_3}{k_2} = k_5^* \alpha_n, \quad \frac{k_4}{K_3} = k_6^* \quad \text{and} \quad \frac{k_3}{k_2} = k_7^* \quad (6.2.30)$$

and substituting equations (6.2.29) and (6.2.30) into (6.2.27) gives

$$\frac{V}{A} \frac{d(\overline{\text{Fe}})}{dt} = \frac{k_5^* \alpha_n (A) (\overline{B}) - k_6^* \frac{(\overline{\text{Fe}})}{(\overline{B})}}{1 + k_7^* (\overline{B})} \quad (6.2.31)$$

Writing equation (6.2.31) in terms of bulk concentrations gives

$$\frac{V}{A} \frac{d(\overline{\text{Fe}})}{dt} = \frac{k_5^* \alpha_n (\text{Fe}) (\overline{\text{TOAHCl}}) - k_6^* \frac{(\overline{\text{Fe}})}{(\overline{\text{TOAHCl}})}}{1 + k_7^* (\overline{\text{TOAHCl}})} \quad (6.2.31)$$

It can be seen in equation (6.2.12) that k_2 refers to the desorption of the Fe-chlorocomplex into the aqueous phase, which should be a relatively fast process, whereas k_3 refers to the desorption of the Fe-TOAHCl complex into the organic phase, which should be also a fast process, but not as fast as the former reaction; it would be expected that k_2 is greater than k_3 . As the TOAHCl concentration was always below 0.1 M it can be assumed that

$$\frac{k_3}{k_2} (\overline{\text{TOAHCl}}) = k_7^* (\overline{\text{TOAHCl}}) \ll 1 \quad (6.2.32)$$

and equation (6.2.31) becomes

$$\frac{V}{A} \frac{d(\overline{\text{Fe}})}{dt} = k_5^* \alpha_n (\text{Fe}) (\overline{\text{TOAHCl}}) - k_6^* \frac{(\overline{\text{Fe}})}{(\overline{\text{TOAHCl}})} \quad (6.2.33)$$

The fact that k_2 and k_3 refer to relatively fast reactions and appear also in k_5^* (equation (6.2.31)) does not invalidate

the derived rate equation, since only their ratio is involved. It is difficult to speculate about the expected values of k_5^* and k_6^* , but these will be considered further in the following section when the rate equation will be evaluated. It is obvious that under conditions favourable to extraction

$$k_5^* \alpha_n(\text{Fe}) \overline{(\text{TOAHCl})} > k_6^* \frac{\overline{(\text{Fe})}}{\overline{(\text{TOAHCl})}}$$

and vice-versa for conditions favourable to stripping.

As

$$\frac{d(\overline{\text{Fe}})}{dt} = - \frac{d(\text{Fe})}{dt} \quad (6.2.34)$$

the initial extraction rate will be given by

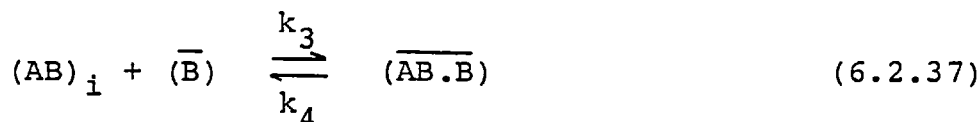
$$\frac{V}{A} \frac{d(\overline{\text{Fe}})}{dt} = k_5^* \alpha_n(\text{Fe}) \overline{(\text{TOAHCl})} \quad (6.2.35)$$

and the initial stripping rate

$$\frac{V}{A} \frac{d(\text{Fe})}{dt} = k_6^* \frac{\overline{(\text{Fe})}}{\overline{(\text{TOAHCl})}} \quad (6.2.36)$$

Equation (6.2.35) predicts that the initial extraction rate should be first order with respect to the total aqueous iron and TOAHCl concentrations and that it should be related in some way to the concentration of the active chlorocomplex²⁵. Equation (6.2.36) predicts that the initial stripping rate should be first order with respect to the organic Fe concentration and inverse first order with respect to the TOAHCl concentration and independent of the aqueous chloride concentration. These predictions agree with the experimental results and indicate that the proposed mechanism is consistent with the experimental kinetic data.

Some alternative mechanisms were also considered. If reaction (6.2.13) was the final extraction step, then

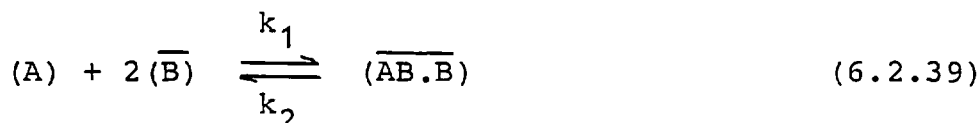


Using the same assumptions and the same procedure, a rate equation was derived giving the following expression

$$\frac{V}{A} \frac{d(\overline{Fe})}{dt} = k_5^{**} \alpha_n (Fe) (\overline{TOAHCl}) - k_6^* (\overline{Fe}) \quad (6.2.38)$$

This mechanism would explain the extraction rates but it would be inconsistent with the stripping rates since these should be independent of TOAHCl concentration, which was not the case.

The possibility that the reaction takes place in a single step, such as



should be ruled out since the derived rate equation is

$$\frac{V}{A} \frac{d(\overline{Fe})}{dt} = k_1 (A) (\overline{B})^2 - k_2 (\overline{AB.B}) \quad (6.2.40)$$

and this is inconsistent with the results, since a second order dependence with respect to TOAHCl concentration would be predicted for extraction and also the stripping rates should be independent of TOAHCl concentration, contrary to the experimental evidence. Equation (6.2.39) is also a third order reaction for the extraction and such mechanisms are not often observed. It would require one metal ion to react simultaneously with two TOAHCl molecules, and this would seem a much more unlikely and difficult reaction path than the interfacial mechanism proposed. Another reason to reject this mechanism is that there is no interfacial reaction involved and the extraction rate has been shown to be controlled by an interfacial process.

The possibility that the reaction mechanism could be represented by



should also be ruled out. The derived rate equation would have the same form as given by the proposed mechanism (equation (6.2.33)) and thus would explain the extraction and stripping rates, but it would be inconsistent with other experimental evidence, since either no interfacial reaction is involved or at best it would require the reaction to take place in a plane interface with the adsorption of the metal ions at the interface, contrary to the evidence of interfacial studies which indicate that metal ions are not surface active. Only a mechanism involving reactions near the interface can explain satisfactorily all the experimental results. Therefore, reactions (6.2.7.) to (6.2.11) are considered the most likely mechanism for the extraction of iron (III) chloride by TOAHCl. The validity of this mechanism is investigated in the following section.

6.2.6. Rate equation evaluation

It has been established using a preliminary analysis of the experimental results, and other known information that equations (6.2.7) to (6.2.11) represent the most likely reaction mechanism. The full rate equation derived is represented by equation (6.2.31) and this includes all forward and reverse rate constants for the two rate controlling steps. This model was tested with the experimental results to see whether it was consistently adequate and whether it could predict the mass transfer rates. For testing the model all data at 25°C for extraction

and stripping rates at 1 M chloride were used, except those used to investigate the effect of interfacial area. Extraction and stripping rates were investigated separately and the combined effect of both was considered when the rate equation was integrated.

For the full model the initial extraction rate is given by

$$\vec{R} = \frac{d(\overline{\text{Fe}})}{dt} \frac{V}{A} = \frac{k_5^* \alpha_n (\text{Fe}) (\overline{\text{TOAHCl}})_A}{1 + k_7^* (\overline{\text{TOAHCl}})_B} \quad (6.2.43)$$

where the subscript A or B indicates TOAHCl total (M), monomer (M_1) or dimer (M_2) concentration. This equation is not linear in the coefficients k_5^* and k_7^* and so linear regression analysis is not directly possible.

However, if equation (6.2.43) is re-written as

$$\frac{(\text{Fe}) (\overline{\text{TOAHCl}})_A}{\vec{R}} = \frac{1}{k_5^* \alpha_n} + \frac{k_7^*}{k_5^* \alpha_n} (\overline{\text{TOAHCl}})_B \quad (6.2.44)$$

the model becomes linear. Statistical analysis of the results were carried out using a computer library package called MINITAB²²⁸. The best equation to fit the experimental results is the one which minimises the residual sum of squares.

All the possibilities involving TOAHCl species were considered in order to verify whether $(\overline{\text{TOAHCl}})_A$ or $(\overline{\text{TOAHCl}})_B$ was the monomer, dimer or total TOAHCl concentration. Monomer and dimer concentrations were calculated, as shown in Appendix B.1, using the determined and estimated dimerisation constants (K_2). Figure 6.2.5.5. shows the concentration of monomer and dimer TOAHCl as a function of total TOAHCl concentration. The best overall fitting was always associated with the monomer and dimer TOAHCl concentrations calculated using

$K_2 = 45$, which confirms the adequacy of the assumptions leading to this K_2 value.

The square of the correlation coefficient (R_c^2) was the parameter used to select the best model. R_c^2 is a measure of the fraction of the total variation that can be accounted for by the model. The difference between 1.0 and the value of R_c^2 contains two contributions, the experimental error which should be random, and the lack of fit which shows the inadequacy of the model. This inadequacy, if present, can be detected by any systematic trends in the residuals. As the experimental error was less than $\pm 5\%$, high values of R_c^2 would be expected if the model was adequate to represent the data. Low R_c^2 values would indicate a large lack of fit and the inadequacy of the model.

Table D.1 (Appendix D) shows the computer output for the regression analysis of the best full extraction model. All the other possibilities gave worse fits. This model indicates that $(\text{TOAHCl})_A$ and $(\text{TOAHCl})_B$ should both be the monomer TOAHCl, which should be the active TOAHCl species involved in the forward and reverse reaction (6.2.9) and the forward reaction (6.2.10). An unimpressive value of 0.6 for R_c^2 indicates a large lack of fit. If $k_7^*(\text{TOAHCl})_B \ll 1$, then $(k_7^*/k_5^* \alpha_n)(\text{TOAHCl})_B$ is close to zero and $(\text{Fe})(\text{TOAHCl})_A/\bar{R} \simeq \text{constant}$. The best estimate of the value of a constant is its average and the result of the application of regression analysis to determine the value of a constant would be a non-sense. The value of k_7^* is statistically not significant as shown by the low value of its T-ratio.^(*) The inadequacy of the model can be seen in the plot of residuals presented in Figure 6.2.6.1., which shows that they are not randomly distributed about zero.

(*) The T-ratio of a coefficient measures the relative significance of this coefficient. The T-ratio is given by the value of the coefficient divided by its standard deviation.

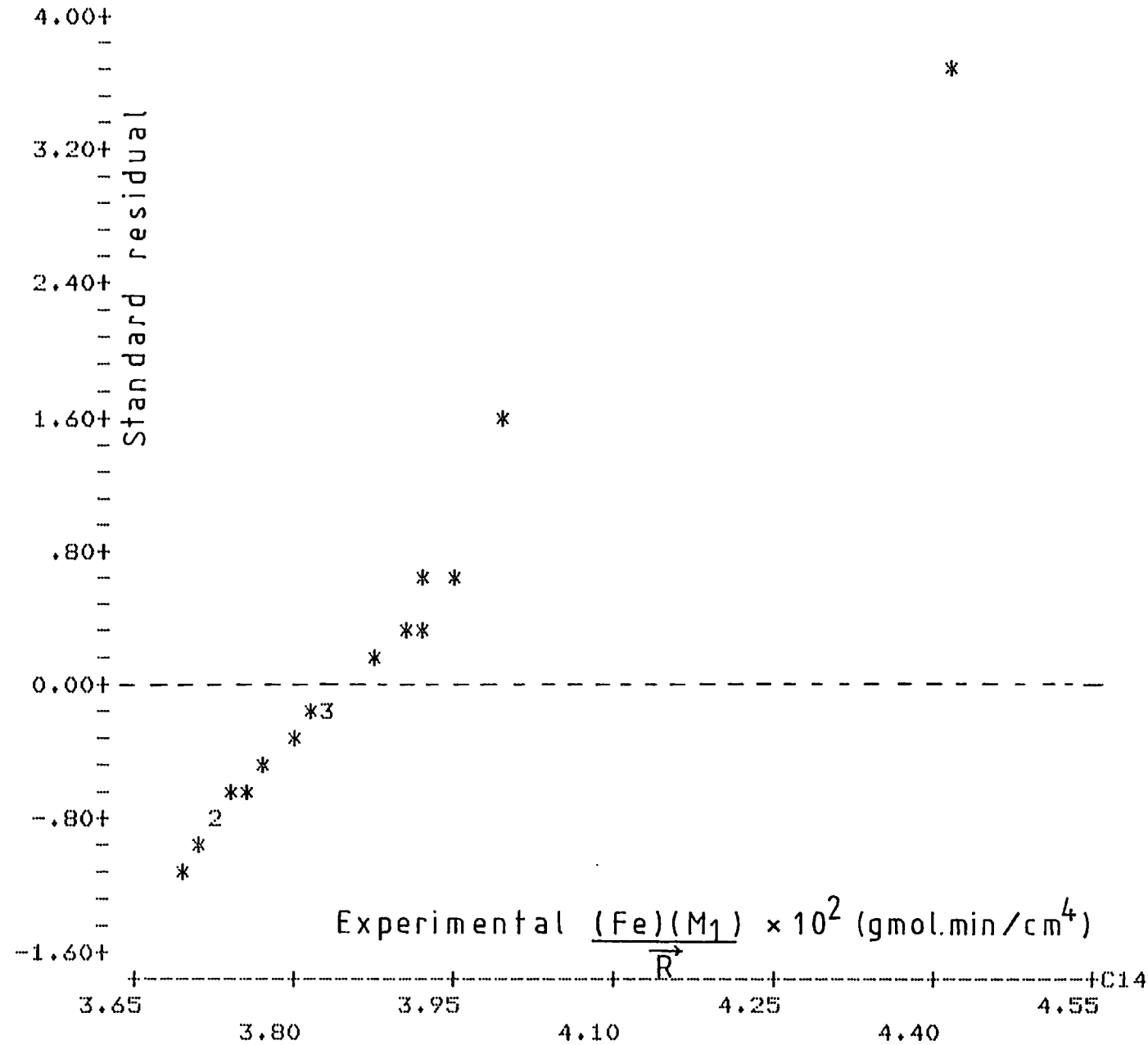


FIGURE 6.2.6.1. PLOT OF RESIDUALS. BEST FULL MODEL (EXTRACTION 1 M Cl⁻).

However, the predicted extraction rate was not as bad as the inadequacy of the model may suggest and this is possibly accounted for by the high statistical significance of $k_5^* \alpha_n$, as indicated by its high T-ratio. This model gave the following values for $k_5^* \alpha_n$ and k_7^* :

$$k_5^* \alpha_n = (2.58 \pm 1.88) \times 10^{-9} \text{ (cm}^4\text{/gmol.min)}$$

$$k_7^* = -(1.32 \pm 9.95) \times 10^{-2} \text{ (cm}^3\text{/gmol)}$$

The great uncertainty in the values of $k_5^* \alpha_n$ and k_7^* means that they could not provide a reliable estimate of the extraction rate. The negative value of k_7^* implies that this model has no physical meaning, as there cannot be a negative rate constant. Negative values for k_7^* were found in all the other cases considered, which definitely indicates the inadequacy of the full model. Therefore, the full extraction model should be ruled out. It can be seen in equation (6.2.9) that k_2 refers to the desorption of the Fe-chloro complex into the aqueous phase, which should be a relatively fast process, whereas in equation (6.2.10) k_3 refers to the desorption of the Fe-TOAHCl complex into the organic phase which should be also a fast process, but not as fast as in the first case. The value of k_7^* given above (apart from the negative sign) indicates that k_2 is at least 1 or 2 order(s) of magnitude greater than k_3 . As the TOAHCl concentration was always below 0.1 M, it can be assumed that

$$\frac{k_3}{k_2} \overline{(\text{TOAHCl})}_B = k_7^* \overline{(\text{TOAHCl})}_B \ll 1 \quad (6.2.45)$$

The fact that k_2 and k_3 refer to relatively fast reactions and both are included in k_5^* (equation 6.3.31) does not invalidate the derived rate equation, since only their ratio is involved.

Having shown that the full extraction model was inadequate, it was then thought that a reduced model may represent the data better than the full model. The reduced model assumes that $k_7^*(\text{TOAHCl})_B \ll 1$ and then it follows that

$$\vec{R} = k_5^* \alpha_n (\text{Fe}) (\overline{\text{TOAHCl}})_A \quad (6.2.46)$$

Equation (6.2.46) was fitted to the experimental data.

Table D.2 (Appendix D) shows the computer output for the regression analysis of the best reduced extraction model. All the other possibilities gave worse fits. This model indicates that the active TOAHCl species involved in the extraction was the monomeric one. A high value of R_c^2 ($\sim 100\%$) indicates also a very good fit and the high statistical significance of $k_5^* \alpha_n$ is indicated by the high value of its T-ratio. The adequacy of the model is confirmed in the plot of fitted rate versus experimental rate presented in Figure 6.2.6.2., where good agreement was achieved, and in the plot of residuals versus experimental rate presented in Figure 6.2.6.3., where they are reasonably randomly distributed. The plot of normal scores of residuals against residuals presented in Figure 6.2.6.4. is a reasonable straight line with a correlation coefficient (R) equal to 0.945, indicating a probability over 95% that the residuals are randomly distributed. The value of $k_5^* \alpha_n$ was then obtained giving

$$k_5^* \alpha_n = (2.59 \pm 0.03) \times 10^{-9} \text{ (cm}^4\text{/gmol.min)}$$

The rate constant k_5^* presented in equation (6.2.30) is represented by the equation

$$k_5^* = \frac{k_1^* k_3}{k_2} = \frac{k_1(B)_1 k_3}{k_2} \quad (6.2.47)$$

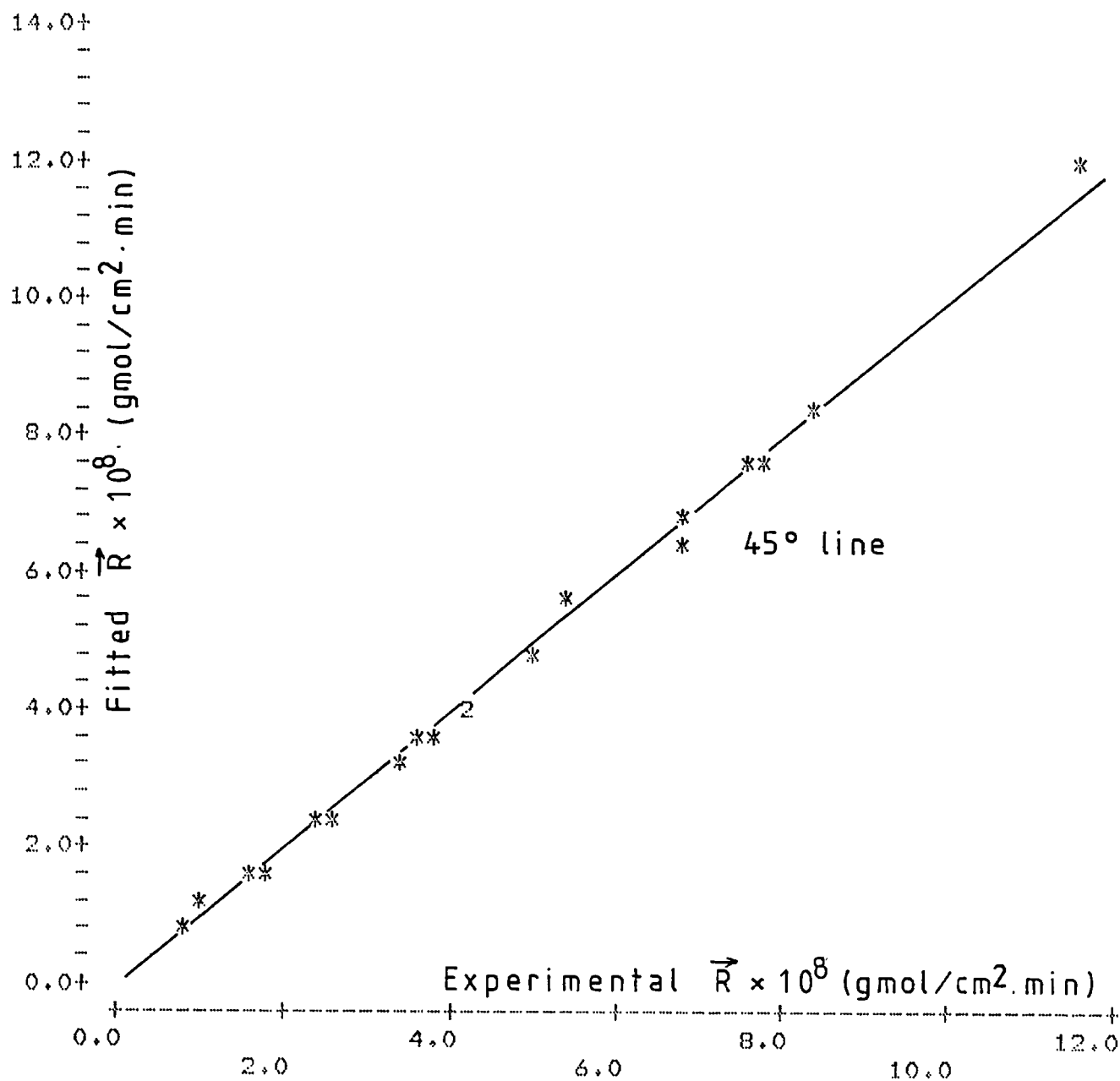


FIGURE 6.2.6.2. FITTED RATE AGAINST EXPERIMENTAL VALUE.
BEST REDUCED MODEL (EXTRACTION 1 M Cl⁻).

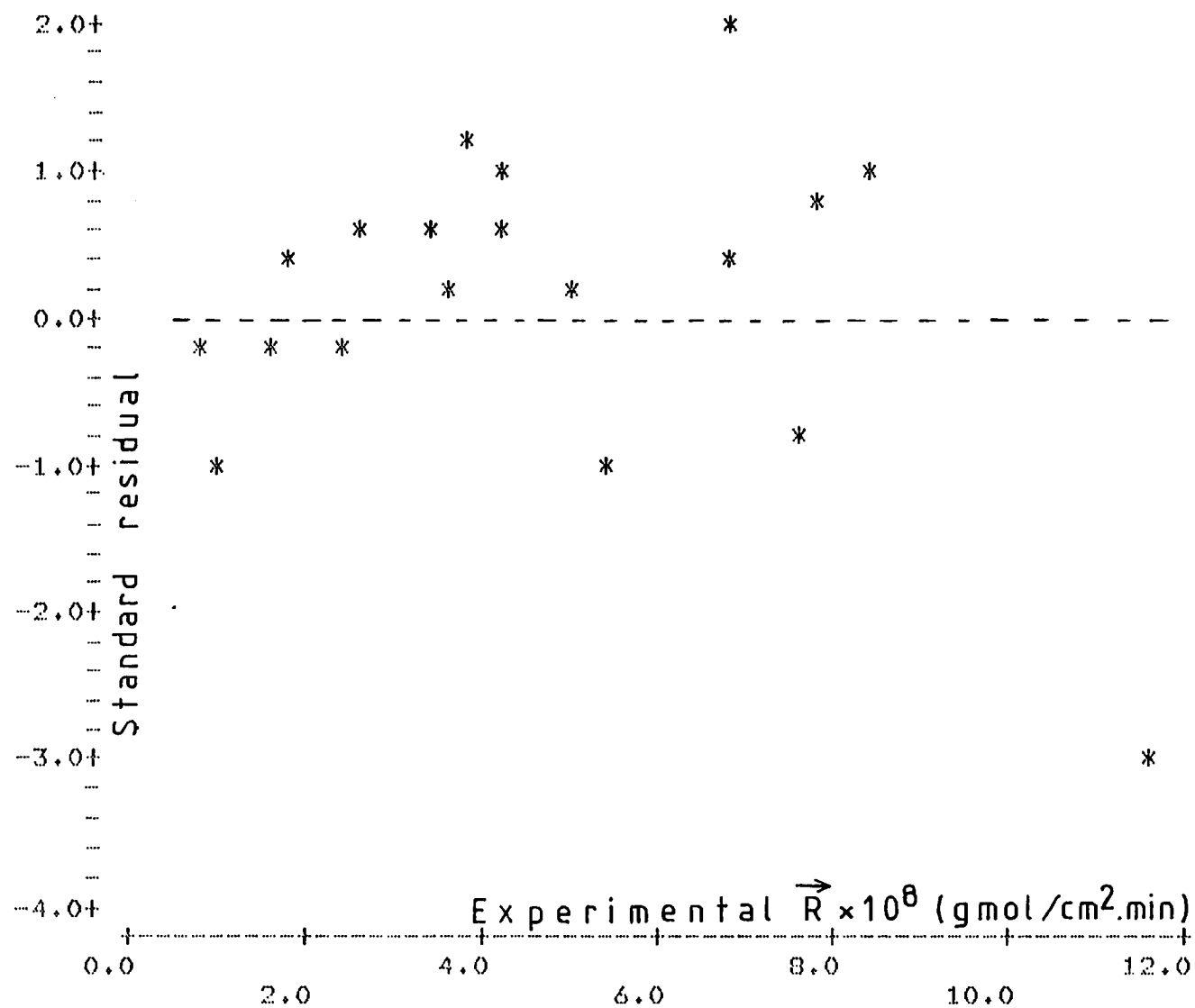


FIGURE 6.2.2.3. RESIDUAL AGAINST EXPERIMENTAL RATE. BEST REDUCED MODEL (EXTRACTION 1 M Cl⁻).

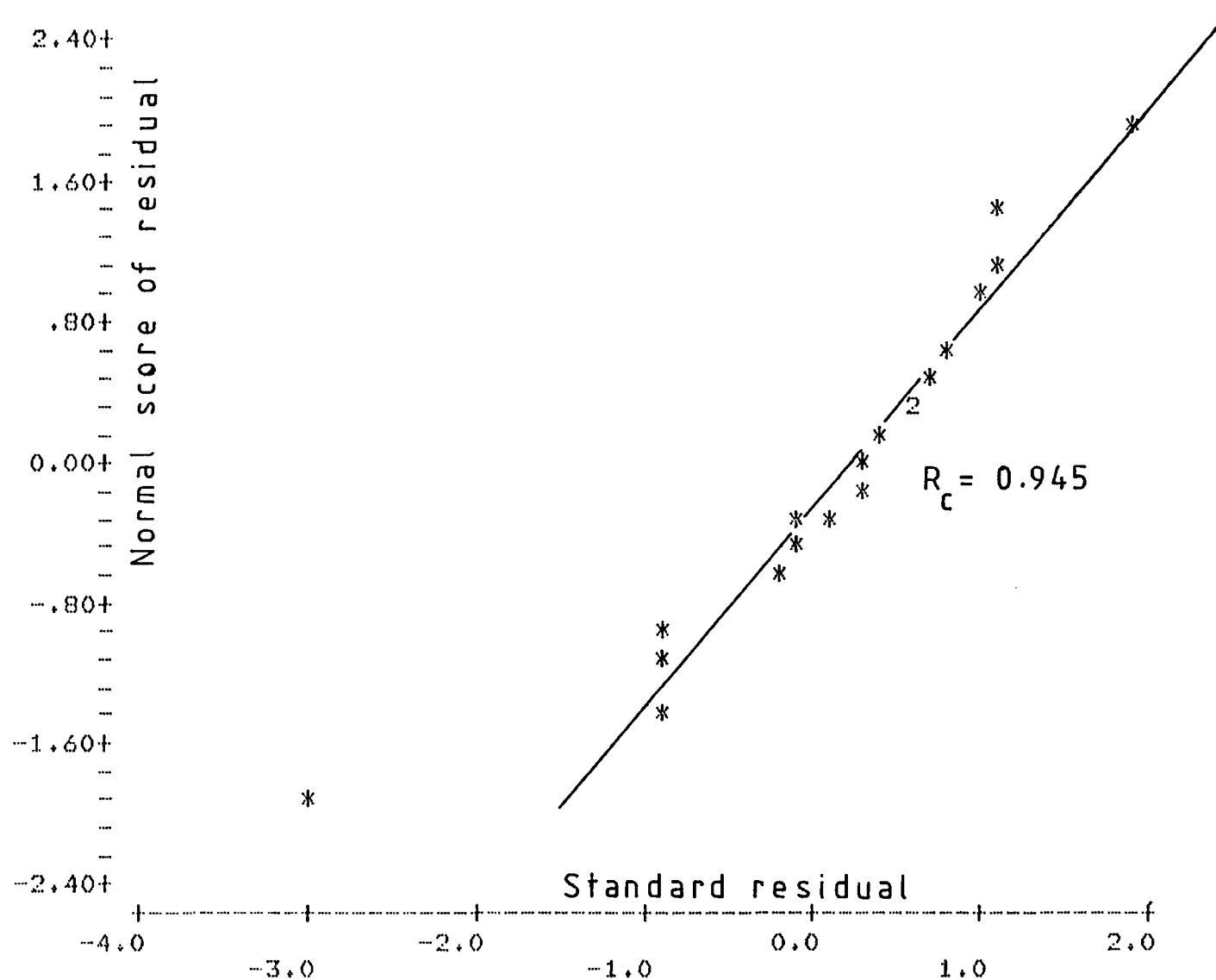


FIGURE 6.2.6.4. NORMAL SCORES AGAINST RESIDUAL. BEST REDUCED MODEL (EXTRACTION 1 M Cl^-).

where:

k_1 and k_2 are the rate constants for the forward and reverse reaction represented in equation (6.2.9);

k_3 is the rate constant for the forward reaction represented in equation (6.2.9);

$(B)_i$ is the interfacial TOAHCl concentration.

It is obvious, that it is not possible to evaluate the individual rate constants. However, in the light of the experimental evidence and other known results, it is possible to speculate about the slowest step involved in the extraction process. For the reason outlined in the full extraction model concerning k_2 and k_3 , it is unlikely that the desorption of the Fe chlorocomplex(es) or the Fe-TOAHCl complex would be slow processes. It is also unlikely that the adsorption of TOAHCl at the interface, as discussed in Section 6.2.5., is a slow process. This elimination process reduces the choice of the slowest extraction step to the reaction between interfacial monomeric TOAHCl and the Fe chlorocomplex. This reaction occurs, probably, in the aqueous phase, near the interface, as indicated by the dependence of extraction rate on stirring speed in the aqueous phase and its independence of stirring speed in the organic phase (Section 6.2.3.). The resistance to the mass transfer was found to be almost entirely in the aqueous side of the interface. Metal ions are not surface active as shown by their tendency to increase interfacial and surface tension. Therefore, it would be easier for the Fe chlorocomplex(es) to react with monomeric TOAHCl protruding into the aqueous phase, rather than having to adsorb onto the interface. It was then concluded that the difficulty of the Fe chlorocomplex(es) reaching the interface and reacting with monomeric TOAHCl near the interface, in the aqueous phase, was the most probable slowest extraction step.

Having established that the reduced extraction model could explain the effect of total Fe and TOAHCl concentrations on the extraction rate at 1 M chloride, it was thought to

be unnecessary to repeat the same calculations at 4 and 7 M chloride, as the same dependences are observed, as shown in Figures (6.2.5.2.), (6.2.5.6.) and (6.2.5.7). The effect of aqueous chloride concentration on the extraction rate will be considered later.

For the full model, the initial stripping rate is given by

$$\overleftarrow{R} = \frac{d(\text{Fe})_V}{dt} \frac{V}{A} = \frac{k_6^* \frac{(\overline{\text{Fe}})}{(\overline{\text{TOAHCl}})_C}}{1 + k_7^* (\overline{\text{TOAHCl}})_B} \quad (6.2.48)$$

where the subscripts B and C indicate TOAHCl total (M), monomer (M_1) or dimer (M_2) concentration. As with the extraction rate, equation (6.2.48) is not linear in the coefficients k_6^* and k_7^* , but it can be linearized by re-writing it as

$$\frac{(\text{Fe})}{(\overleftarrow{R}) (\overline{\text{TOAHCl}})_C} = \frac{1}{k_6^*} + \frac{k_7^*}{k_6^*} (\overline{\text{TOAHCl}})_B \quad (6.2.49)$$

The same statistical analysis as used in the extraction model was carried out and all the possibilities involving $(\overline{\text{TOAHCl}})_B$ and $(\overline{\text{TOAHCl}})_C$ (equation 6.2.49)) were considered.

Table D.3 (Appendix D) shows the computer output for the regression analysis of the best full model. Some other possibilities also gave high R_c^2 values and could not be rejected without further analysis, as shown below:

	$(\overline{\text{TOAHCl}})_C$		
	M	M_1	M_2
R^2 (%)	99.0	98.7	97.6
$k_6^* \times 10^7$	12.7 ± 2.0	7.3 ± 0.6	6.3 ± 0.5
$k_7^* \times 10^5$	1.11 ± 8.63	0.41 ± 1.23	1.42 ± 15.18

In all these cases, $(\text{TOAHCl})_B$ was monomeric TOAHCl. All the other possibilities were not statistically significant and were rejected. It can be seen from the table above that there is a great uncertainty in the value of k_7^* , and that also it is very small, so that $k_7^*(\text{TOAHCl})_B \ll 1$ in all cases. The full stripping model does not differentiate the active TOAHCl species involved in the stripping process and apparently, monomer, dimer or total TOAHCl could be possible. There is some inadequacy in this model, as basically it is a reduced model, with an extra parameter which is not statistically significant. The same conclusions regarding k_2 and k_3 , as discussed in the full extraction model, would apply.

A reduced model was then fitted to the experimental data. The reduced stripping model assumes that $k_7^*(\text{TOAHCl})_B \ll 1$ and then

$$\bar{R} = k_6^* \frac{(\overline{\text{Fe}})}{(\text{TOAHCl})_C} \tag{6.2.50}$$

Table D.4 shows the computer output for the regression analysis of the best reduced stripping model. The other possibilities could not be rejected outright without further considerations as they all gave high R^2 values and were statistically significant as shown below.

	$(\text{TOAHCl})_C$		
	M	M_1	M_2
$R^2 (\%)$	99.8	97.6	99.1
$k_6^* \times 10^7$	9.225 ± 0.343	5.52 ± 0.65	1.73 ± 0.12
T-ratio	60.61	19.20	31.60

The statistical analysis indicates that an inverse first order dependence with respect to the total TOAHCl is most likely but the other possibilities cannot be ruled out.

A possible way to sort out this problem would be to use the rate equation, including all possible stripping models, to predict the distribution ratio under equilibrium conditions and then compare the calculated values with the ones obtained experimentally. Under equilibrium conditions the extraction and stripping rates should be equal and then, from equation (6.2.33)

$$k_5^* \propto_n (\text{Fe})(\overline{\text{TOAHCl}})_{M_1} = k_6^* \frac{(\overline{\text{Fe}})}{(\overline{\text{TOAHCl}})_{M, M_1 \text{ or } M_2}} \quad (6.2.51)$$

and

$$D_{\text{Fe}} = \frac{\overline{\text{Fe}}}{\text{Fe}} = \frac{k_5^* \propto_n}{k_6^*} (\overline{\text{TOAHCl}})_{M_1} (\overline{\text{TOAHCl}})_{M, M_1 \text{ or } M_2} \quad (6.2.52)$$

Experimental and predicted D_{Fe} values are presented in Figure 6.2.6.5. It can be seen that the assumption that total TOAHCl concentration is responsible for the stripping rate gives D_{Fe} values and a slope most consistent with the experimental results. It was thus concluded that the stripping rate was inverse first order with respect to the total TOAHCl concentration and first order with respect to the organic iron concentration. The adequacy of the reduced stripping model is confirmed in the plot of fitted rate versus experimental rate presented in Figure 6.2.6.6., where good agreement was found, and in the plot of residuals versus experimental rate presented in Figure 6.2.6.7, where they are reasonably random distributed. The plot of normal scores of residuals against residuals presented in Figure 6.2.6.7. is a reasonable straight line with a correlation coefficient (R_c) equal to 0.928, indicating a probability of over 95% that the residuals are randomly distributed.

The fact that monomer TOAHCl gave the worst fit in the reduced stripping model may indicate that the starting point of the stripping process was not TOAHFeCl_4

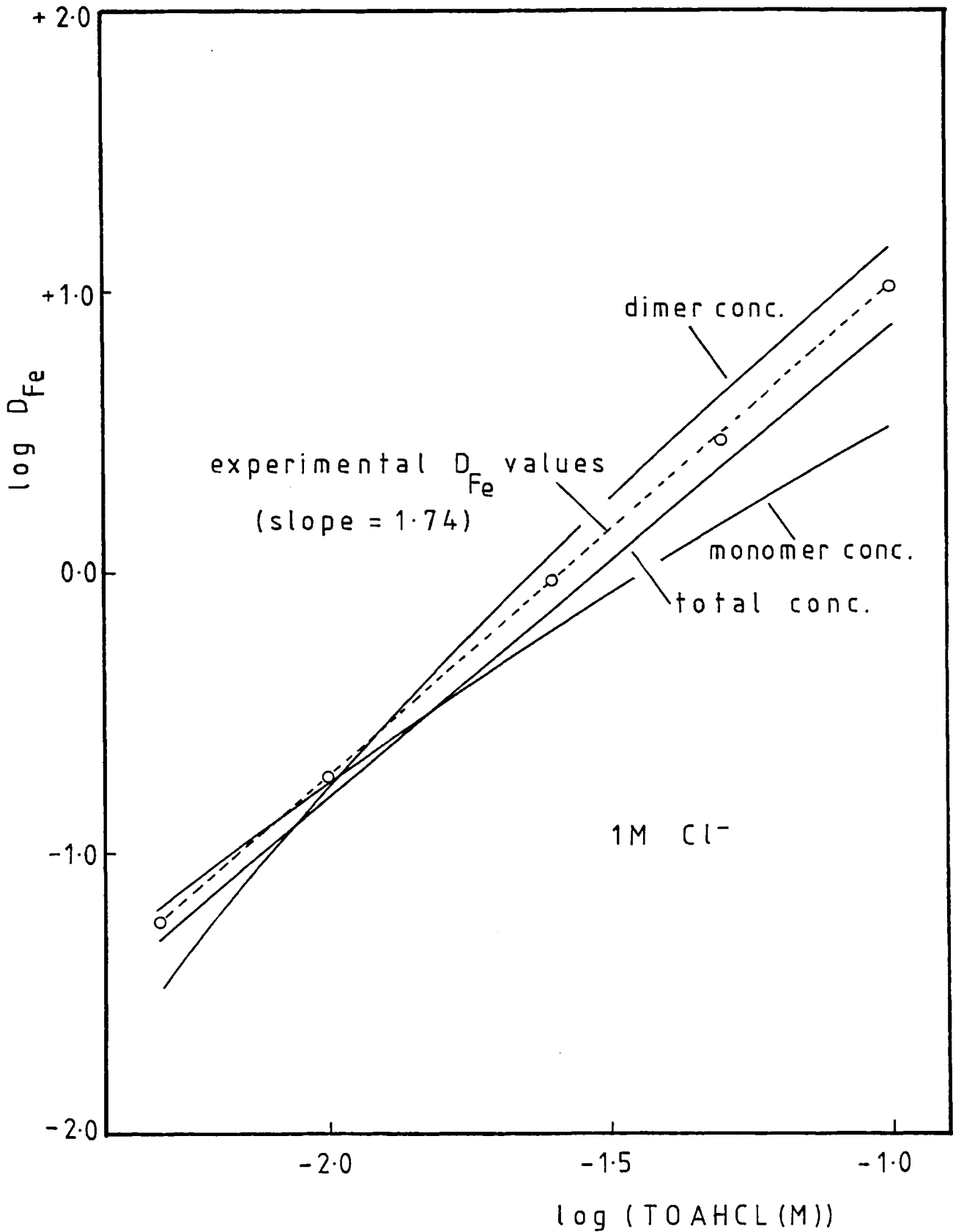


FIGURE 6.2.6.5. PLOT OF EXPERIMENTAL AND PREDICTED LOG DISTRIBUTION COEFFICIENT VERSUS LOG TOAHCl CONCENTRATION FOR TESTING THE REDUCED STRIPPING MODEL ($1\text{ M } Cl^-$).

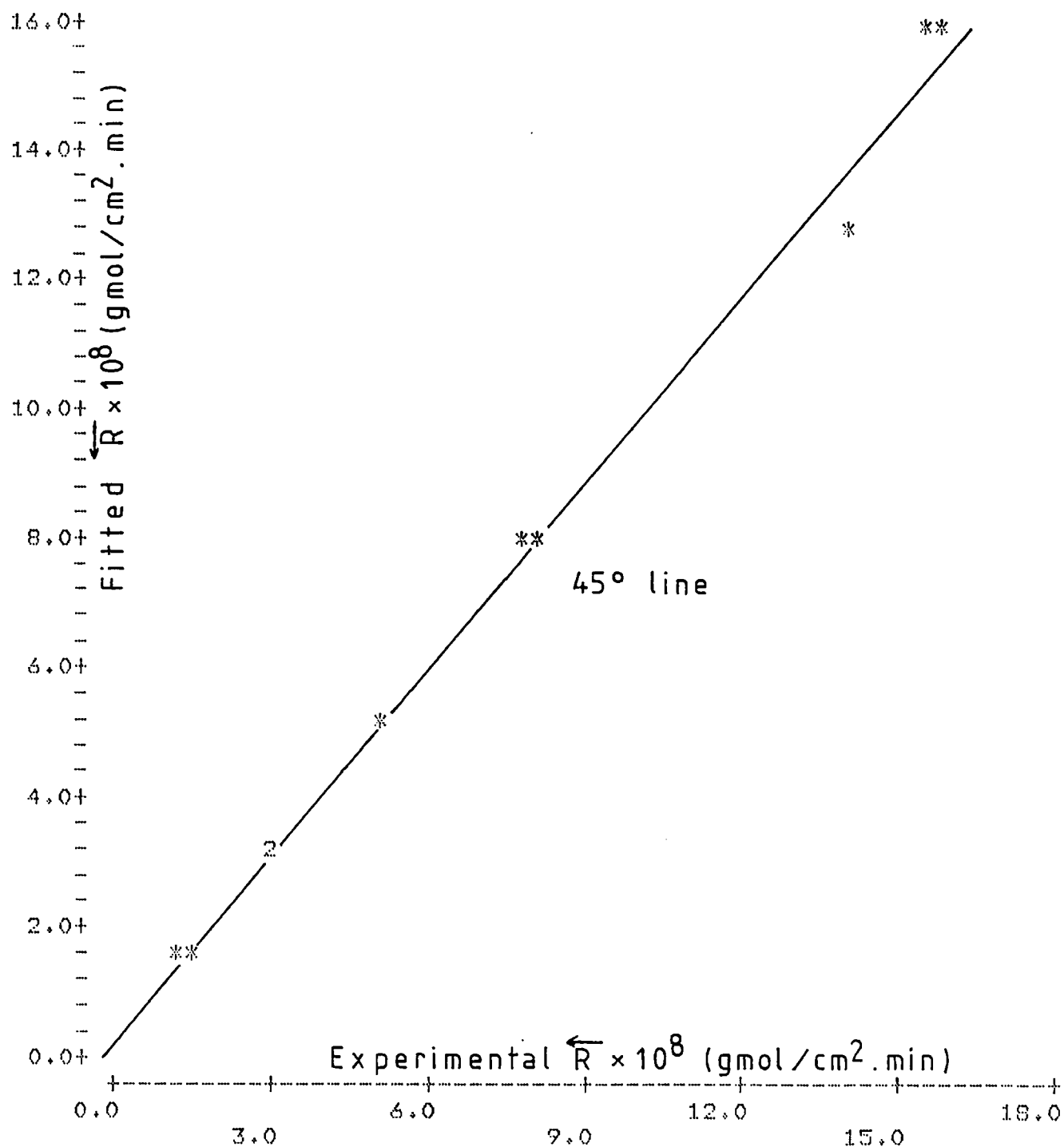


FIGURE 6.2.6.6. FITTED RATE AGAINST EXPERIMENTAL VALUE.
BEST REDUCED MODEL (STRIPPING 1 M Cl^-).

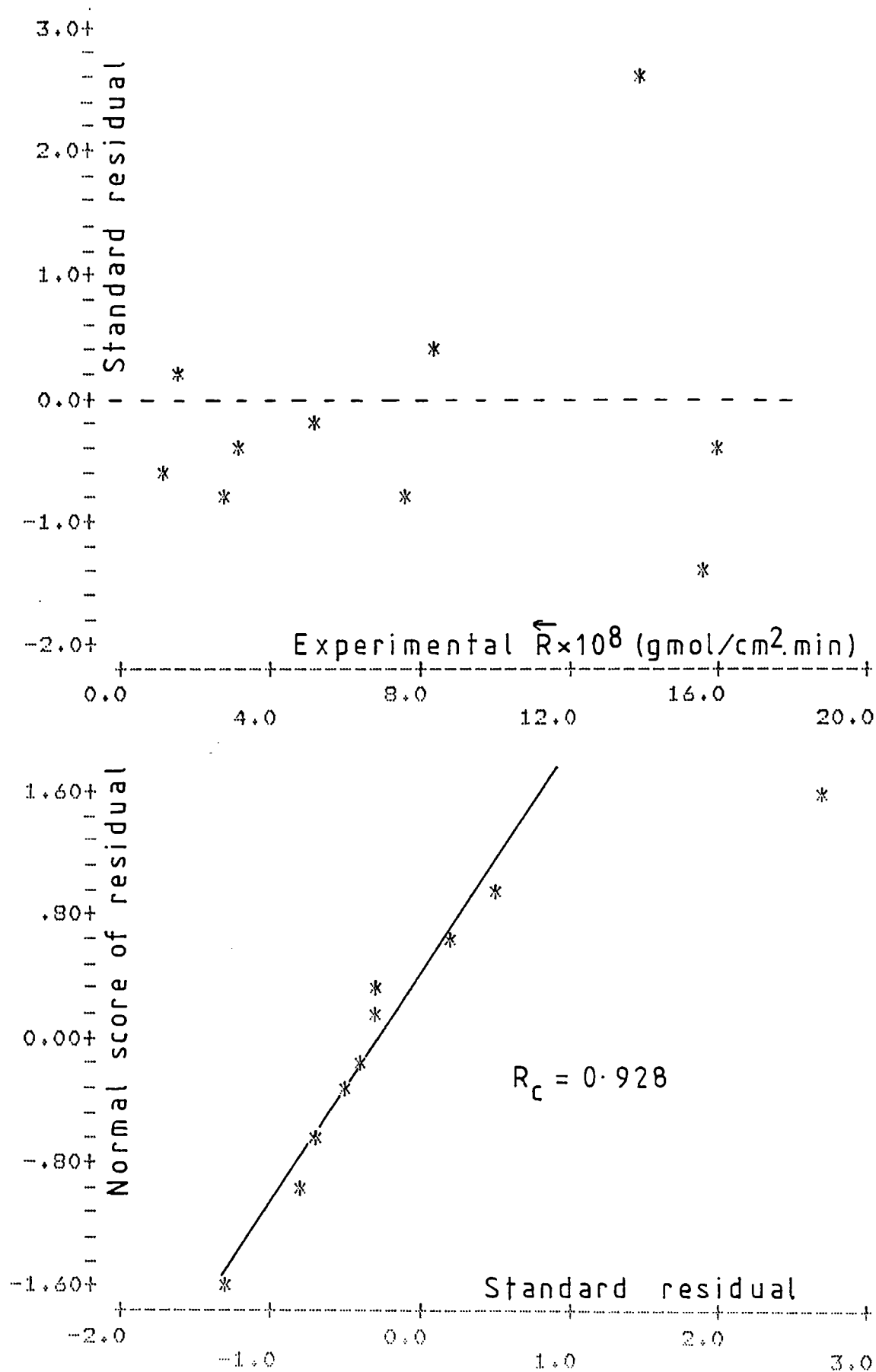


FIGURE 6.2.6.7. PLOT OF STANDARD RESIDUAL AGAINST EXPERIMENTAL RATE AND NORMAL SCORES OF RESIDUALS AGAINST STANDARD RESIDUALS. BEST REDUCED MODEL (STRIPPING 1 M Cl^-).

but $\text{TOAHFeCl}_4 \cdot \text{TOAHCl}$ as indicated by the better fitting obtained when dimer TOAHCl was assumed. The best overall fitting obtained with total TOAHCl may indicate that in the formation of $\text{TOAHFeCl}_4 \cdot \text{TOAHCl}$ (a bulk reaction), either monomer or dimer TOAHCl can react with equal facility with TOAHFeCl_4 to give $\text{TOAHFeCl}_4 \cdot \text{TOAHCl}$, as shown by the full loading requirements (Appendix B.1.7), where it was found that the ratio TOAHCl/Fe was independent of TOAHCl concentration. Although the equilibrium conditions in the full loading experiments are quite different from the conditions where initial mass transfer rate measurements were carried out, this could be considered as some experimental evidence for the above hypothesis. The rate constant k_6^* refers to the reverse reaction (6.2.10), which is related to the adsorption of the Fe-TOAHCl complex onto the interface. The Fe-TOAHCl complex should have an interfacial activity lying between monomeric TOAHCl and free TOA , as shown by McDowell and Coleman⁷⁵ for the uranium DDAS system. It was thus concluded that the difficulty of displacing monomer TOAHCl from the interface by TOAHFeCl_4 in the organic phase should be the slowest stripping step. In other words, the adsorption of TOAHFeCl_4 onto the interface should be the rate controlling step for the stripping process.

It has been shown in Figure 6.2.5.10 the dependence of the extraction rate on the aqueous chloride concentration, whereas the stripping rate (Figure 6.2.5.11) was found to be independent of this parameter. If the reduced extraction model and all the assumptions made to derive it are correct, a constant value of k_5^* would be predicted for all the runs at different Cl^- concentrations. From equation (6.2.46) the value of k_5^* is given by

$$k_5^* = \frac{\vec{R}}{\alpha_n (\text{Fe}) (\text{TOAHCl})_{M_1}} \quad (6.2.53)$$

where $\alpha_n (\text{Fe})$ is the concentration of the active chloro-complex(es).

Using the α_n values calculated from the stability constants given in reference (215), values of k_5^* were calculated. The results are presented in Figure 6.2.6.8. It can be seen that the assumption that only FeCl_3 or FeCl_4^- is the active chlorocomplex involved in the extraction process does not lead to a constant k_5^* value, whereas the assumption that FeCl_3 and FeCl_4^- are the active species gives a reasonably constant k_5^* value, except at 1 M Cl^- . This discrepancy at 1 M Cl^- could be due to the different interfacial behaviour in the presence of LiCl in the aqueous phase. If this is the case, the results indicate that aqueous LiCl concentrations had a small effect on the extraction rate, but concentrations greater than 1 M would not have any significant effect. It is assumed also that the extraction rate of FeCl_3 and FeCl_4^- are represented equally well by the rate constant k_5^* . The fact that FeCl_3 and FeCl_4^- should have different diffusion coefficients should not affect the results, as the extraction process is (mainly) chemically controlled. The assumptions that other cationic species (Fe^{3+} , FeCl^{2+} and FeCl_2^+) could be involved, either alone or in different combinations with FeCl_3 and/or FeCl_4^- did not give a constant k_5^* value. In fact they lead to a worse fit and if the stability constants used to calculate the distribution of the chlorocomplexes really represents the system, the cationic species definitely should not be involved in the extraction process, as indicated by the lack of a constant k_5^* value.

In order to check whether the α_n values calculated from the stability constants given in references (210), (212) and (214) would lead to different conclusions from those above, the same calculations were carried out. The results showed no constant k_5^* value, except for the α_n values from reference 212, when FeCl_3 and FeCl_4^- were assumed to be the active species. The results are presented in Figure 6.2.6.9 where the active chlorocomplexes were assumed to be FeCl_3 and FeCl_4^- in all cases. It can be seen

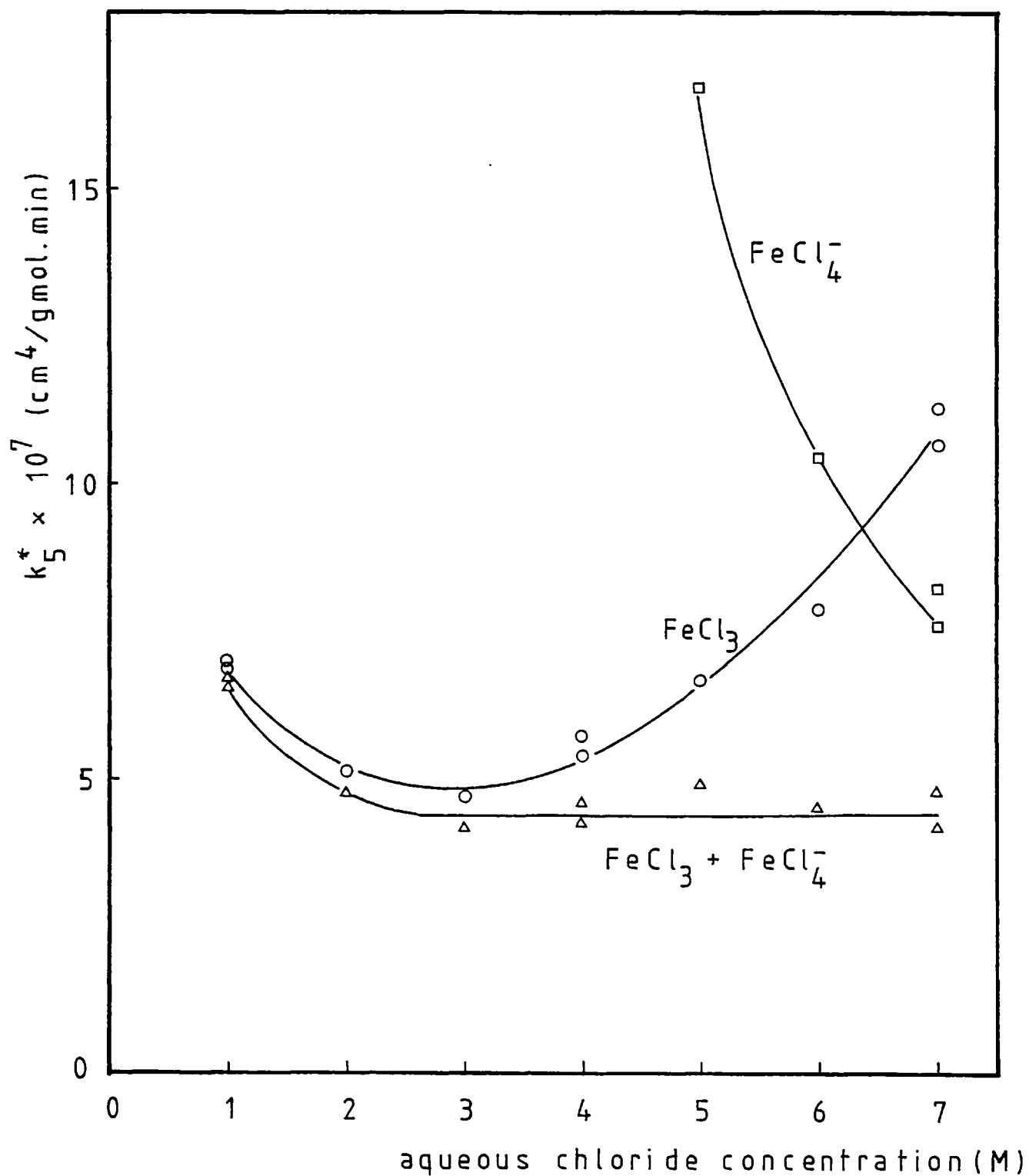


FIGURE 6.2.6.8. CALCULATED k_5^* VALUE AS A FUNCTION OF AQUEOUS CHLORIDE CONCENTRATION FOR THE DIFFERENT POSSIBILITIES INVOLVING THE ACTIVE CHLOROCOMPLEX(ES). α_3 and α_4 calculated using the stability constants given in reference 215.

$$k_5^* = \vec{R} / (\alpha_n) (\text{Fe}) (\text{TOAHCl}).$$

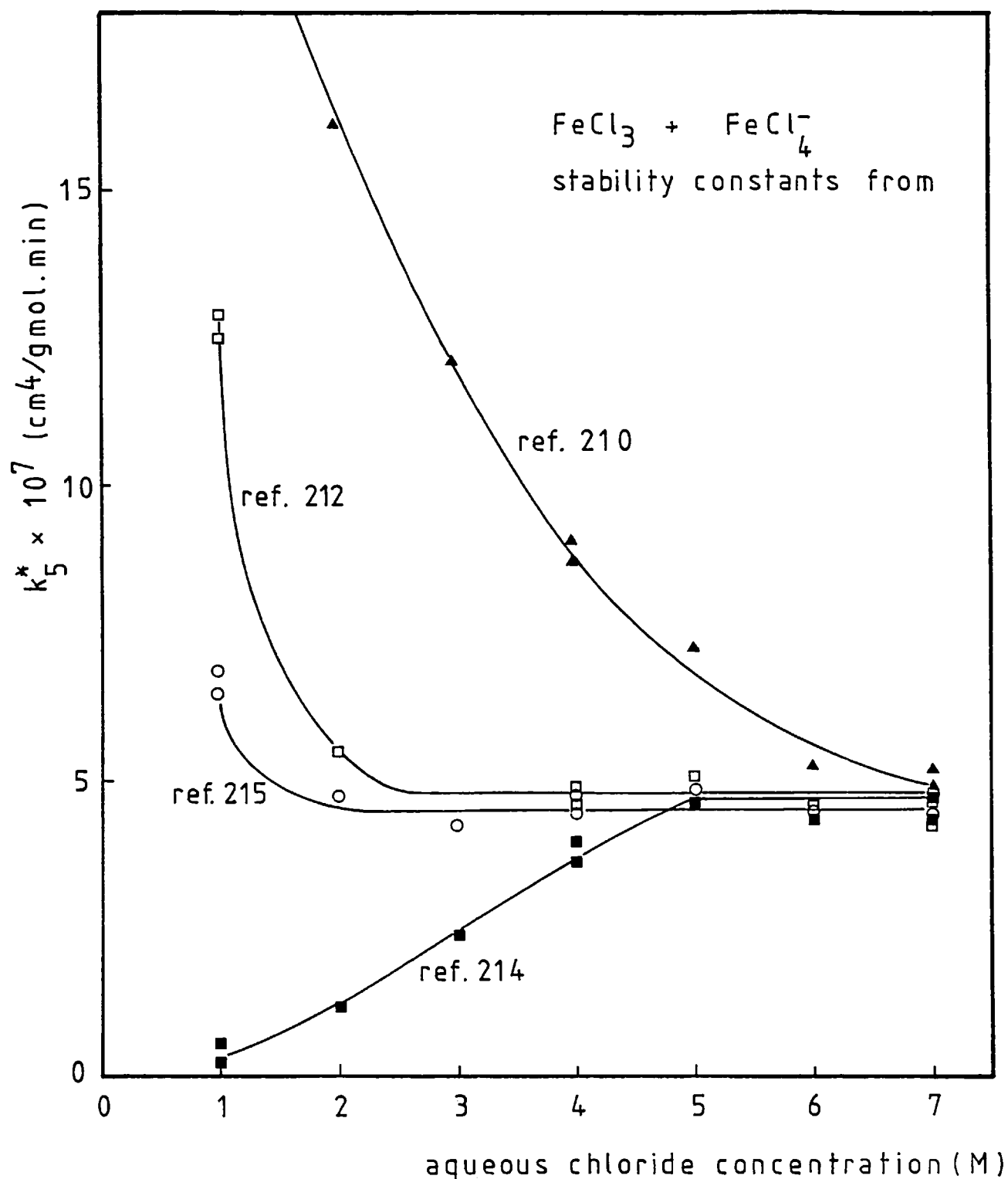


FIGURE 6.2.6.9. CALCULATED k_5^* VALUE AS A FUNCTION OF AQUEOUS CHLORIDE CONCENTRATION. α_3 and α_4 calculated using the stability constants given in references 210, 212, 214 and 215. $k_5^* = \vec{R} / ((\alpha_3 + \alpha_4) (\text{Fe}) (\text{TOAHCl})_{M_1})$

that the k_5^* values calculated using the α_n values from reference 210 and 214 give no constant k_5^* value, except for the α_n values from reference 214 at high aqueous chloride. As discussed in Section 3.6. it is difficult to comment on the reliability of the different sets of stability constants or the likelihood that they represent the actual system. The difficulties inherent in the Fe(III)-chloride system preclude reliable conclusions regarding the determination of the stability constants. It seems remarkable that the α_n values calculated from data in reference 212 and 215, being so different, gave almost the same ($\alpha_3 + \alpha_4$) result. Since in both cases the stability constants have been determined by least square analyses of solvent extraction distribution measurements, this may indicate that either the assumption that only FeCl_3 or FeCl_4^- is the extractable species, which was assumed to calculate the stability constants is not correct, but the determined values give the correct FeCl_3 plus FeCl_4^- concentrations (and then they would indicate that in the present study FeCl_3 and FeCl_4^- are the active species) or they are meaningless, being just the result of a best fitting exercise. If the determined stability constants are meaningless, then no conclusion regarding the active chlorocomplex(es) can be obtained with the present analysis. However, the $\alpha_3 + \alpha_4$ calculated using data from reference 212 and 215 should provide at least a reasonable empirical fitting for the experimental extraction results.

Figure 6.2.6.10 shows the predicted initial extraction rates using α_3 and α_4 values calculated using data from reference 212 and 215. In both cases a good agreement is obtained. Due to the lack of reliability of the stability constants, it is not possible to conclude whether FeCl_3 and FeCl_4^- are in fact the active species or these good agreements happened by chance (in this case they would represent just good empirical fittings).

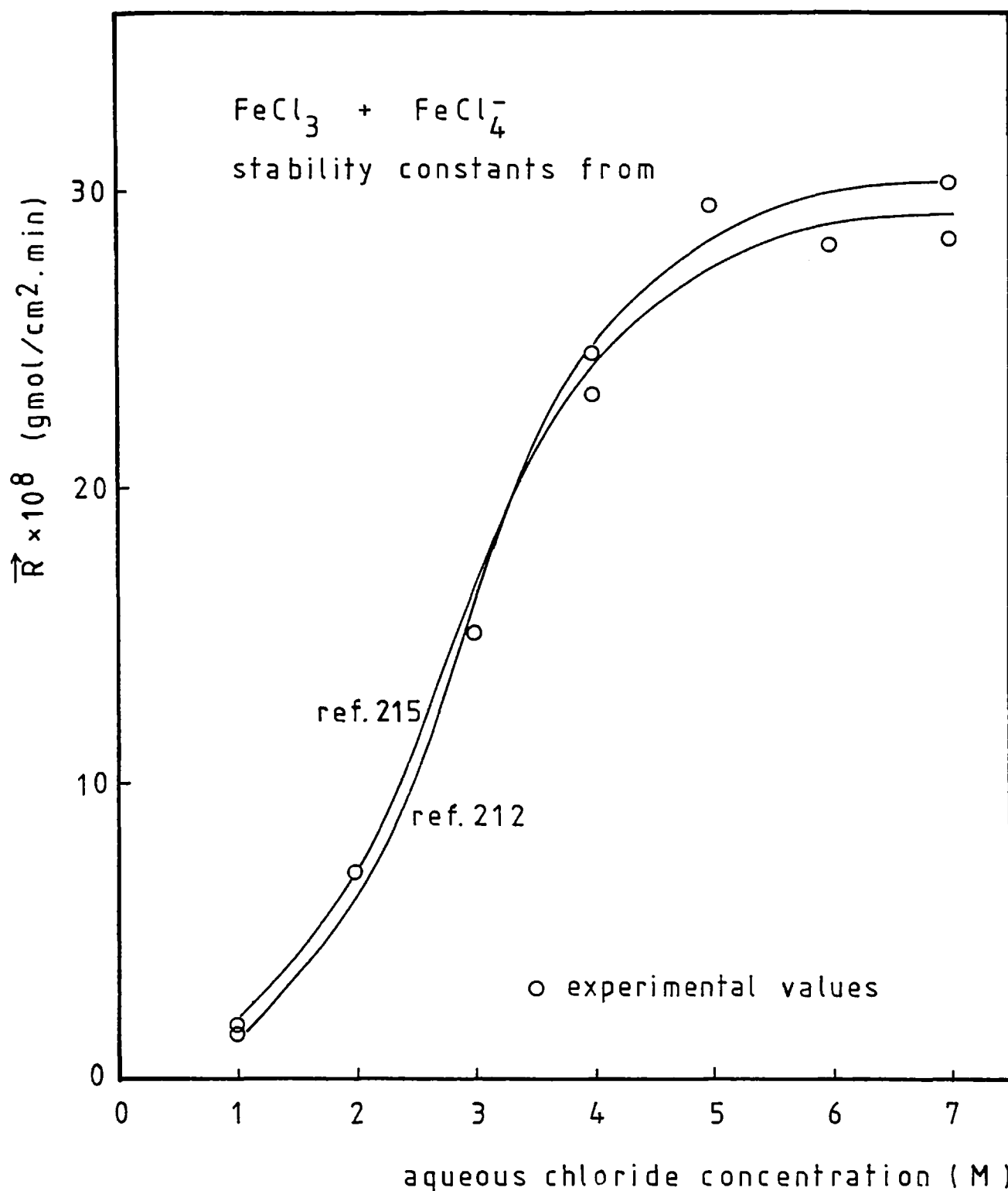


FIGURE 6.2.6.10. FITTED RATE (EQUATION 6.2.46)) AGAINST EXPERIMENTAL VALUE. α_3 and α_4 calculated using the stability constants given in references 212 and 215.

$$\vec{R} = \kappa_5^* (\alpha_3 + \alpha_4) (\text{Fe}) (\text{TOAHCl})_{M1}$$

The agreement between the predicted distribution ratio at equilibrium (D_{Fe}) as a function of Cl^- concentration with the values determined experimentally was not good. The slope of the plot $\log D_{Fe}$ versus $\log [Cl^-]$ found experimentally was about 3, whereas the calculated values did not lead to a constant slope and these D_{Fe} values were much less than the experimental ones. It is possible that this discrepancy could be due to some inconsistency in the proposed model or to some experimental error. Apparently, the rate equation derived from the proposed mechanism is consistent with the experimental kinetic evidence and some replicate runs showed that the experimental data were reproducible. For the rate equation to predict the expected D_{Fe} value as a function of aqueous chloride concentration, it would be necessary to have an inverse dependence of the stripping rates on the Cl^- concentration, which was not observed. It is possible that the experimental results at high Cl^- concentrations were not in a true plateau region and in this case the assumption of chemical control would not apply. The experimental evidence indicates that this was not the case. Other reasons that could explain this apparent discrepancy would be a different mechanism at high Cl^- concentration and then the derived rate equation would not apply (which is rather unlikely) or that the extraction of $FeCl_3$ and $FeCl_4^-$ cannot be represented by the same rate equation, as the k_5^* value would be different in each case. As the extraction of $FeCl_3$ and $FeCl_4^-$ cannot be monitored separately this possibility cannot be investigated. Finally, the lack of any significance at all in the values of the stability constants could be the only reason that would explain satisfactorily this discrepancy.

Having established that the reduced extraction and stripping models could predict adequately the initial mass transfer rates and were consistent with the experimental kinetic results, indicating that equations (6.2.7) to

(6.2.11) represent the most likely mechanism under the investigated conditions in this work, the obtained rate equation was integrated and the resulting function examined to see if it could predict concentration-time profiles of the form observed, in order to verify that the mass transfer rate data were not fitted by the proposed model by chance.

The linear reduced model is given by

$$\frac{V}{A} \frac{d(\overline{\text{Fe}})}{dt} = k_5^* \alpha_n (\text{Fe}) (\overline{\text{TOAHCl}})_{M_1} - k_6^* \frac{(\overline{\text{Fe}})}{(\overline{\text{TOAHCl}})_M} \quad (6.2.54)$$

where M_1 and M refer to the monomer and total TOAHCl concentration. But, under the investigated conditions $(\overline{\text{TOAHCl}})_M$ and $(\overline{\text{TOAHCl}})_{M_1}$ are much greater than the extracted organic Fe, so that they can be assumed constant. The initial conditions are given by
At $t = 0$ $(\overline{\text{Fe}}) = 0$ $(\text{Fe}) = (\text{Fe})^0$

$$(\overline{\text{TOAHCl}})_M = (\overline{\text{TOAHCl}})_M^0 \quad (\overline{\text{TOAHCl}})_{M_1} = (\overline{\text{TOAHCl}})_{M_1}^0$$

and at any time the conditions are

$$t = t \quad (\overline{\text{Fe}}) = (\overline{\text{Fe}}) \quad (\text{Fe}) = (\text{Fe})^0 - (\overline{\text{Fe}})$$

$$(\overline{\text{TOAHCl}})_M = (\overline{\text{TOAHCl}})_M^0 \quad (\overline{\text{TOAHCl}})_{M_1} = (\overline{\text{TOAHCl}})_{M_1}^0$$

Integration of equation (6.2.54) between $t = 0$ and $t = t$ and re-arrangement of the resulting equation gives

$$(\overline{\text{Fe}}) = \frac{a}{b} (1 - e^{-\frac{A}{V} b t}) \quad (6.2.55)$$

where $a = k_5^* \alpha_n (\text{Fe})^0 (\overline{\text{TOAHCl}})$

$$b = k_5^* \alpha_n (\overline{\text{TOAHCl}})_{M_1} + \frac{k_6^*}{(\overline{\text{TOAHCl}})_M}$$

$$\overline{(\text{TOAHCl})}_{M_1} = \frac{-1 \pm \sqrt{1 + 8 K_2 (\text{TOAHCl})_M}}{4K_2}$$

$$K_2 = 45$$

Using the integrated equation (6.2.55) and the fitted $k_5^* \alpha_n$ and k_6^* values at 1 M chloride, the organic Fe concentration was calculated as a function of time. The predicted concentration-time profiles for typical extraction experiments at 1 M chloride are presented in Figure 6.2.6.11, where they are compared with the experimental results. It can be seen that a good agreement is obtained in all cases.

The prediction of the concentration-time profiles in the stripping experiments requires the integration of equation (6.2.54) in a different form. The relationship between the mass transfer rate of aqueous and organic Fe is given by

$$\frac{d(\text{Fe})}{dt} = \frac{d(\overline{\text{Fe}})}{dt} \quad (6.2.34)$$

and equation (6.2.54) can be re-written as

$$\frac{V}{A} \frac{d(\text{Fe})}{dt} = k_6^* \frac{(\overline{\text{Fe}})}{(\text{TOAHCl})_M} - k_5^* \alpha_n (\text{Fe}) (\overline{\text{TOAHCl}})_{M_1} \quad (6.2.56)$$

Using the same assumptions regarding $(\text{TOAHCl})_M$ and $(\text{TOAHCl})_{M_1}$, the initial conditions are given by

$$\text{at } t = 0 \quad (\text{Fe}) = 0 \quad (\overline{\text{Fe}}) = (\overline{\text{Fe}})^0.$$

and at any time the conditions are

$$t = t \quad (\overline{\text{Fe}}) = (\overline{\text{Fe}})^0 - (\text{Fe}) \quad (\text{Fe}) = (\text{Fe})$$

Integration of equation (6.2.56) between $t = 0$ and $t = t$

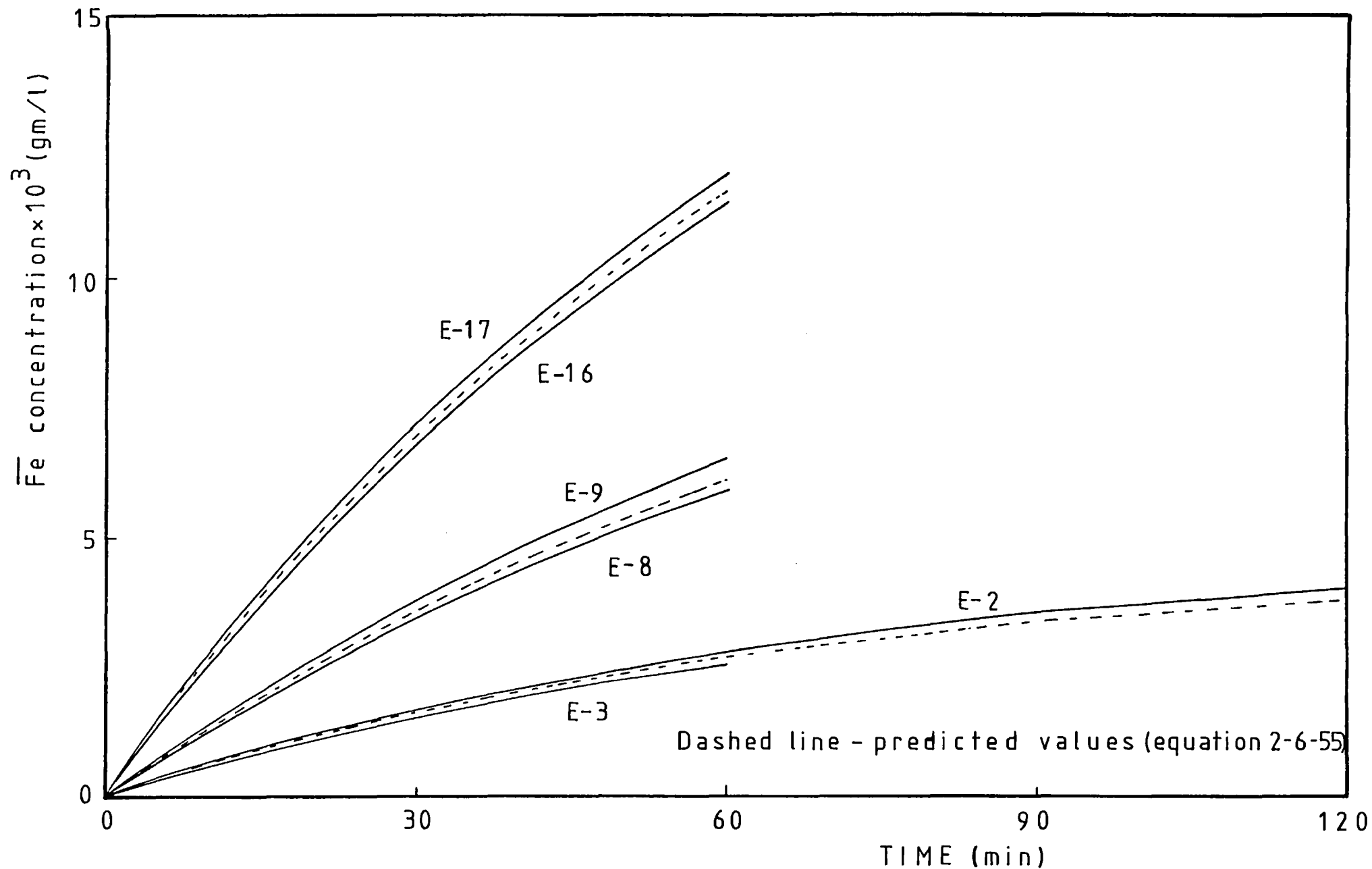


FIGURE 6.2.6.11. COMPARISON OF PREDICTED AND EXPERIMENTAL CONCENTRATION-TIME PROFILES FOR TYPICAL EXTRACTION RUNS (AQUEOUS $\text{Cl}^- = 1 \text{ M}$).

and re-arrangement of the resulting equation gives

$$(\text{Fe}) = \frac{c}{b} \left(1 - e^{-\frac{A}{V} b t} \right) \quad (6.2.57)$$

where $c = k_6^* \frac{(\overline{\text{Fe}})^0}{(\text{TOAHCl})_M}$

and b , $(\overline{\text{TOAHCl}})_{M_1}$ and K_2 is as defined in equation (6.2.55).

Using the integrated equation (6.2.56) and the fitted values of $k_5^* \propto_n$ and k_6^* at 1 M chloride, the aqueous Fe concentration was calculated as a function of time. The predicted concentration-time profiles for typical stripping experiments at 1 M chloride are presented in Figure 6.2.6.12, where they are compared with the experimental results. It can be seen that good agreement is obtained in all cases.

The good agreement obtained with the predicted and experimental concentration-time profiles indicated that the proposed mechanism was valid and could justifiably represent the kinetic data. The consistency of the derived rate equation with the experimental evidence confirms that the proposed mechanism is the most likely one. The investigation of the interfacial behaviour of the system and a reliable estimate of the stability constants of the chlorocomplexes are essential in order to reach definite conclusions about the reaction mechanism of the studied system.

To conclude this section it should be stressed that a thorough statistical analysis of the rate equation is essential in order to check the validity of the proposed model. It should be also stressed that adequate planning of the experiments is very important. In the present work, the planning showed some inadequacy, as the experiments were carried out using the conventional method of one

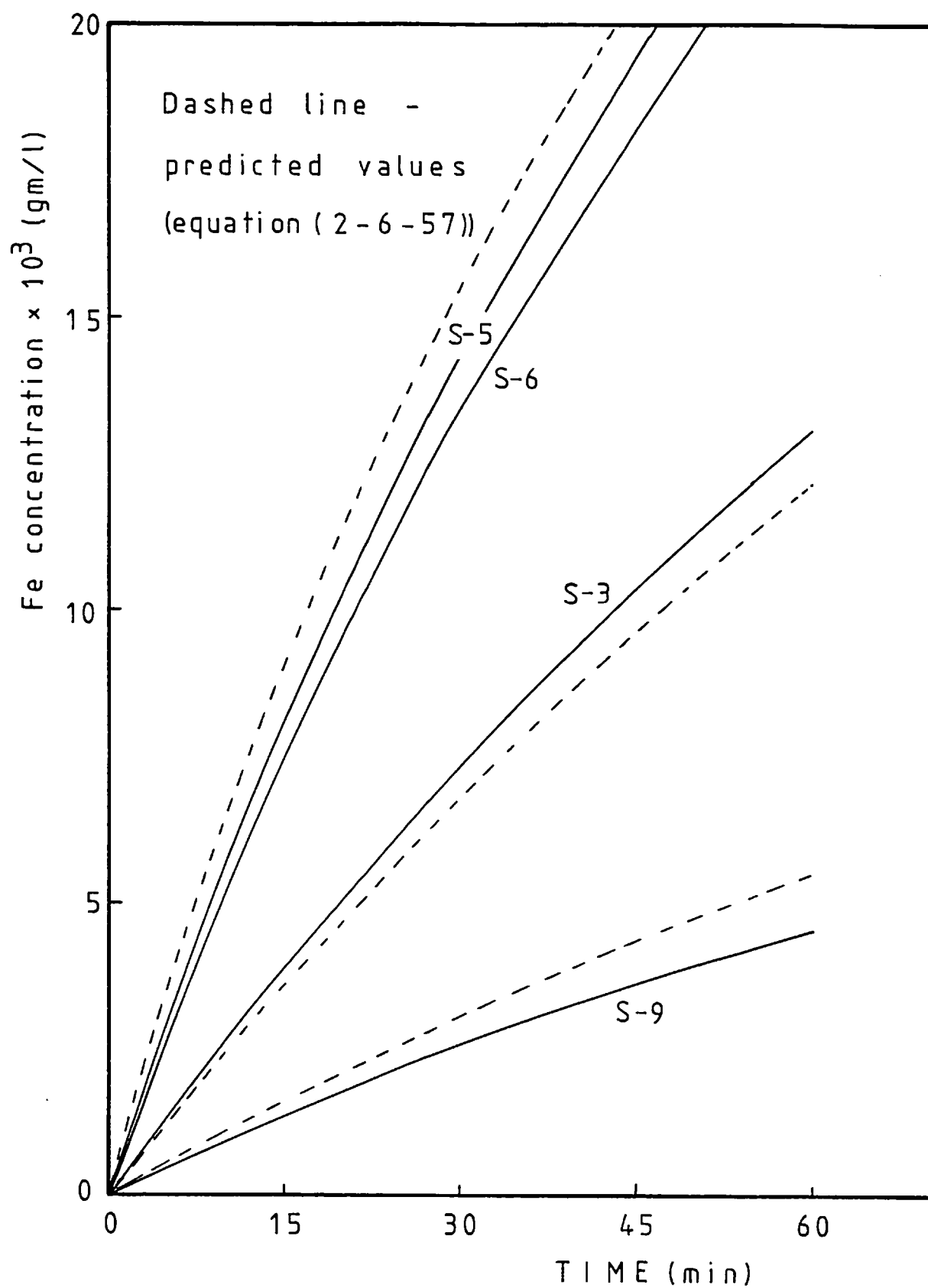


FIGURE 6.2.6.12. COMPARISON OF PREDICTED AND EXPERIMENTAL CONCENTRATION-TIME PROFILES FOR TYPICAL STRIPPING RUNS (AQUEOUS $\text{Cl}^- = 1 \text{ M}$).

variable at a time, keeping the others constant. This method is very useful for a preliminary investigation as it clearly shows the trends. However, there is a tendency to over-weight the variable which is allowed to change, when all data are used to test the model and the results may not be as statistically significant as those obtained by a matrix¹⁴⁹ or simplex²³³ design. In the conventional method it is possible that the effect of interactions, if any, could be neglected or not detected. The selection of the best model showed also that if one model contains more parameters than another it will not be necessarily better. If the hypothetical model is not close to the true model, probably it will be inadequate, no matter how many parameters are used to represent it, or an overfitting may happen and in any case it may lead to misleading conclusions.

6.2.7. Effect of temperature on initial mass transfer rate

The activation energy or the dependence of reaction rate on temperature can provide some useful information about the reaction mechanism for simple systems. However, for the activation energy to be meaningful it must refer to the temperature dependence of a true rate constant for the reaction. For multi-step reactions with irreversible steps the overall activation energy will be the sum of the step energies. With reversible steps, the forward rate constant activation energy will be the sum of the forward step energies and vice-versa for the reverse rate constant activation energy. The difference between forward and reverse energies will be the energy change in each step and the total of these the energy change for the overall stoichiometric reaction. The individual activation energies cannot be obtained from Arrhenius plots ($\ln k$ vs $\frac{1}{T}$ ($^{\circ}\text{K}^{-1}$)) for the individual step reactions, unless single forward and reverse constants can be factored out

of the rate expression. The overall energy change can be obtained from an Arrhenius plot of the overall equilibrium constant, or in the case of metal extraction, the equilibrium metal distribution coefficient, where chemical conditions are kept constant.

Hughes et al.¹⁴⁸ obtained activation energy values in the range 41-51 kJ/mol for the rate of extraction of copper (II) from sulphate solutions with LIX 64N. These values are typical of other solvent extraction systems, i.e. copper (II) with KELEX¹⁴⁹, zinc with HDEHP¹⁵⁰, etc. These activation energy calculations were based on the initial forward reaction rates, which are not rate constants, but it may be possible to relate these values in some way to the activation energy for the forward reaction. Activation energies around 45 kJ/mol are quite low for chemical reaction controlled processes, but it is known that in some processes an interface can catalyse the reaction and so lower the activation energy because the adsorption of reactants onto the interface is energetically favourable.

It is also important to consider the effect that reaction at an interface may have on the activation energy. The degree of saturation of the interface with reactant is known to affect the activation energy for a chemical process, independent of other chemical considerations²³¹. It is known that as the surface pressure increases and the interfacial film changes from an expanded to a condensed type, the activation energy increases. It has been postulated that this increase is a result of the stronger electrostatic field exerted by the dipoles in the condensed film and also of the change in orientation and mobility of the surface molecules as the film is concentrated. Activation energies of 42 kJ/mol increasing to 67 kJ/mol are typical for systems where this effect has been observed. The fundamental differences between a reversible heterogeneous

system makes it difficult to compare activation energies for heterogeneous systems using values from homogeneous reactions as a guide.

For the range of conditions studied in this work, it has been shown that the rate equation for the proposed mechanism reduced to a simple linear relationship involving only two overall rate constants k_5^* and k_6^* . The constant k_5^* refer to a group of forward and reverse rate constants and the interfacial monomeric TOAHCl concentration, whereas k_6^* represents the ratio between the forward reaction of equation (6.2.10) and the equilibrium constant K_3 (equation (6.2.11)). It has been shown that it is not possible to calculate the individual rate constants with the present analysis, so that the calculated activation energies will give only the energy change or apparent activation energy for the forward and reverse reactions, but not the activation energy of the individual steps.

Runs were performed at temperatures from 14.7°C to 36.0°C at 1 M, 4 M and 7 M aqueous chloride concentration for extraction and at 1 M Cl^- for stripping, to evaluate the effect of this variable. Apparent activation energies were calculated using Arrhenius plots and are given in Table 6.2.7.1. Hydrodynamic conditions were kept constant (i.e. Reynolds number, interfacial area, etc.). Based on initial mass transfer rates, reasonably constant values for the forward reaction energy change were obtained which, combined with the reverse reaction energy change, gave an estimate for the energy change for the overall reaction (ΔE):

$$\Delta E = 34.8 \pm 9.8 \text{ kJ/mol}$$

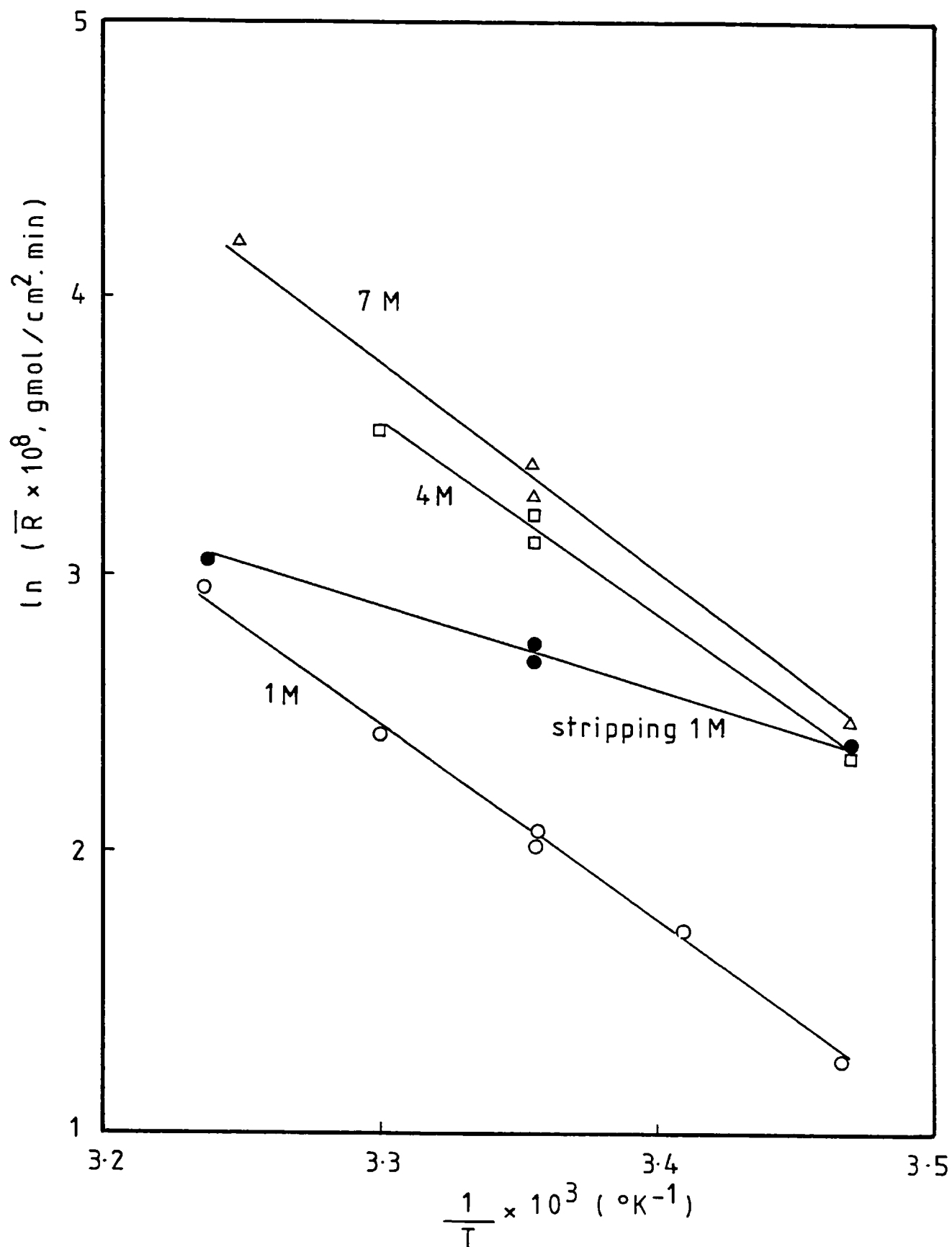


FIGURE 6.2.7.1. EFFECT OF TEMPERATURE ON INITIAL MASS TRANSFER RATE.

TABLE 6.2.7.1. Apparent activation energy (E_A)

	Cl^- (M)	Fe (M x 10^3)	TOAHCl ₂ (M x 10^2)	E_A (kJ/mol) based on R values	E_A (kJ/mol) based on k* values
Extraction	1	2.5	2.5	59.2 $\pm$ 2.6	49.0 $\pm$ 3.0
Extraction	4	1.0	1.0	58.8 $\pm$ 8.2	49.7 $\pm$ 8.2
Extraction	7	1.0	1.0	59.9 $\pm$ 11.0	51.2 $\pm$ 11.9
Stripping	1	1.74	1.0	24.5 $\pm$ 2.5	32.6 $\pm$ 3.4

Using equations (6.2.35) and (6.2.36) rate constants were calculated and Arrhenius plots gave the apparent activation energies shown in Table 6.2.7.1. The enthalpy value used to calculate the dimerization constants of TOAHCl and hence TOAHCl monomer concentrations was $\Delta H = -8 \text{ kcal/mol}^{224}$. This value was shown to be adequate for the present system since the evaluated rate equation represented reasonably well the kinetic data. Under these conditions an estimate of the overall energy change gave:

$$\Delta E = 17.4 \pm 11.5 \text{ kJ/mol}$$

The good straight lines on the Arrhenius plots indicate that only one reaction at each time (extraction or stripping) is being dealt with and that it is not likely that the mechanism at the higher temperatures is significantly different from the mechanism at 25°C . The variation of k_7^* (equation 6.2.32) with temperature is not such as to make it possible that $k_7^*(\text{TOAHCl}) \ll 1$ is untrue at the higher or lower temperatures. The estimated overall energy change using rate constants was about half of the value using initial mass transfer rates. If both methods were equivalent, they should give the same result. The variation of the reacting species with temperature is not considered when using the initial rate method, which indicates the inadequacy of this method to estimate the energy change when this situation occurs. The magnitude of the apparent activation energy of about 50 kJ/mol for extraction and 32.6 kJ/mol for stripping indicates that both refer to a chemical controlled process, although these values are at the low end of the range for chemical control.

Hughes et al.¹⁴⁸ studied the temperature dependence of viscosity and attempted to relate the slope of an Arrhenius plot for a mass transfer controlled process to that of the viscosity of the appropriate medium. The

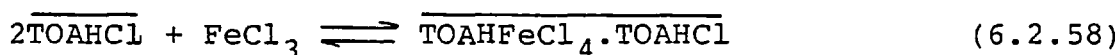
activation energy expected for mass transfer control alone was found to be about one third the value obtained for the extraction and it was concluded that the extraction was probably under mixed or chemical control. For the reasons outlined above it is questionable whether the behaviour of homogeneous systems as indicated by their activation energies can be related to the behaviour of heterogeneous systems when activation energy measurements are carried out. In homogeneous system only bulk properties are important, whereas in metal extraction by any commercial extractant such as high molecular weight tertiary amines, where reactions at or near the interface take place, interfacial properties may be more important than bulk properties. Since interfacial properties are not identical to the bulk properties and not necessarily even simply related to them, only by knowing the temperature dependence of those interfacial properties (interfacial viscosity, interfacial potential and interfacial tension) may definite conclusions be obtained regarding the relationship between activation energy and type of control of the extraction system. Apparently, to date no such study has been carried out, at least for the system under investigation. The temperature dependence of the viscosity of TOAHCl-toluene and HCl-LiCl-water solutions were not determined and were not available in the literature. The activation energies for the viscosity of pure water (16.4 kJ/mol) and of toluene (8.6 kJ/mol) were estimated, which, compared to the estimated value for extraction (50 kJ/mol) and stripping (32.6 kJ/mol) for the present system, would indicate chemical or mixed control. The apparent activation energies at 1 M, 4 M and 7 M chloride, which have quite different aqueous phase bulk viscosities, are all about the same. As diffusivity is strongly dependent on the viscosity of the medium, the fact that there was no significant difference in the forward apparent activation energies, strongly suggests that the rate controlling step under the investigated conditions was a chemical reaction.

The apparent activation energies for the forward reaction based on initial mass transfer rates are consistent with values obtained in a similar manner for other systems¹⁴⁸⁻¹⁵⁰.

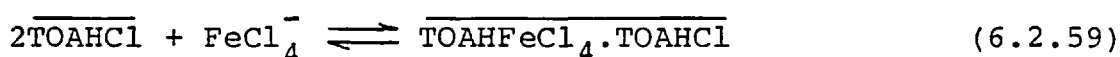
The apparent activation energy for the process will be also a function of all the experimental parameters: diluents, modifiers, degree of association of the extractant, hydrodynamic conditions and any other factors which will affect the extraction mechanism. This makes it more difficult to obtain mechanistic information from the activation energies determined for complex extractions reactions.

6.2.8. The nature of the transferred species

The overall reaction for the proposed mechanism at low organic Fe concentration is given by:



or



Since reactions (6.2.58) and (6.2.59) yield the same reaction product, the position of the extraction equilibrium is independent of the particular reaction responsible for the formation of the extracted complex, whatever the phase composition. As a result, equilibrium studies will not show which chlorocomplex is involved in the extraction process, even though extensive experimental material on the subject is available. So, a kinetic study is essential for the solution of this problem if indeed it is possible to solve it.

In the previous section, it has been shown that the lack of reliable stability constants for the Fe chlorocomplexes preclude definite conclusions regarding the nature of the

transferred species, although strong evidence was found that mixed (neutral and anionic) transfer is most likely.

In order to elucidate the reaction mechanism a different approach must be used without involving the stability constants. There is one difference between reactions (6.2.58) and (6.2.59) which can be exploited. If the neutral chlorocomplex is the active species, then the ratio Cl/Fe transferred will be 3, whereas if the anionic species is the active one, this ratio will be 4. If it is possible to differentiate in some way the neutral and anionic species, it should be possible to follow the transfer of the chlorocomplex involved in the extraction process. The use of radioactive labelled chloride (^{36}Cl) should allow this possibility.

The theory of the kinetic isotope method is described elsewhere²³⁴. Tikhomirov et al.²³⁵ developed theoretical models for the kinetics of the isotope exchange through a liquid-liquid interface. However, these models involve the use of several parameters which are difficult to determine and so the models cannot be applied in the present study.

The results from the isotopic transfer investigation presented in Section 6.1.3. indicated that, on a molar basis for comparable situations, the mass transfer rate under conditions of transport control is at least one order of magnitude greater than the mass transfer rate under conditions of chemical control. So, the experiments could not be carried out in the range of conditions where chemical control would be expected, as the increase in the chloride concentration in the organic phase associated with the Fe transfer would have the same order of magnitude of the experimental error involved in the isotopic transfer measurements. The experiments had to be carried out under conditions of mixed or transport control. It is unlikely

that FeCl_3 and FeCl_4^- have the same diffusivity. However, it is assumed that this difference in diffusivity is not significant and does not affect the measured Cl/Fe ratio. It is assumed also that there is no isotope effect and that ^{36}Cl ions behave in the same way as the other chloride ions.

To calculate the chloride concentration associated with the Fe transfer, a simple model was used. It was assumed that the net chloride transfer would be given by:

$$(\text{Cl})_{\text{net}} = (\text{Cl})_{\text{during Fe extraction}} - (\text{Cl})_{\text{during isotopic transfer}}$$

and the Cl/Fe ratio by:

$$\text{Cl/Fe} = (\text{Cl})_{\text{net}}/\text{Fe}$$

So, two separate kinetic experiments are required to calculate the Cl/Fe ratio. It is assumed also that there is no interaction between the chemical reaction and the isotopic transfer. If the experimental conditions in the two experiments are the same except for the absence or presence of Fe it seems reasonable to expect that the mixing and diffusion effects will remain the same.

The analysis of ^{36}Cl in the presence of Fe is not simple as shown in Section 5.4. However, the colour quenching problem can be overcome by working under conditions where the organic Fe concentrations is less than 0.2 gm/l. The β -counting analysis of ^{36}Cl required relatively large samples under the investigated conditions. Sampling of the aqueous phase was not possible as this would have affected the hydrodynamic conditions at the interface, by displacing its level. So, the samples had to be collected from the organic phase. Usually, up to 10 samples of 6 ml each were taken and the variation of volume was assumed to have negligible effect (initial volume of organic phase = 480 ml).

The experimental procedure was the same as described in Section 6.1.3. (isotopic transfer). The radioactive chloride (^{36}Cl as HCl) was added to the aqueous phase in the extraction experiments or to the organic phase in the stripping experiments.

The first series of experiments was carried out at 1 M Cl^- . Using concentrations of TOAHCl and Fe in the aqueous phase of 0.1 M each and operating the cell at 250 rpm (contra-rotating stirrers) gave a fast Fe extraction. The Fe content in the organic phase was above 0.2 gm/l within a few minutes and so the samples could not be analysed for the ^{36}Cl content. Reducing the TOAHCl and Fe concentrations to 0.01 M and using the same stirring conditions gave a slow Fe extraction and the isotopic transfer was much faster than the Fe extraction. However, using TOAHCl and Fe concentrations of 0.025 M each, good results were obtained, which are presented in Figure 6.2.8.1. The chloride concentration during Fe extraction was corrected for the colour quenching of β -counting using equation 5.4.1. The Cl/Fe ratio calculated is presented in Figure 6.2.8.2. It can be seen that the results are rather scattered. Attempts to "smooth" the data using "smoothed" concentrations or derivative values and extrapolation to time zero gave results which were inconsistent with the expected value and also this type of analysis when applied to the other results gave inconsistent trends. It was then decided that the average of the Cl/Fe ratios would give the most probable value.

Under the same conditions, experiments were carried out at 3, 5, 7 and 9 M Cl^- . The results are given in Appendix C. The experiment of 9 M Cl^- produced erratic results and these are not reported. The average Cl/Fe values are presented in Figure 6.2.8.3. The theoretical Cl/Fe ratio was calculated by assuming mixed transfer and using the α_n values calculated from the stability constants

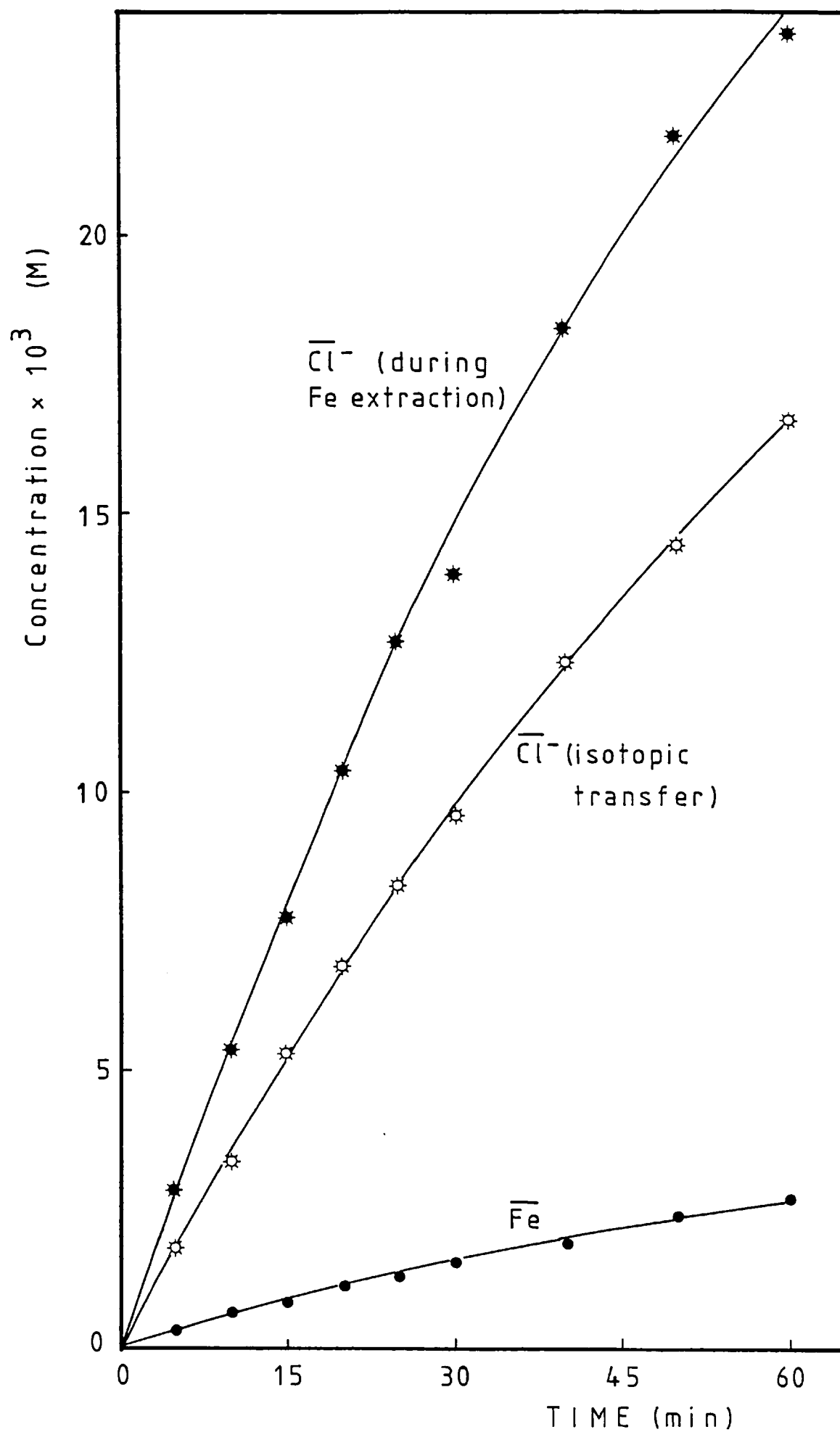


FIGURE 6.2.8.1. EXPERIMENTAL CONCENTRATION-TIME PROFILES (EXTRACTION 1 M Cl^-).

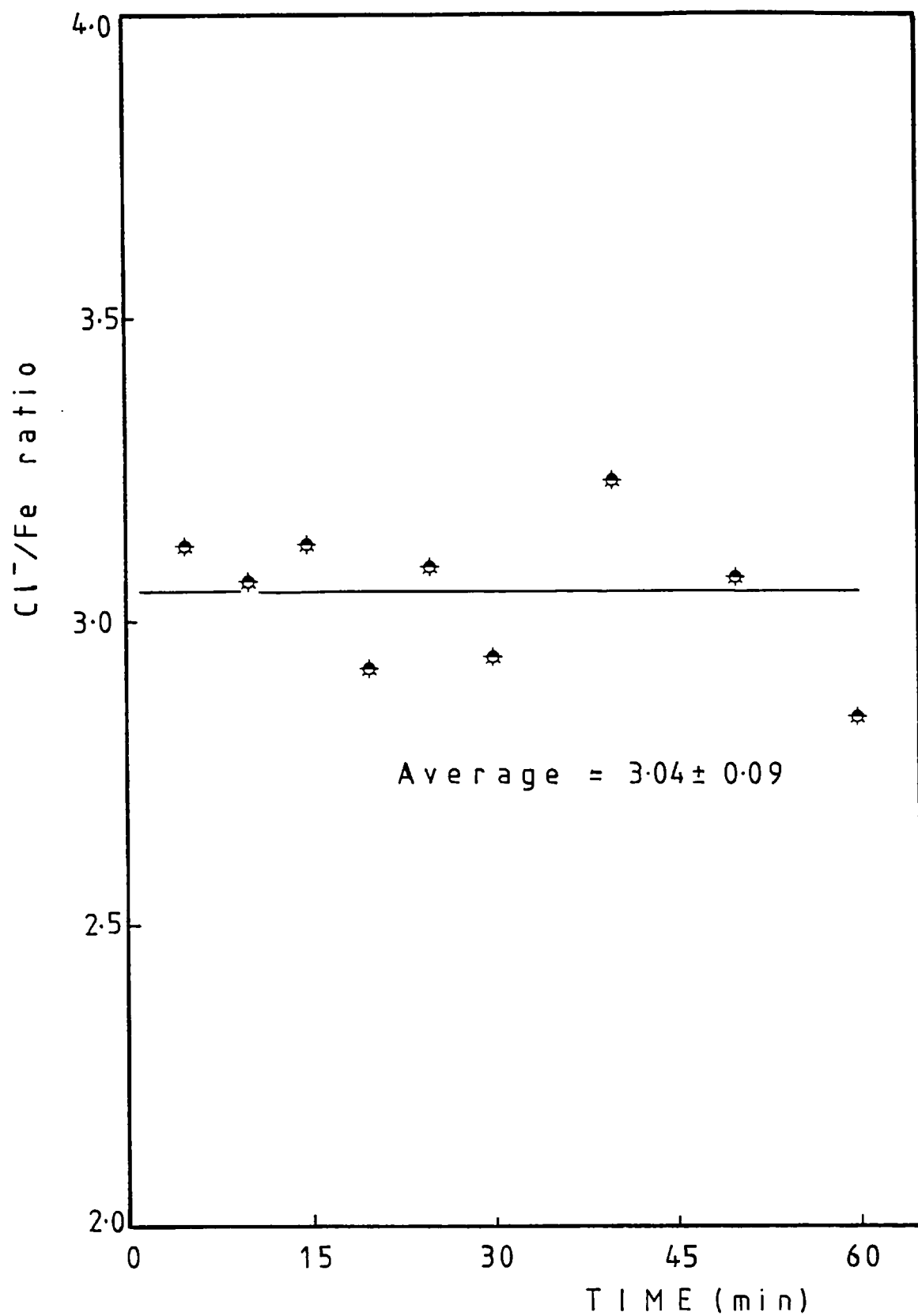


FIGURE 6.2.8.2. Cl/Fe RATIO AS A FUNCTION OF TIME.
(EXTRACTION 1 M Cl^-).

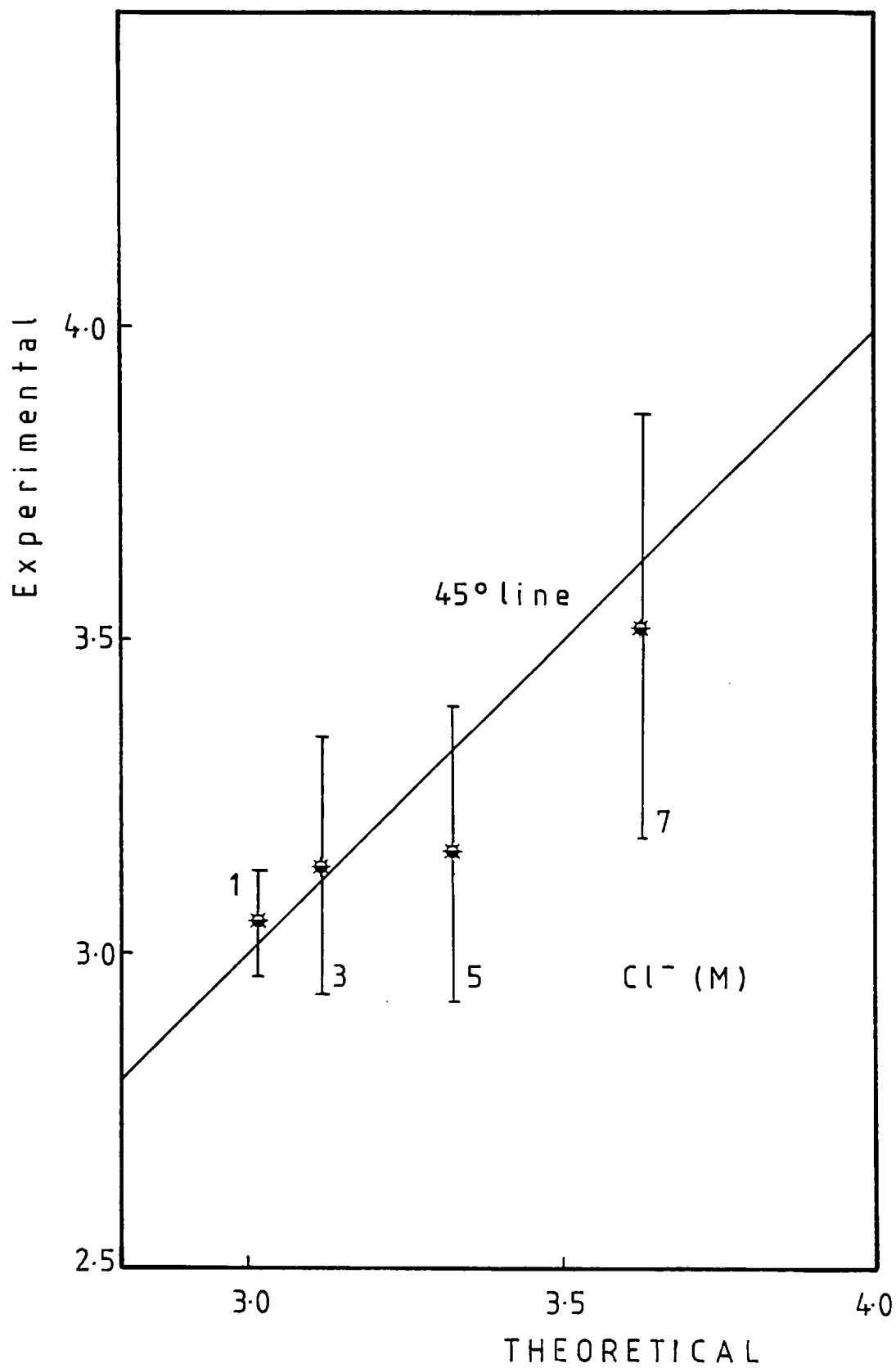


FIGURE 6.2.8.3. PLOT OF EXPERIMENTAL VERSUS THEORETICAL Cl/Fe RATIO.

given in reference 215, which in the previous section was shown to be the most consistent with the kinetic data under chemical control. The agreement between experimental and theoretical Cl/Fe ratio is not very good, but the trends are very clear. If the average Cl/Fe ratio as calculated is accepted to represent the extraction process, then the results show clearly that mixed transfer is most likely. Under the range of conditions investigated pure neutral or anionic transfer seems to be most unlikely. Therefore, the transfer mechanism that predominates depends on the availability of both species. Apparently, the rate of extraction seems to be proportional to the concentration of these species.

It can be seen in Figure 6.2.8.3. that the uncertainty in the experimental Cl/Fe ratio increases with the increase of the chloride concentration. This is associated with the error in the β -counting analysis. As the aqueous chloride concentration increases, the rate of iron extraction increases, so that samples had to be taken at short periods of time and therefore had low count rates.

Attempts to measure the Cl/Fe ratio by adding the tracer to the organic phase during the Fe stripping were unsuccessful. The experiment at 1 M Cl using TOAHCl = 0.01 M and Fe = 1.74×10^{-3} M showed that the isotopic transfer was much faster than the Fe extraction. The same situation happened at 0.1 M Cl using the same TOAHCl and Fe concentrations. Lowering the aqueous chloride concentration to 0.05 produced hydrolysis of the Fe complex in the organic phase. Increasing the organic Fe concentration was not possible, as the chloride content could not be analysed either in the organic (above 0.2 gm/l) or in the aqueous phase (no sampling).

CHAPTER VIICONCLUSIONS

1. In the range of conditions where mass transfer is affected by diffusion, a dependence of mass transfer rate on the stirring speed in the cell is always observed. For the chloride isotopic transfer under the investigated conditions, the dependence of the overall mass transfer coefficient on the stirring speed was correlated by the equation:

$$K = 1.072 \times 10^{-3} \times 10^{\frac{N}{602}}$$

2. The initial extraction and stripping rate of iron under the experimental conditions was controlled by the rate of chemical reactions taking place at or near the interface between the two phases. This conclusion was supported by the independence of the mass transfer rate with respect to stirring speed. The location of the reactions at or near the interface was indicated by the linear dependence of mass transfer rate on specific interfacial area. The apparent activation energy also supported a chemical reaction mechanism with due regard for the special problems in considering activation energies for interfacial and multi-step processes.

3. Depending on the chemical composition of the system the plateau region, where mass transfer rate is independent of stirring speed, shifts or disappears completely. At high reactant concentrations or at aqueous chloride concentration above 7 M, no plateau region was found. If the transfer rate is very fast, the stirring conditions necessary for chemical control are incompatible with the requirement of a quiescent interface. Therefore, under these conditions chemical control cannot be achieved

in the stirred cell. If the physical properties of the bulk phases change significantly, the location of the plateau region shifts and a criterion of hydrodynamic similarity for the mixing conditions must be used. For the investigated system the criterion used was a constant aqueous Reynolds number ($Re = 2680$).

4. A mechanism was proposed for the reactions involved (equations (6.2.7) to (6.2.11)) and a rate equation was derived based on the proposed mechanism (equation (6.2.31)). The evaluation of the rate equation indicated that the initial extraction rate was first order with respect to the total aqueous iron and TOAHCl monomer concentration, whereas the initial stripping rate was first order with respect to the organic iron concentration and inverse first order with respect to the TOAHCl total concentration. At 1 M chloride, this model was able to predict the initial extraction and stripping rates and the equilibrium distribution ratio, and in the integrated form it was used to predict concentration-time profiles of the form observed experimentally. These results indicated that the proposed mechanism was valid and could justifiably represent the kinetic data.

5. From the evaluation of the rate equation and other known results it was concluded that the difficulty of the iron chlorocomplex(es) reaching the interface and reacting with monomeric TOAHCl near the interface, in the aqueous phase, should be the slowest extraction step, whereas the difficulty of displacing monomer TOAHCl at the interface by $TOAHFeCl_4$ should be the rate controlling step for the stripping process.

6. The derived rate equation could also predict the dependence of the initial extraction rate on the aqueous chloride concentration. It was found that apparently the initial extraction rate was related to the concentrations

of the neutral (FeCl_3) and anionic (FeCl_4^-) iron chloro-complexes, whereas the initial stripping rate was found to be independent of the aqueous chloride concentration. From the evaluation of the rate equation no definite conclusion was possible regarding the nature of the chlorocomplexes involved in the extraction process, due to the lack of reliability and consistency of the stability constants of the chlorocomplexes available in the literature. Assuming that FeCl_3 and FeCl_4^- were the active species and using the stability constants $K_1 = 4.02$, $K_2 = 0.045$, $K_3 = 0.339$, $K_4 = 0.0105$ or $K_1 = 0$, $K_2 = 0.2$, $K_3 = 0.04$, $K_4 = 0.012$ gave good predictions of the initial extraction rate as a function of the aqueous chloride concentration. However, the agreement between the predicted distribution ratio at equilibrium with the values determined experimentally was not good, which indicated that the values of the stability constants were unreliable.

7. The determination of the ratio Cl/Fe transferred from the aqueous to the organic phase using labelled radioactive ^{36}Cl (as HCl) indicated that mixed (neutral and anionic) extraction transfer is the most likely possibility.

8. The investigation of the interfacial behaviour of the system and a reliable estimate of the stability constants of the chlorocomplexes are essential in order to reach definite conclusions about the reaction mechanism of the investigated system. However the proposed mechanism is consistent with the available experimental data.

CHAPTER VIII
GENERAL COMMENTS

This work has indicated a considerable range of topics which may be of interest in future studies.

These may be divided into three main areas, namely: stirred cell design; practical applications of the stirred cell technique; and the elucidation of amine reaction mechanisms.

Although the present stirred cell proved to be adequate for kinetic investigation, there is still the need for further improvements. It appears that the cell is over-baffled, as indicated by the unexpected shape of the curve when extraction rate was plotted as a function of stirring speed in the region of mixed or mass transfer control. Different types of vertical baffles should be tested and their effects on the hydrodynamic conditions optimised. Before it is at all possible to compare the fundamental results of different investigators directly, a standard apparatus must be accepted, much as with the AKUFVE for equilibrium studies. There is a great deal of work to be done on the stirred cell itself. It needs to be developed. There is room for much improvement in the engineering of the cell. Cell design, hydrodynamics and improvements of the ease with which experiments can be carried out are all subjects of interest. The stirred cell technique could also be used for comparing the extraction rates of different commercial extractants. Such work would again require the development of a standard cell. Important work could be done to investigate if there was any way to relate rates observed in a stirred cell under chemical control, to those seen in industrial contactors where mixed or mass transfer control might occur, otherwise these studies

would be of no use. In a way, it is difficult to foresee the application of the stirred cell technique as a tool of extractant selection. Commercially available amine extractants are already fast enough so that small discriminations in extraction rate, which could be determined in a stirred cell, are of no consequence on the economics of a commercial process. The difficulty of obtaining kinetic information makes the stirred cell technique rather unattractive. Interfacial tensions studies may be easier and may give just as much comparative information. There is some evidence to show that this is the direction being taken in solvent extraction kinetic studies^{49,236}.

The lack of reliability and consistency of the stability constants of the iron (III) chlorocomplexes, as well as the restrictions imposed on the experimental conditions when determining the ratio Cl/Fe transferred indicates the inadequacy of this system for a kinetic investigation aimed towards the elucidation of the amine reaction mechanism. It appears that zinc chloride should be a better system, as there are less discrepancies amongst the determined stability constants, as well as the fact that the colour quenching problem during the β -counting analysis would be avoided. However, the chemical analysis of zinc could be a problem. Zinc-TOAHCl complexes are colourless, which means that direct spectrophotometric analysis is not possible. Probably on-stream analysis of the γ -emitter ^{65}Zn (half-life 245 days) would be an adequate method. The determination of the ratio Cl/Zn transferred using ^{36}Cl (as HCl) could be difficult, as an alternative analytical method would have to be used for the zinc analysis. Atomic absorption cannot be used when the samples contain radioactive material (safety regulations). Perhaps, an electrochemical method as described by Danesi et al.⁸¹ could overcome this difficulty. In this case, special electrodes are required. During the

course of the present work this possibility was considered but the cell had little room for these special electrodes and major modifications in the design of the cell would have been necessary. However, if a new cell is designed it would be convenient to have facilities for electrochemical analysis (amperometry). The Hg(II)-chloride system may be the ideal one to investigate the ratio Cl/metal transferred, as the Hg(II)-TOAHCl complexes are colourless and Hg is fully extracted at low Cl^- concentrations, which should increase the precision of the β -counting analysis. However, the determination of the Hg concentrations and the lack of reliability in the stability constants would be serious inconveniences.

A new approach should be attempted in order to find a reliable method of determination of the stability constants. It is possible that new developments in Raman spectroscopy may provide an answer to this problem. Without reliable stability constants, no definite conclusions are possible regarding the nature of the transferred species.

These types of kinetic investigations should be carried out in parallel with interfacial studies of the system. This is needed to obtain information about the nature of the reactants and products at the interface and the nature of the interface itself. The effect of diluent and modifiers, as well as synergistic extractants could be investigated. All these parameters and more need to be investigated before there is any hope that a complete understanding of the extraction mechanism has been obtained. It can be seen that the complete elucidation of the reaction mechanism of any system may involve a large effort.

Apparently, most of the industrial problems related to solvent extraction are concerned with phase separation (coalescence and entrainment). If solvent extraction is

to have in the future the large industrial application that is predicted today, research must be directed to the solution of the separation problem, otherwise, developments in ion exchange, not having this problem, will offer a tremendous advantage.

SYMBOLS

Capital letters

A	- interfacial area (cm^2)
A	- of the aqueous phase
C	- concentration (gm/l or gmol/l)
C_b	- bulk concentration (unit as C)
C_i	- hypothetical interfacial concentration (unit as C)
D	- diffusivity or diffusion coefficient (cm^2/sec)
D_{eff}	- effective diffusivity (unit as in D)
D_{Fe}	- equilibrium distribution ratio of iron (dimensionless)
F	- single mean activity coefficient as defined in context
J	- mass flux ($\text{gmol}/\text{cm}^2.\text{sec}$)
$\overline{J}$	- average mass flux (unit as J)
K	- mass transfer coefficient (cm/sec or cm/min)
K_1, K_2, K_3, K_4	- thermodynamic stepwise equilibrium constant (stability constants)
K_2	- dimerisation constant (M^{-1})
K_n	- thermodynamic equilibrium constant as defined in context.
L	- characteristic length or dimension (cm)
M	- total TOAHCl concentration (M)
M_1	- monomer TOAHCl concentration (unit as M)
M_2	- dimer TOAHCl concentration (unit as M)
N	- stirring speed (rpm, rps)
NSCORES	- normal scores of standard residuals
O	- of the organic phase
R	- initial mass transfer rate - dC/dt ($\text{gm}/\text{l}.\text{min}$)
$\overline{R}$	- initial specific mass transfer rate - $(V/A)(dC/dt)$ ($\text{gmol}/\text{cm}^2.\text{min}$)
$\rightarrow R$	- initial specific extraction rate (unit as R)
$\leftarrow R$	- initial specific stripping rate (unit as R)
R_c	- linear correlation coefficient
R_c^2	- coefficient of determination or fraction explained
T	- temperature ($^{\circ}\text{C}$, $^{\circ}\text{K}$)

- U - velocity (cm/sec)
 V - phase volume (ml)
 A, B, C, D, E, F, G, H also used as various constants in specific instances in the text.

Small letters

- $a_1, a_2, \dots, a_n$ - linear coefficients (polynomial)
 d - specific gravity (gm/cm^3)
 g - gravitational constant
 k_1, k_2, k_3, k_4 - chemical-rate constants as defined in context.
 $k_1^*, k_1^{**}, k_4^*, k_5^*, k_6^*, k_7^*$ - grouped chemical rate constants as defined in context.
 s - fractional rate of renewal
 t - time (sec, min)
 $\bar{t}$ - average residence time (sec, min)
 t^* - mean surface exposure time in surface renewal theory

Greek letters

- α_n - fraction of iron (III) present as the nth chlorocomplex
 γ - activity coefficient as defined in context
 δ - effective film thickness (cm)
 ϵ - eddy diffusivity (cm^2/sec)
 μ - absolute viscosity ($\text{gm/cm} \cdot \text{sec}$)
 ν - kinematic viscosity (cm^2/sec)
 σ - interfacial tension (dynes/cm)
 $\phi(t)$ - surface age distribution in surface renewal theory

Dimensionless groups

- Re - Reynolds number = (NL^2/ν) where L = tip to tip stirrer length
 Sc - Schmidt number = (ν/D)

- Sh - Sherwood number = (KL/D) where L = tip to tip stirrer length
- We/Fr - ratio of Weber and Froude numbers = $(\Delta d \ g \ L^2 / \sigma)$ where L = interface annulus width

Subscripts

- a - of the aqueous phase
- b - of the bulk phase when used in conjunction with C as concentration
- c - refer to the linear correlation coefficient when used in conjunction with R , otherwise it indicates critical value.
- i - of or at the interface
- o - of the organic phase

Superscripts and other symbols

- t - at time = t
- o - at initial value at $t = 0$
- $()$ - aqueous phase concentration
- $()_i$ - interfacial concentration
- $\overline{()}$ - organic bulk concentration
- $\overline{\quad}$ - organic phase species. Formulae with no overline are for species in the aqueous phase or at the interface when subscripted i
- $[]$ - activity as defined in the context
- (A) - FeCl_3 or FeCl_4^- concentration
- $\overline{(B)}$ - TOAHCl concentration
- $(B)_i$ - $(\text{TOAHCl})_i$ or $(\text{TOAH}^+)_i$ concentration

Chemical names

Alamine 336	- Tri-n-alkylamine ⁽¹⁾
Aliquat 336	- Methyl-tri-n-alkylamine ⁽¹⁾
BTHAHC1	- bis(3,5,5-trimethylhexyl) ammonium chloride
DDA	- di-n-decylamine
DDAS	- di-n-decylamine sulphate
DEHA	- bis(2-ethylhexylamine)
HDEHP	- di(2-ethylhexyl) phosphoric acid
KELEX 100	- chelating extractant ⁽²⁾
LA-1	- Amberlite LA-1 ⁽³⁾
LA-2	- Amberlite LA-2 ⁽³⁾
LIX 64N	- chelating extractant ⁽²⁾
PrJM-T	- Primene JM-T ⁽³⁾
Solvesso 100	- Aromatic diluent ⁽⁴⁾
TOA	- Tri-n-octylamine
TOAHC1	- Tri-n-octylamine hydrochloride
TOAS	- Tri-n-octylamine sulphate
TBP	- Tributyl phosphate
TiOA	- Tri-iso-octylamine
TLA	- Tri-n-laurylamine (tri-n-dodecylamine)
TLAHC1	- Tri-n-laurylamine hydrochloride

-
- (1) General Mills Chemicals, Inc.
 (2) Ashland Chemical Co.
 (3) Rohm and Haas Co.
 (4) Exxon Co.

APPENDIX ADETAILED CELL DRAWINGS

- A-1 The stirred cell (Section AA')
- A-2 The stirred cell (Section BB')
- A-3 The stirred cell (Section CC')
- A-4 Detail of the bottom section AA'
- A-5 Ring baffle
- A-6 Upper stirrer
- A-7 Central baffle
- A-8 Vertical baffles
- A-9 Lower stirrer

COMPONENTS OF LEWIS CELL

1. Glass ring
2. Top plate (stainless steel) (Fig. A-1 to A-3)
3. Top plate
4. Bottom plate (stainless steel)
5. Bottom plate
6. Upper stirrer (Fig. A-6)
7. Lower stirrer (Fig. A-9)
8. Central baffle (Fig. A-7)
9. Glass tube support
10. Vertical baffles (Fig. A-8)
11. Ring baffle (Fig. A-5)
12. Sampling/filling plugs
13. Base plate (steel)
14. Water jacket (perspex)
15. Water from thermostat
16. Water to thermostat
17. Stirrer bearing/seal
18. Bearing
19. Stopcock (glass)
20. Plug
21. Ring
22. Support (stainless steel)
23. Plug
24. Plug
25. Vertical baffle support (rod)
26. Plug
27. Sampling lower phase (continuous reading), (glass tube)
28. Plug
29. Sampling upper phase (continuous reading), (glass tube)

NOTE: ALL PARTS ARE MADE OF PTFE UNLESS OTHERWISE STATED

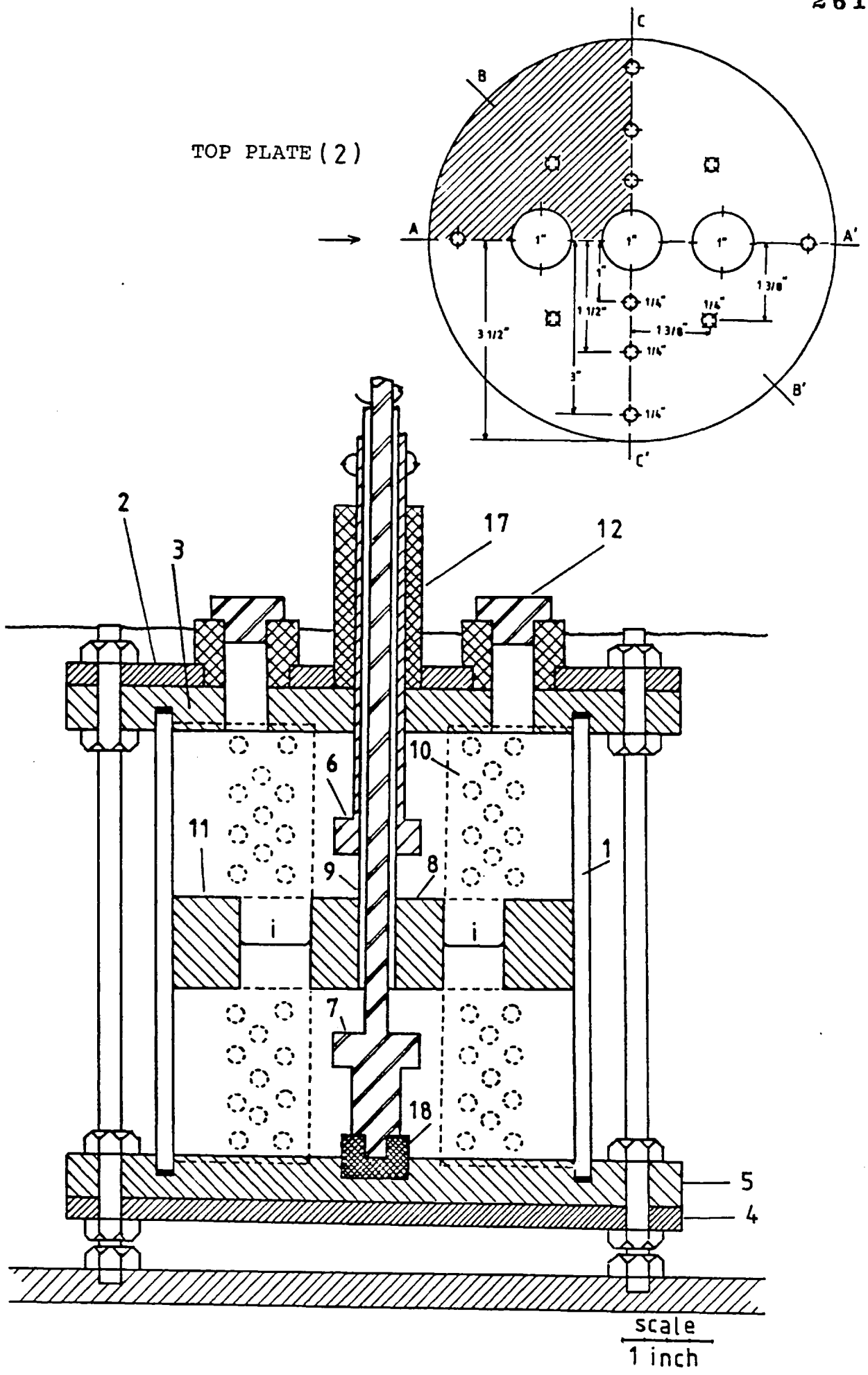


FIGURE A.1. THE STIRRED CELL (SECTION ALONG AA').

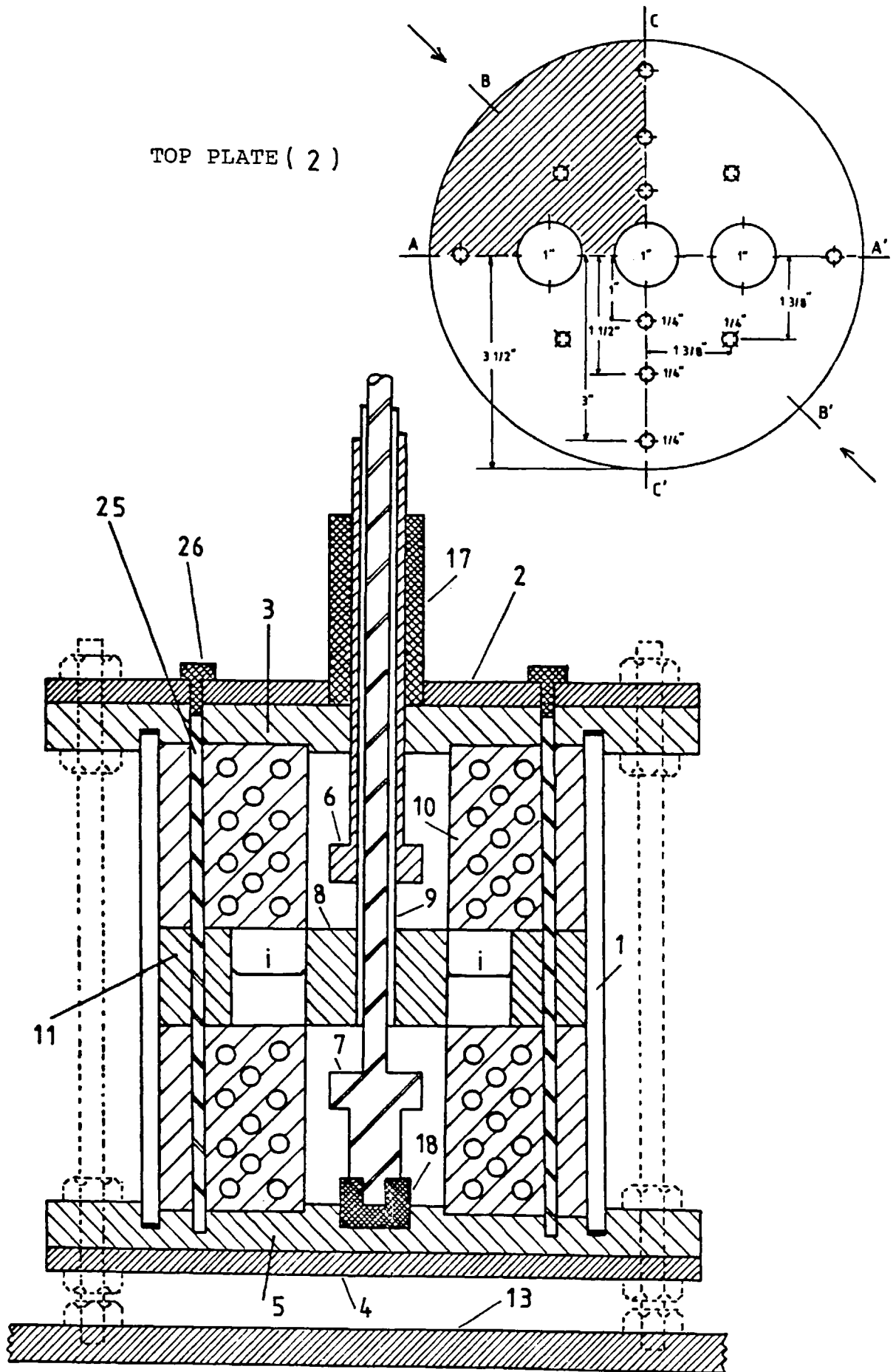


FIGURE A.2. THE STIRRED CELL (SECTION ALONG BB').

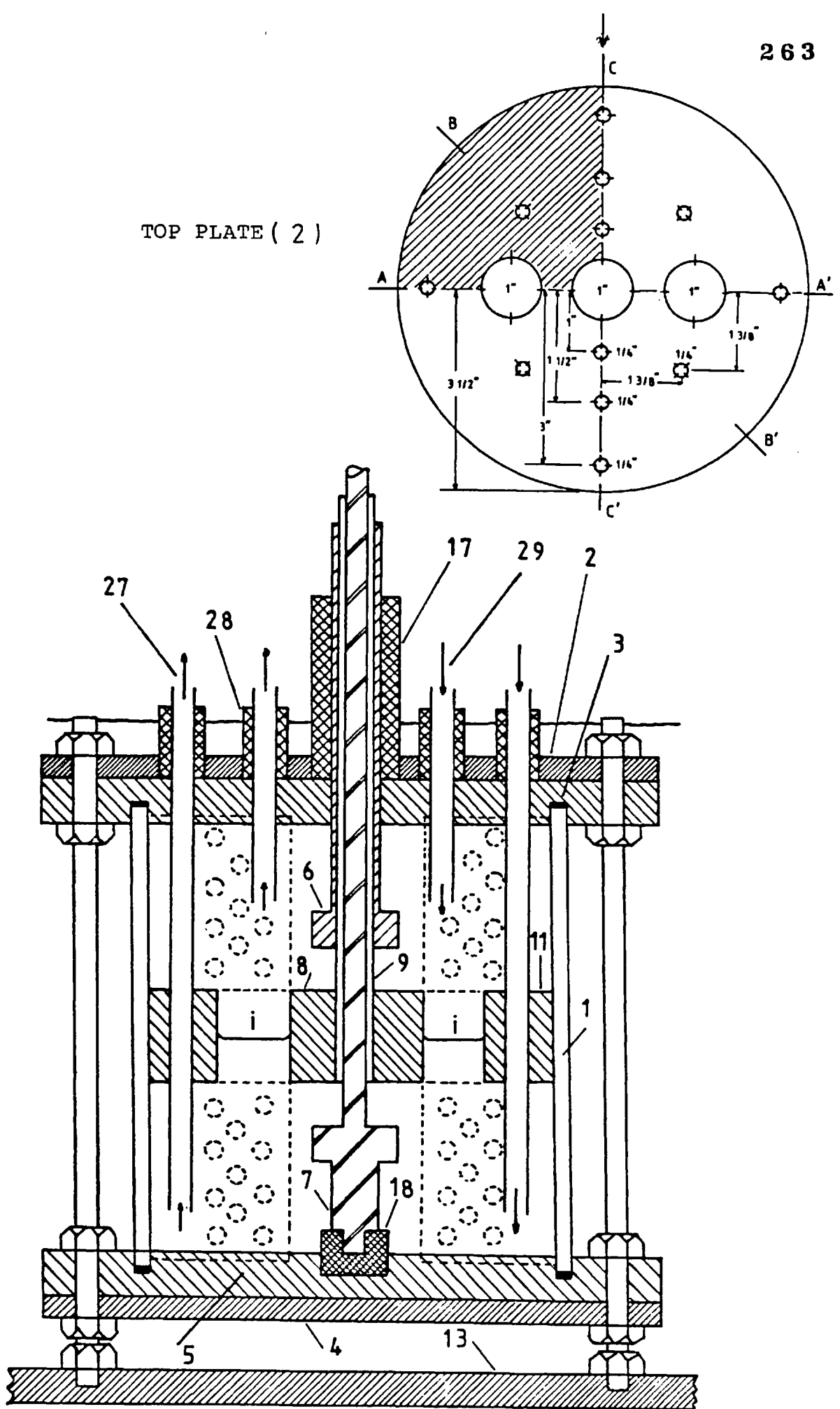


FIGURE A.3. THE STIRRED CELL (SECTION ALONG CC').

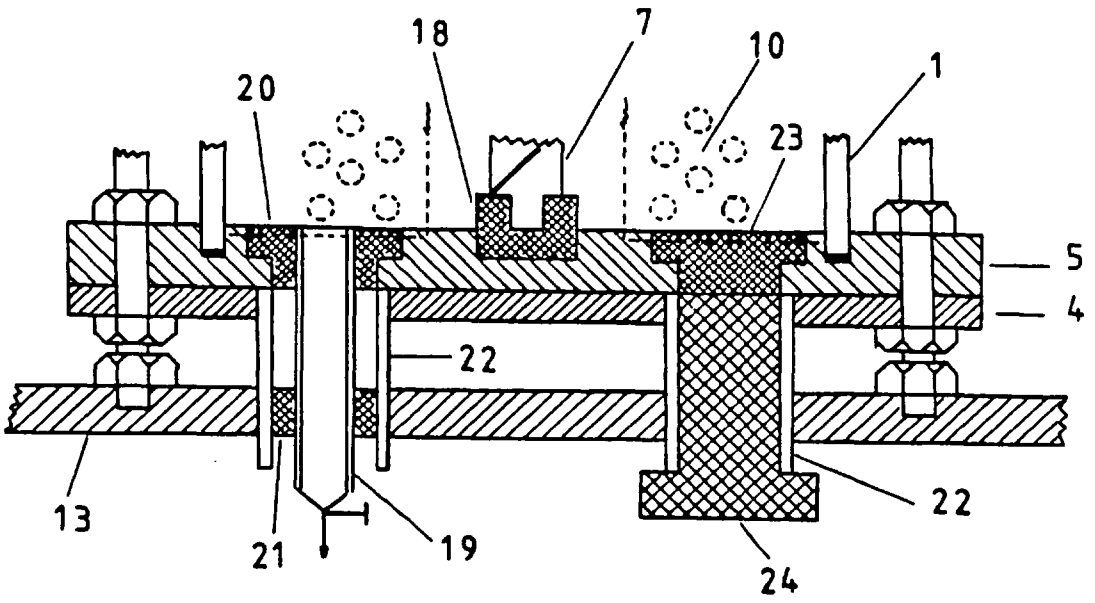


FIGURE A.4. DETAIL OF THE BOTTOM SECTION AA'

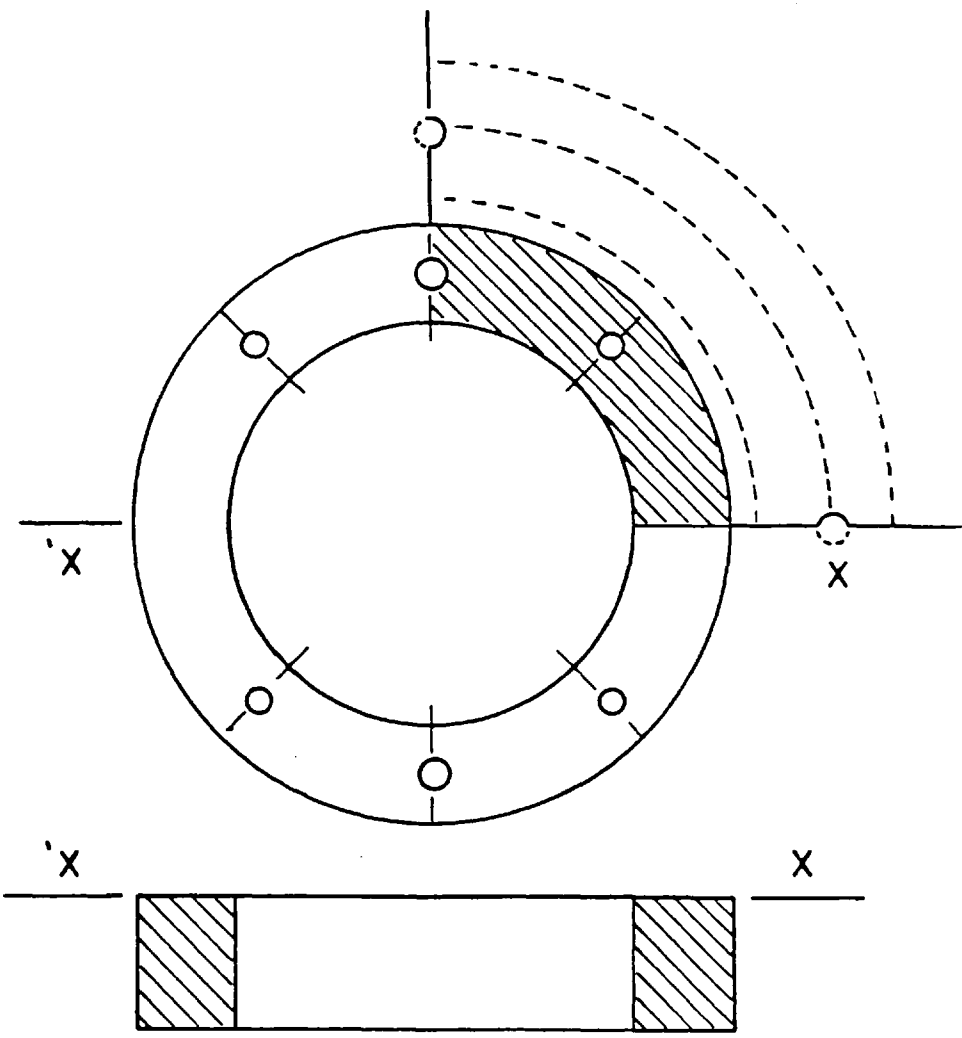


FIGURE A.5. RING BAFFLE (11)

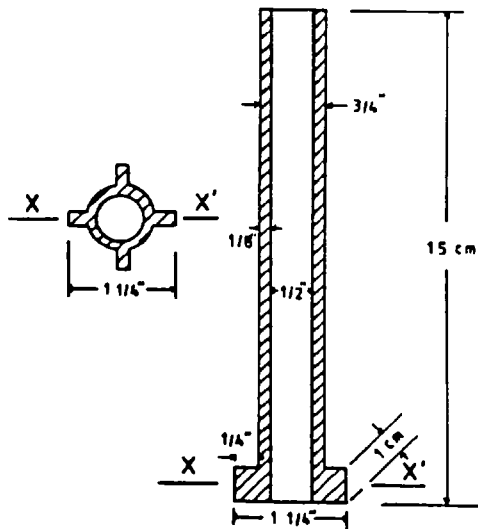


FIGURE A.6. UPPER STIRRER.
(6)

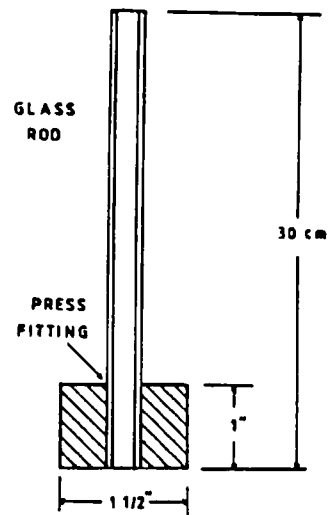


FIGURE A.7. CENTRAL BAFFLE
(8)

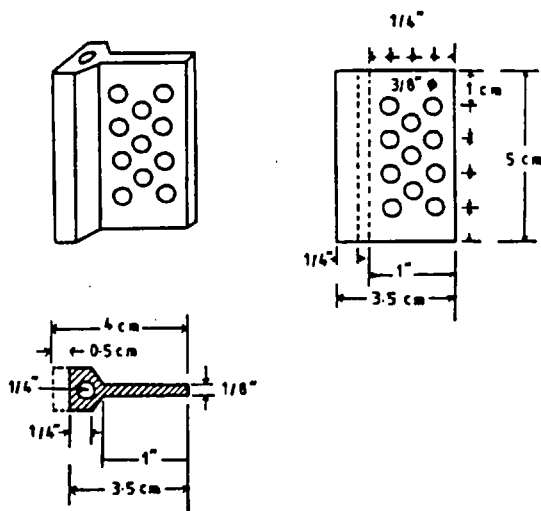


FIGURE A.8. VERTICAL BAFFLES
(10)

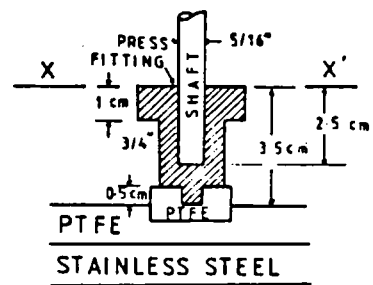


FIG. A.9. LOWER STIRRER
(7)

APPENDIX B-1
VAPOUR PRESSURE OSMOMETRY

- B.1.2 Materials
- B.1.3. Experimental technique
- B.1.4. Calibration
- B.1.5. Molecular weight of TOA
- B.1.6. TOAHCl
- B.1.7. Fe(III) - TOAHCl complexes

B.1. VAPOUR PRESSURE OSMOMETRY

It is known that aggregation of the extractant plays an important role in the kinetics of the extraction process. Therefore in order to make a proper interpretation of the kinetic data, molecular weights of TOA and TOAHCl were determined by vapour pressure osmometry (v.p.o.). Monomer and dimer concentrations and the dimerization constant were calculated by using the experimental data.

The technique of v.p.o. is very simple; it comprises essentially of the measurement, via a Wheatstone bridge circuit, of the temperature difference developed between two identical thermistor beads, suspended in an accurately thermostated chamber saturated with solvent vapour, when one of them carries a drop of pure solvent and the other a drop of a solution of known concentration of the substance under investigation. The difference in temperature results from the net condensation of solvent onto the bead carrying the solution with respect to that carrying the pure solvent, and it is manifested experimentally as an electrical bridge output, which rises to a pseudo-equilibrium value which is maintained until dilution of the drop of solution becomes appreciable.

B.1.1. Theory

For a solution obeying Raoult's Law, the lowering of the solvent vapour pressure (p) due to a solute of mole fraction concentration x_2 is given by

$$p = p_1^{\circ} \cdot x_2 \quad (\text{B.1.1.})$$

where p_1° is the vapour pressure of the pure solvent.

If the solvent is assumed to behave ideally

$$\frac{1}{\bar{p}} \frac{dp}{dT} = \frac{\Delta H_v}{RT^2} \quad (\text{B.1.2.})$$

where H_v = enthalpy of vapourization

R = gas constant

T = absolute temperature

A v.p.o. operates on the principle of the solution drop temperature being raised by condensation of solvent vapour until the vapour pressure of the solution is equal to the vapour pressure of the pure solvent.

When temperature is increased from T_1 to T_2 , integration of equation (B.1.2.)

$$\int_{p_1}^{p_2} dp = \frac{\bar{p} \Delta \bar{H}_v}{R \bar{T}^2} \int_{T_1}^{T_2} dT$$

gives

$$\Delta T = \frac{RT^2}{\bar{p} \Delta \bar{H}_v} \cdot \Delta p \quad (\text{B.1.3.})$$

by substitution of equation (B.1.1.) into (B.1.3.)

$$\Delta T = \frac{RT^2}{\bar{p} \Delta \bar{H}_v} p_1 x_2$$

or $\Delta T = K_1 x_2$

but $\Delta T = K_2 V$

where V is the v.p.o. bridge output (mV)

by substitution

$$x_2 = \frac{K_2 V}{K_1} \quad (\text{B.1.4.})$$

In dilute solutions

$$x_2 = \frac{C}{M_2^*} \times \frac{M_1^*}{1000} \quad (\text{B.1.5.})$$

where C is the solute concentration in g/kg, M_1^* is the solvent molecular weight and M_2^* the solute molecular weight.

Combining equations (B.1.4.) and (B.1.5.)

$$\frac{V}{C} = \frac{K}{M_2^*} \quad (\text{B.1.6.})$$

where K is an empirical constant dependent on the temperature, solvent and instrument characteristics.

For non-Raoultian solutions a power series may be used to correlate the data

$$\frac{V}{C} = \left(\frac{V}{C} \right)_{C=0} \cdot (1 + AC + BC^2 + \dots) \quad (\text{B.1.7.})$$

where, A , B , etc. are the second, third, etc., virial coefficients.

The intercept at $C = 0$ of a plot of V/C against C gives the value of $(V/C)_{C=0}$. Since all solutions approach Raoultian behaviour at low solute concentrations, the value of $(V/C)_{C=0}$ may be used in equation (B.1.6.) to give a value of K/M_2^* .

K is an empirical constant, and it must be determined by calibrating the instrument. This is done by determining $(V/C)_{C=0}$ for a solute which behaves ideally in the chosen solvent. The calibration is carried out at the same temperature as that to be used for the unknown determinations. The value of K is then given by

$$K = \left(\frac{V}{C} \right)_{C=0} \cdot M_S \quad (\text{B.1.8.})$$

where M_S is the molecular weight of the standard solute.

B.1.2. Materials

(i) Benzil

Benzil (M.W. 210.23) purissimo (Koch Light product) was weighed and dissolved in a weighed amount of toluene A.R. (sulfur free) to form a solution with a known concentration expressed in g solute/kg solvent and molality. Several solutions were prepared in this fashion (always weight solute/weight solvent).

(ii) TOA

TOA (Fluka product) solutions were prepared by dissolving weighed amounts of TOA in weighed amounts of Toluene A.R. (sulfur free) to give solutions of known weights of TOA/weights of Toluene.

(iii) Pure TOAHCl (Fluka)

Solid TOAHCl was prepared from TOA (Fluka product) by shaking solutions of TOA in petroleum ether (b.p. 40-60°C) with HCl 0.5 M, followed by recrystallisation, as described in Chapter 5. TOAHCl solutions were prepared by dissolving weighed amounts of solid TOAHCl in weighed amounts of Toluene A.R. (sulfur free) to give solutions of known weights of TOAHCl/weights of Toluene.

(iv) Pure TOAHCl (Eastman-Kodak)

TOAHCl (Eastman-Kodak product) properties are described in Chapter 5. Solutions of known weights of TOAHCl/weights of toluene were prepared as described above.

(v) Practical TOAHCl (Fluka)

TOA (Fluka product) solutions were prepared weight/weight, as described before. These solutions were equilibrated

with equal volumes of 0.5 M HCl. It was assumed that only the monohydrate of TOAHCl was formed. The weight of $\text{TOAHCl} \cdot \text{H}_2\text{O}$ was calculated and concentrations expressed as required.

B.1.3. Experimental Technique

A Hewlett-Packard Vapour Osmometer (v.p.o.) was used for the molecular weight determinations. The bridge output from the v.p.o. was recorded on a LINSEIS Type LS4 recorder, set to give 1 mV full-scale deflection with up to 10 mV back-off available.

In order to maintain thermal stability within the v.p.o., it is necessary to operate the thermostatic chamber of the instrument at least 12°C above ambient. For this reason all measurements were carried out at 37°C.

The instrument was calibrated with benzil and the calibration constant K was determined.

Molecular weight determinations were carried out on solutions described before. The results obtained are presented graphically in Figures B.1.1. to B.1.5. and the numerical values of the results are contained in Tables B.1.1. to B.1.6. All results reported are the average of at least three, and in some cases many more, determinations on each solution.

B.1.4. Calibration

Benzil was chosen as the solute for calibration in this investigation, since it is expected to behave ideally in toluene solution.

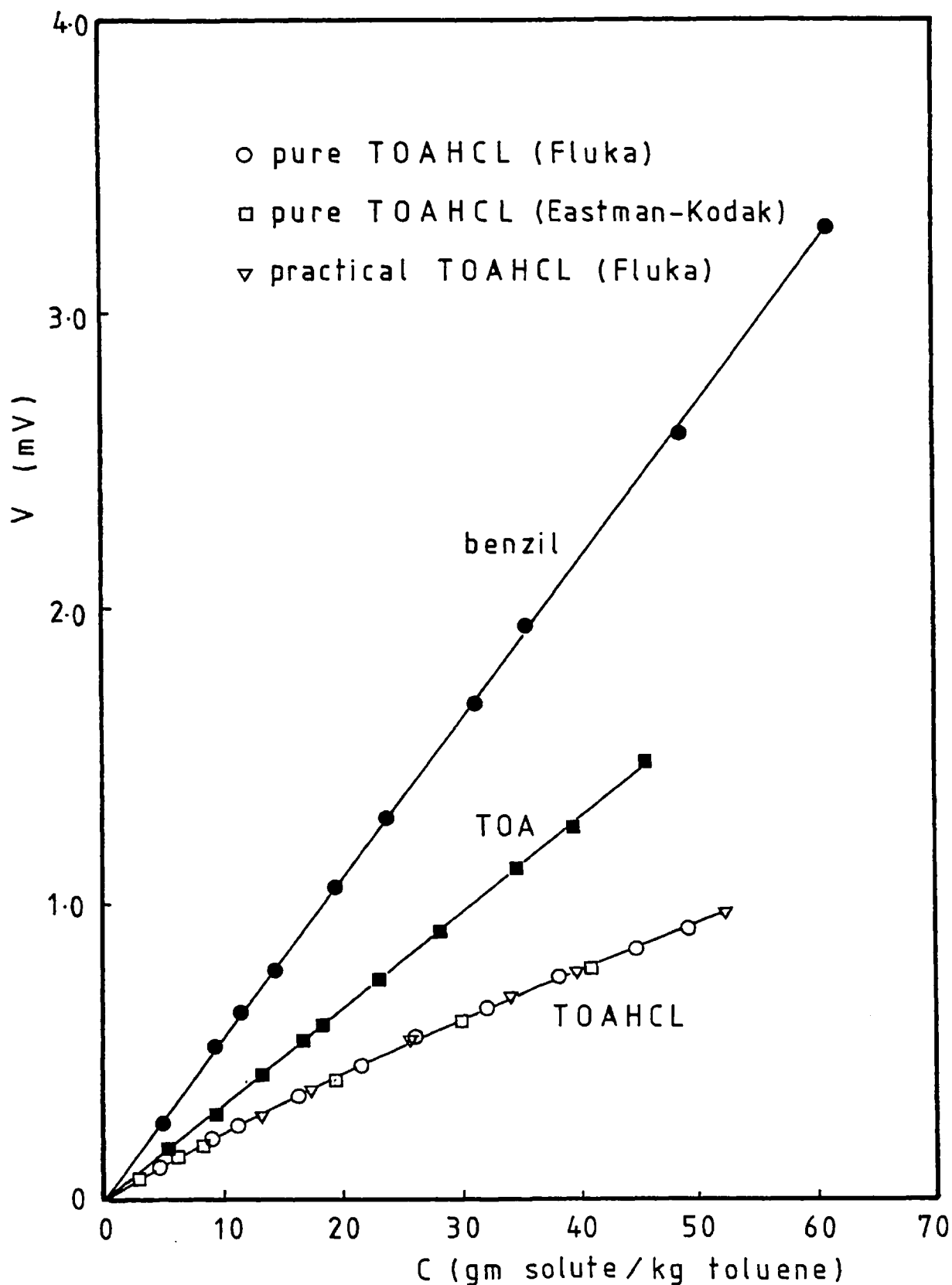


FIG · B-1-1 - V.P.O. BRIDGE OUTPUT AGAINST
SOLUTE CONCENTRATIONS

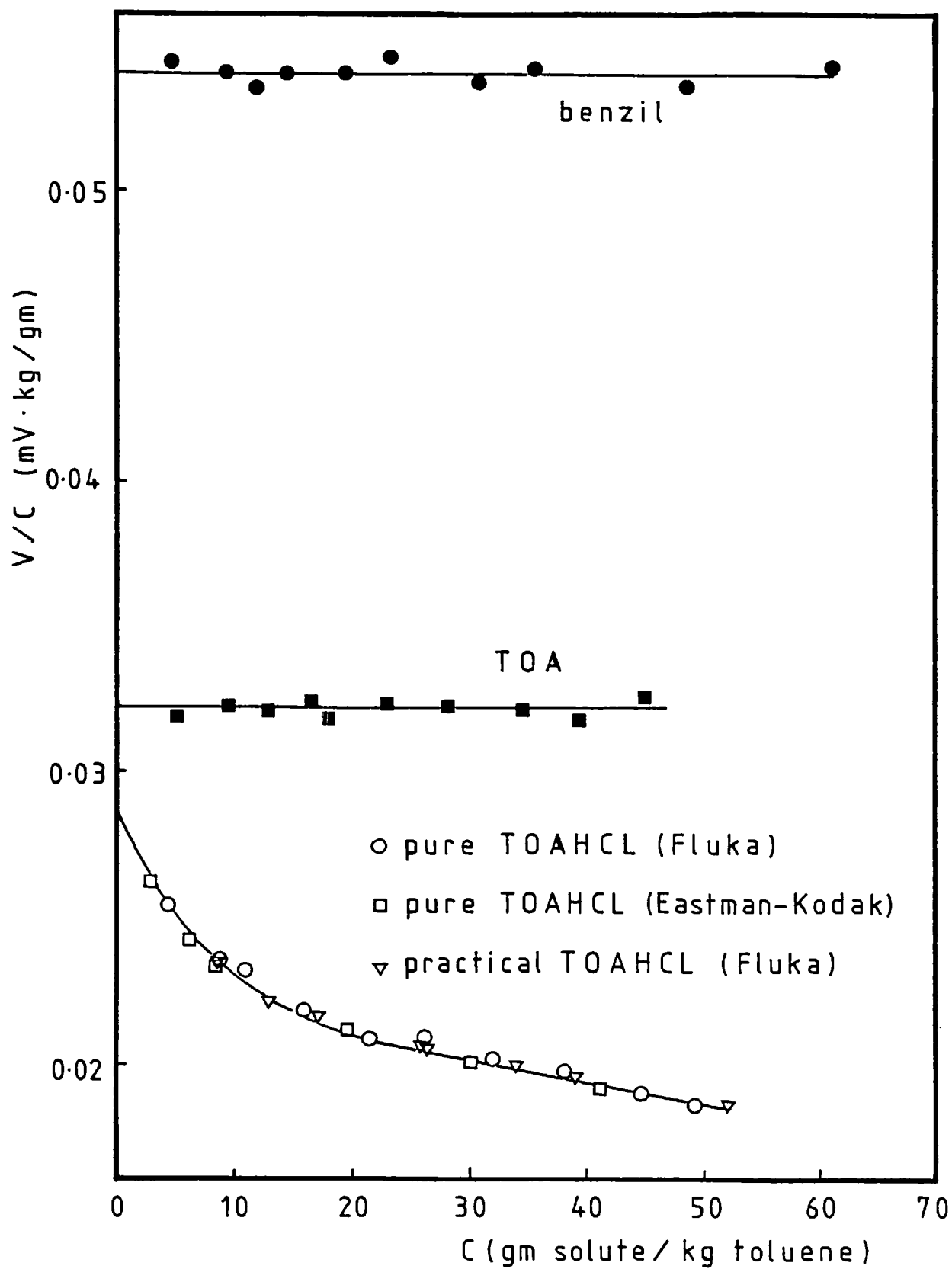


FIG. B-1-2 - V/C AGAINST C FOR VARIOUS SOLUTES

A plot of V/C versus C for benzil in toluene at 37°C is given in Figure B.1.2. Statistical analysis of data presented in Table B.1.1. gave the following results:

$$\text{slope} = 0.0000 \text{ mV}/(\text{gm}/\text{kg})^2$$

$$\left(\frac{V}{C}\right)_{C=0} = 0.0540 \pm 0.0003 \text{ mV}/(\text{gm}/\text{kg})$$

$$\text{Standard deviation} = 0.000220$$

$$\text{T-ratio (coef/st.dev.)} = 245.20$$

The slope being equal to zero indicates that benzil behaves ideally in toluene. The value of K was calculated using equation (B.1.6.) combined with the obtained value of $(V/C)_{C=0}$ to give

$$K = 11.352 \pm 0.063 \text{ mV/molal}$$

B.1.5. Molecular Weight of TOA(Fluka)

A plot of V/C versus C for TOA in toluene is given in Figure B.1.2. The results lie on a straight line with slope zero, indicating that TOA behaves ideally in toluene solutions and it is unaggregated. The results include both "dry" and "wet" solutions. Apparently the presence of water in the organic phase has no significant effect on the molecular weight determination.

Statistical analysis of the data gave the following results:

$$\text{slope} = 0.0000 \text{ mV}/(\text{gm}/\text{kg})^2$$

$$\left(\frac{V}{C}\right)_{C=0} = 0.0321 \pm 0.0003 \text{ mV}/(\text{gm}/\text{kg})$$

Standard deviation = 0.000220

T-ratio = 145.12

If this value of $(V/C)_{C=0}$ and K , which was calculated before, are substituted into equation (B.1.6.), the molecular weight of TOA is obtained:

$$\text{M.W. TOA} = \frac{11.352 \pm 0.063}{0.0321 \pm 0.0003} = 353 \pm 5$$

This value is in agreement with the theoretical value (353.68) indicating a good degree of purity.

B.1.6. TOAHCl

The V/C versus C plot for solutions of TOAHCl in toluene is shown in Figure B.1.2. The points lie on a curve which approaches linearity as the solute concentration increases. This type of plot is indicative of highly non-ideal behaviour.

The behaviour of practical and pure TOAHCl are compared in Figure B.1.1. to B.1.4. Apparently, the results show no significant difference, indicating that TOAHCl from the different sources behaves similarly. Another feature of the results is that water in the organic phase has a negligible effect in the aggregation process. The agreement of the results for pure TOAHCl (Fluka and Eastman-Kodak) and practical TOAHCl can be considered reasonable and all the results were combined to calculate the dimerization constant.

An empirical relationship relating molal and molar concentration was derived:

$$m = 1.1875 M$$

(B.1.9.)

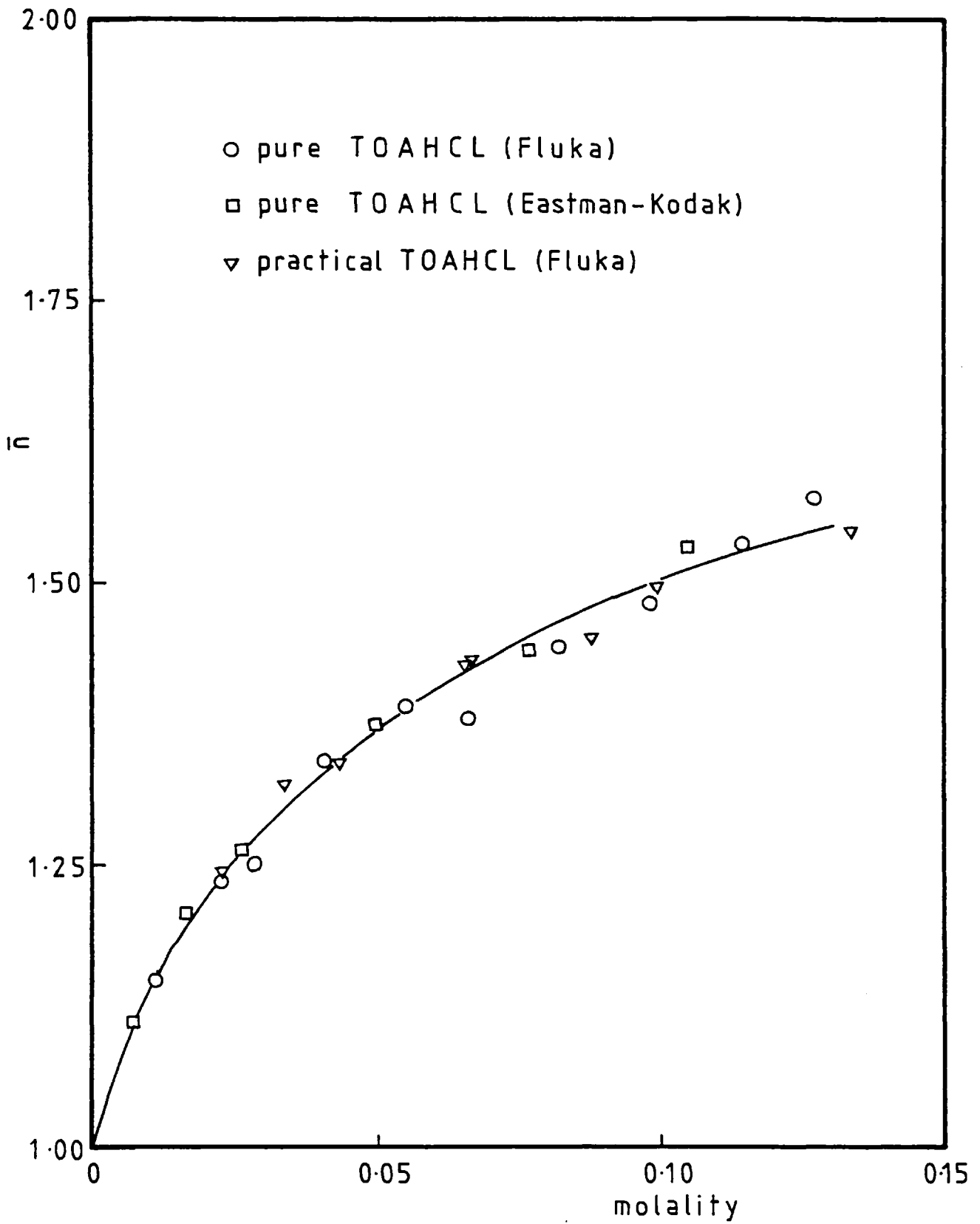


FIG. B-1-3 - COMPARISON OF $\bar{n}$ VALUES FOR
DIFFERENT TOAHCL

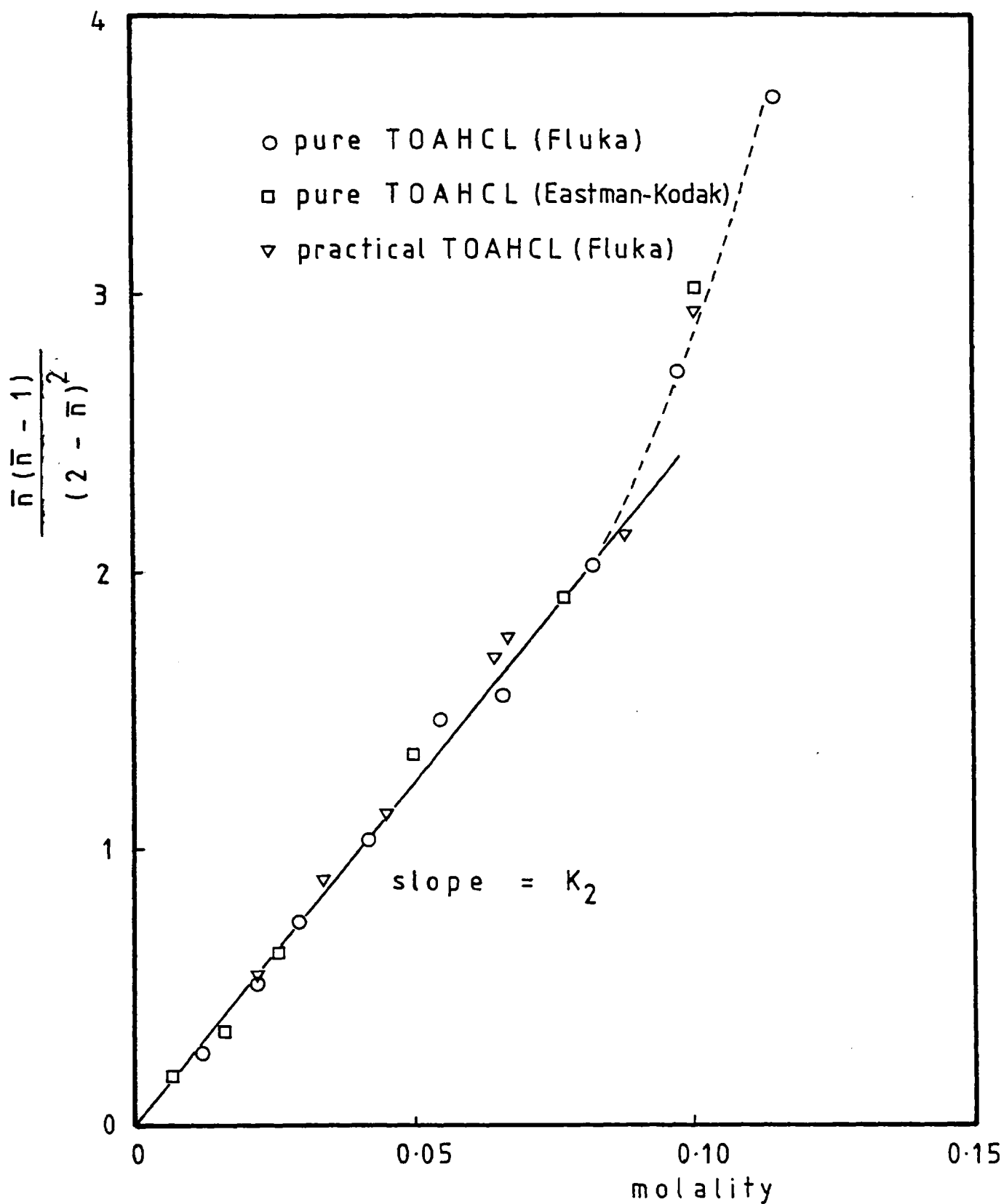


FIG. B-1-4- CALCULATION OF THE DIMERISATION
CONSTANT OF TOAHCL

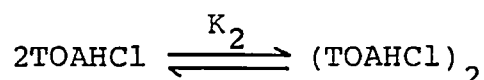
This relationship could be applied equally well to solutions of TOA and TOAHCl in toluene.

Non ideal behaviour of long chain amine salts in many solvents is generally attributed to aggregation of the salts into dimers and higher polymers. Previous works on this type of system have been discussed in Chapter III.

The data obtained for TOAHCl were analysed on the assumption that the non-ideal behaviour was due to aggregation. The apparent molecular weight was calculated by introducing each measured V/C value into equation (B.1.6.). Dividing the apparent molecular weight by the monomer molecular weight of TOAHCl gave the average aggregation number $\bar{n}$ for each solution.

The basic assumption is that all the various species in solution behave ideally and the observed non-ideality is due to polymerisation of the solute (the individual polymeric species behave ideally). In order to calculate the dimerization constant, it is assumed that the major species existing in solution are monomers and dimers. The validity of this assumption is demonstrated by the analysis that follows.

The equilibrium reaction is



$$\text{then, } M_2 = K_2 M_1^2$$

where M_2 = molal concentration of dimer

M_1 = molal concentration of monomer

K_2 = dimerisation constant

The total molal concentration of monomers and dimers, M , is given by:

$$M = M_1 + M_2 = M_1 + K_2 M_1^2 \quad (\text{B.1.9.})$$

The total stoichiometric molal concentration of TOAHCl, S , is given by:

$$S = M_1 + 2M_2 = M_1 + 2K_2 M_1^2 \quad (\text{B.1.10.})$$

The average aggregation number $\bar{n}$ is defined as the total stoichiometric concentration divided by the total concentration of monomers and dimers:

$$\bar{n} = \frac{S}{M} \quad (\text{B.1.11.})$$

Elimination of M and M_1 from equations (B.1.9.), (B.1.10) and (B.1.11) gives the expression:

$$\frac{\bar{n}(\bar{n}-1)}{(2-\bar{n})^2} = K_2 \cdot S \quad (\text{B.1.12})$$

Thus a plot of the function on the L.H.S. of equation (B.1.12) against the stoichiometric molal concentration of TOAHCl should give a straight line passing through the origin, with a slope equal to K_2 . This plot is given in Figure B.1.4. and the numerical data are contained in Tables B.1.3. to B.1.5. The results lie on a straight line, indicating a monomer-dimer equilibrium, up to approximately 0.095 m TOAHCl. At higher concentrations, the line deviates upwards from linearity, indicating the presence of higher polymers. Linear regression analysis of the data gave the following results:

Intercept = -0.0845

Slope = 32.5 ± 1.4

Correlation coefficient = 98.5%

The slope of the line is equal to the dimerisation constant K_2 , of TOAHCl, thus:

$$K_2 = 32.5 \pm 1.4 \text{ m}^{-1} \text{ at } 37^\circ\text{C}$$

or

$$K_2 = 27.3 \pm 1.4 \text{ M}^{-1} \text{ at } 37^\circ\text{C}$$

No value for the dimerisation constant of TOAHCl in toluene was found in the literature. The value is comparable with the reported values for TOAHCl in benzene and TLAHCl in benzene and toluene presented in Table 3.2.1. (Chapter III).

Having established the concentration range over which only monomers and dimers exist, the concentrations of the two species may be calculated from $\bar{n}$ values. From equations (B.1.9.) and (B.1.11)

$$\bar{n} = \frac{S}{M_1 + M_2}$$

From equation (B-1-10):

$$M_2 = \frac{1}{2} (S - M_1) \text{ and } M_1 = S - 2M_2$$

$$\text{then } \bar{n} = \frac{2S}{S - M_1} = \frac{S}{S - M_2}$$

$$\text{and } M_1 = \frac{S(2 - \bar{n})}{\bar{n}} \quad M_2 = \frac{S(\bar{n} - 1)}{\bar{n}} \quad (\text{B.1.13})$$

Calculated monomer and dimer concentrations are given in Table B.1.6. and the results plotted in Figure B.1.5. The concentrations have been changed from molal to molar so that they are compatible with the solvent extraction results discussed in Chapter VI. Examination of Figure B.1.5. shows that up to 0.095 M the log of monomer and dimer concentration ($\log M_1$ or $\log M_2$) increase linearly with $\log S$. The two lines intercept at

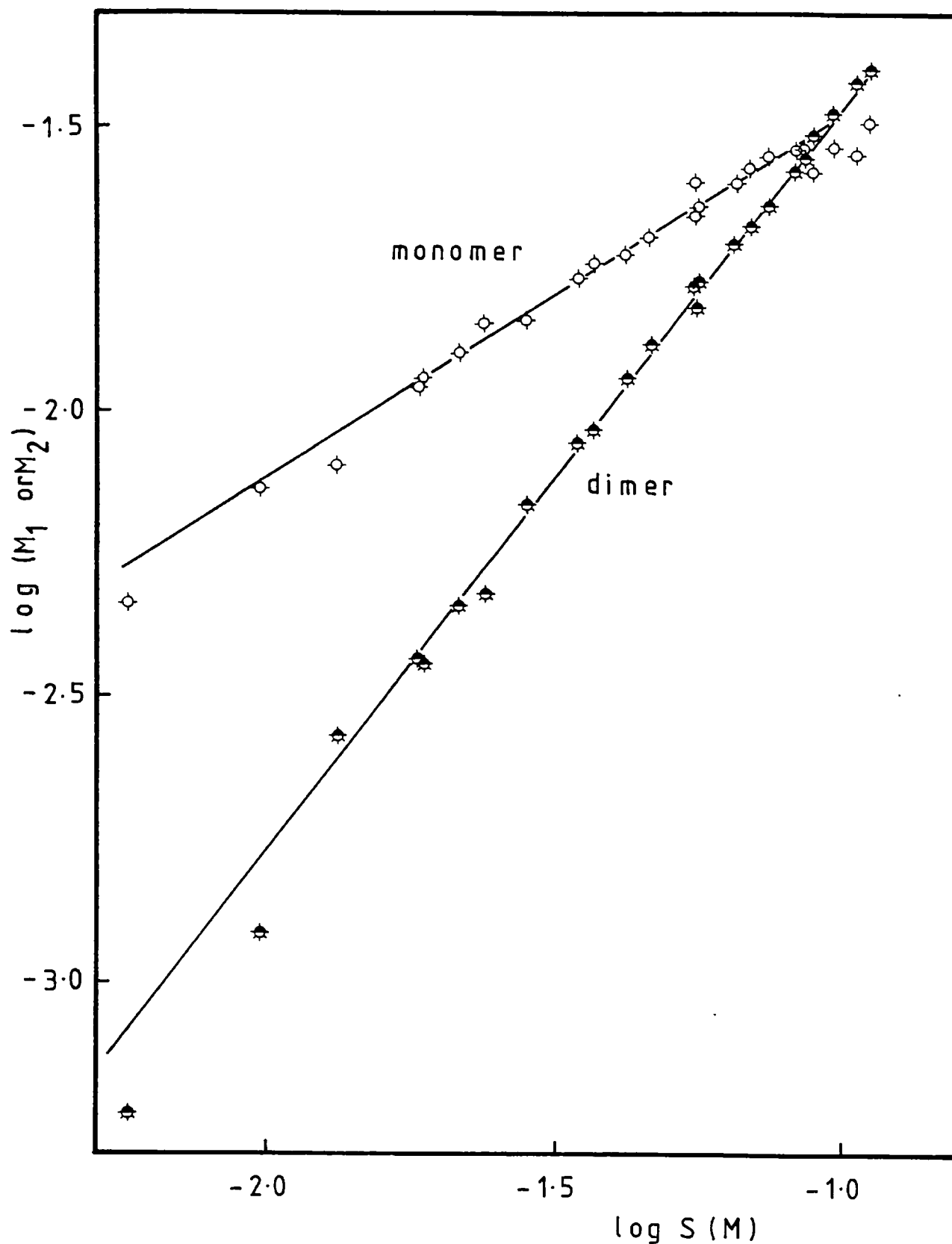


FIG. B-1-5 - VARIATION OF THE CONCENTRATION OF MONOMERS AND DIMERS IN TOAHCL SOLUTIONS.

this value of $\log S$. This is equivalent to a molal concentration of TOAHCl of 0.113, which is lightly greater than the concentration at which deviation was observed in the monomer-dimer equilibrium. At the interception of the lines in Fig. B.1.5., the monomer and dimer concentrations in solution are equal. Thus it appears that higher polymers are not formed until the dimer concentration is approximately equal to the monomer concentration.

Statistical analysis of the results presented in Figure B.1.5. showed that in the range of TOAHCl concentrations where monomer-dimer equilibrium is attained, the concentration of each one can be calculated from the equations:

$$\log M_1 = -0.794 + 0.671 \log (\text{TOAHCl})_M \quad R^2 = 99.6\% \quad (\text{B.1.14})$$

$$\log M_2 = -0.0131 + 1.42 \log (\text{TOAHCl})_M \quad R^2 = 99.8\% \quad (\text{B.1.15})$$

Scibona et al.²²⁴ studied the aggregation of TLAHCl in benzene and found $K_2 = 30 \pm 3$ at 37°C and $K_2 = 50 \pm 5$ at 25°C . The enthalpy of the aggregation was estimated, giving $\Delta H = 8$ kcal. If the same enthalpy is assumed for the present system (which is not unreasonable due to the chemical similarity of both) and the following thermodynamic equation is used

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \quad (\text{B.1.16})$$

a value for K_2 at 25°C is obtained:

$$K_2 = 45 \text{ M}^{-1} \text{ at } 25^\circ\text{C}$$

This value is comparable to the value for K_2 at 25°C for TLAHCl in benzene cited above.

Another way to estimate a value for K_2 at 25°C would be to assume that the free energy of formation of the dimer is independent of temperature in the range $25\text{--}37^\circ\text{C}$, so that the following thermodynamic equation would apply.

$$G_f^\circ = RT \ln K_2 = \text{const.} \quad (\text{B.1.17})$$

This assumption is rather crude and may not give good approximation. However, using equation (B.1.17) a value for K_2 is obtained

$$K_2 = 31 \text{ M}^{-1} \text{ at } 25^\circ\text{C}$$

B.1.7. Fe(III) - TOAHCl Complexes

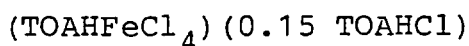
Solutions of TOAHCl in toluene (of known concentrations) were equilibrated with 0.25 M FeCl_3 in 10 M Cl^- ($1 \text{ M HCl} + 9 \text{ M LiCl}$). The organic solutions were analysed for Fe(III) by a spectrophotometric method described in Chapter V and chloride, which was stripped with 6 M HNO_3 , by Volhard's method. The range of TOAHCl concentrations varied from 0.005 M to 0.1 M . In this range of concentrations it was found that the molar ratio of organic Fe to TOAHCl was

$$\text{Fe} : \text{TOAHCl} = 0.87 : 1$$

whereas the molar ratio organic Cl to organic Fe was

$$\text{Cl} : \text{Fe} = 4.11 : 1$$

Then, the Fe(III)-TOAHCl complex under these conditions could be represented by the formula:



Similarly, the same TOAHCl solutions were equilibrated with 2.5×10^{-4} M FeCl_3 in 1 M HCl and the organic and aqueous solutions analysed for Fe(III). The distribution ratio (D_{Fe}) was calculated in each case and the results plotted in a graph of $\log D_{\text{Fe}}$ against $\log \text{TOAHCl}$, which gave a straight line with slope 1.74. This result together with spectrophotometric¹⁹⁶⁻¹⁹⁸ and Raman spectroscopy¹⁹⁹ studies indicated that the Fe(III)-TOAHCl complex, under these conditions, could be represented by the formula:



Based on these formulae the concentrations of the Fe(III)-TOAHCl complex were calculated, as required.

The idea was to determine an aggregation constant in the same way as TOAHCl.

Attempts to calculate average molecular weights using v.p.o. were unsuccessful. At first the results were very scattered and unsuitable for this type of calculation (a high degree of accuracy is required in order to obtain any meaningful aggregation constant) and later the equipment stopped behaving properly. Apparently the thermistor beads were corroded by the organic solutions and the equipment put out of action.

In the present kinetic study the concentration of Fe(III) in the organic phase was kept below 10^{-3} M. Under these conditions it seems reasonable to assume that the Fe(III)-TOAHCl complex is unaggregated.

Monhemius¹¹⁶ studied the aggregation of Co(II)-TOAHCl complexes in benzene and found that at low Co(II) concentrations the organic complex was mostly unaggregated, which gives some support to the assumption above.

TABLE B.1.1. V.P.O. results for benzil

c (gm/Kg)	V (mV)	V/C
4.78	0.26	0.0544
9.45*	0.51	0.0540
11.96	0.64	0.0535
14.26	0.77	0.0540
19.45*	1.05	0.0540
23.63	1.29	0.0546
31.08*	1.67	0.0537
35.64	1.93	0.0542
48.63	2.60	0.0535
61.00	3.31	0.0543

(*) Results for water saturated solutions

TABLE B.1.2. V.P.O. results for TOA

c (gm/Kg)	V (mV)	V/C
5.19	0.165	0.0318
9.16	0.293	0.0320
12.97*	0.415	0.0320
16.56*	0.537	0.0324
18.22	0.580	0.0318
22.90*	0.745	0.0325
28.23	0.913	0.0323
34.64	1.113	0.0321
39.48*	1.250	0.0317
45.52	1.485	0.0326

(*) Results for water saturated solutions.

TABLE B.1.3. V.P.O. results for pure TOAHCl (Fluka)

C (gm/kg)	C (molal)	V (mV)	V/C	App. M.W.	$\bar{n}$	$\frac{\bar{n}(\bar{n}-1)}{(2-\bar{n})^2}$
4.53	0.0116	0.115	0.0254	447	1.146	0.229
8.70	0.0223	0.205	0.0236	481	1.235	0.496
11.04*	0.0283	0.257	0.0233	488	1.250	0.556
16.13	0.0413	0.350	0.0217	523	1.341	1.053
21.50	0.0551	0.450	0.0209	543	1.392	1.476
25.89*	0.0664	0.547	0.0211	537	1.377	1.336
32.19*	0.0825	0.650	0.0202	562	1.441	2.034
38.30	0.0982	0.753	0.0197	577	1.480	2.627
44.71*	0.1146	0.850	0.0190	597	1.532	3.721
49.09	0.1258	0.910	0.0185	613	1.573	4.943

(*) Results for water saturated solutions.

TABLE B.1.4. V.P.O. results for TOAHCl (Eastman-Kodak)

C (gm/Kg)	C (molal)	V (mV)	V/C	App. M.W.	$\bar{n}$	$\frac{\bar{n}(\bar{n}-1)}{(2-\bar{n})^2}$
2.68	0.0068	0.070	0.0261	435	1.114	0.162
6.09*	0.0156	0.147	0.0241	470	1.206	0.394
8.03	0.0258	0.185	0.0230	493	1.263	0.612
19.42*	0.0498	0.410	0.0211	538	1.378	1.346
29.99	0.0768	0.607	0.0202	560	1.438	1.994
40.86*	0.1047	0.773	0.0189	600	1.538	3.877

(*) Results for water saturated solutions.

TABLE B.1.5. V.P.O. results for practical TOAHCl (Fluka)

C (gm/Kg)	C (molal)	V (mV)	V/C	App. M.W.	$\bar{n}$	$\frac{\bar{n}(\bar{n}-1)}{2-\bar{n}}^2$
8.59*	0.0220	0.200	0.0233	487	1.249	0.551
13.03*	0.0334	0.287	0.0220	515	1.321	0.919
17.18*	0.0440	0.373	0.0217	523	1.340	1.046
25.77*	0.0661	0.525	0.0204	556	1.427	1.856
26.07*	0.0668	0.530	0.0203	556	1.432	1.917
34.36*	0.0881	0.690	0.0201	565	1.449	2.143
39.09*	0.1002	0.760	0.0194	583	1.497	2.941
52.13*	0.1336	0.980	0.0188	603	1.548	4.152

(*) Results for water saturated solutions.

TABLE B.1.6. Monomer and dimer concentrations in TOAHCl, calculated from equation (B.1.13). All data.

S (m)	$\bar{n}$	S (M)	log S	T ₁	log T ₁	T ₂	log T ₂
0.0068	1.119	0.0057	-2.242	0.0046	-2.342	0.0006	-3.235
0.0116	1.146	0.0098	-2.010	0.0073	-2.138	0.0012	-2.913
0.0156	1.206	0.0131	-1.882	0.0077	-2.115	0.0027	-2.563
0.0220	1.249	0.0185	-1.732	0.0111	-1.953	0.0037	-2.433
0.0223	1.235	0.0188	-1.726	0.0116	-1.934	0.0036	-2.444
0.0258	1.263	0.0217	-1.663	0.0127	-1.897	0.0045	-2.344
0.0283	1.250	0.0238	-1.623	0.0143	-1.845	0.0048	-2.322
0.0334	1.321	0.0281	-1.551	0.0145	-1.840	0.0068	-2.167
0.0413	1.341	0.0348	-1.459	0.0171	-1.767	0.0088	-2.053
0.0440	1.340	0.0371	-1.431	0.0182	-1.739	0.0094	-2.027
0.0498	1.378	0.0419	-1.377	0.0189	-1.723	0.0115	-1.939
0.0551	1.392	0.0464	-1.333	0.0203	-1.693	0.0131	-1.884
0.0661	1.427	0.0557	-1.254	0.0224	-1.651	0.0167	-1.778
0.0664	1.377	0.0559	-1.252	0.0253	-1.597	0.0153	-1.815
0.0668	1.432	0.0563	-1.250	0.0223	-1.651	0.0170	-1.770
0.0768	1.438	0.0647	-1.189	0.0253	-1.597	0.0197	-1.706
0.0825	1.441	0.0695	-1.158	0.0270	-1.569	0.0213	-1.672
0.0881	1.449	0.0742	-1.130	0.0282	-1.550	0.0230	-1.638
0.0982	1.480	0.0827	-1.083	0.0291	-1.537	0.0268	-1.572
0.1002	1.497	0.0844	-1.074	0.0284	-1.547	0.0280	-1.553
0.1047	1.538	0.0882	-1.055	0.0265	-1.577	0.0308	-1.511
0.1146	1.532	0.0965	-1.015	0.0295	-1.531	0.0335	-1.475
0.1258	1.573	0.1059	-0.975	0.0288	-1.541	0.0386	-1.414
0.1336	1.548	0.1125	-0.949	0.0329	-1.483	0.0398	-1.400

APPENDIX B-2

CALCULATED VALUES FOR THE DISTRIBUTION OF CHLOROCOMPLEXES
AS A FUNCTION OF CHLORIDE ION CONCENTRATION AND ACTIVITIES
OF LiCl and HCl SOLUTIONS

APPENDIX B-3

DENSITY AND VISCOSITY OF HCl AND LiCl SOLUTIONS.

TABLE B.2.1. Distribution of the chlorocomplexes of Fe(III)
as a function of chloride ion concentration

LiCl (M)*	Fe ³⁺ (%)	FeCl ²⁺ (%)	FeCl ₂ ⁺ (%)	FeCl ₃ (%)	FeCl ₄ ⁻ (%)
0.5	39.6	59.5	0.2	0.7	-
1.0	22.8	72.6	0.6	3.8	0.1
1.5	14.1	73.8	1.1	10.6	0.4
2.0	8.5	67.0	1.5	21.7	1.3
2.5	4.9	54.6	1.7	35.7	3.1
3.0	2.5	39.4	1.7	50.3	6.1
4.0	0.5	15.1	1.2	67.8	15.4
5.0	0.1	4.4	0.7	67.0	27.8
6.0	-	1.1	0.3	56.1	42.5
7.0	-	0.3	0.1	41.9	57.7
8.0	-	0.1	-	28.4	71.5
9.0	-	-	-	18.3	81.6
10.0	-	-	-	11.6	88.4

(*) Effective chloride activities presented in Table B.2.7.

$$K_1 = 4.02 \quad K_2 = 0.045 \quad K_3 = 0.339 \quad K_4 = 0.0105 \quad (\text{Ref. 215})$$

TABLE B.2.2. Distribution of the chlorocomplexes of Fe(III)
as a function of chloride ion concentration

LiCl (M)*	Fe ³⁺ (%)	FeCl ²⁺ (%)	FeCl ₂ ⁺ (%)	FeCl ₃ (%)	FeCl ₄ ⁻ (%)
0.5	7.6	87.1	4.9	0.3	-
1.0	3.6	85.0	10.1	1.3	-
1.5	2.0	79.1	15.5	3.3	0.1
2.0	1.2	71.1	20.9	6.6	0.2
2.5	0.7	61.5	25.7	11.6	0.5
3.0	0.4	50.5	29.5	18.6	1.0
4.0	0.1	28.3	31.0	36.8	3.9
5.0	-	12.2	24.5	53.1	10.2
6.0	-	4.1	15.1	59.8	21.0
7.0	-	1.2	7.7	55.6	35.5
8.0	-	0.3	3.4	44.4	52.0
9.0	-	0.1	1.4	32.1	66.5
10.0	-	-	0.5	21.9	77.5

(*) Effective chloride activities presented in Table B.2.7.

$K_1 = 30$ $K_2 = 4.5$ $K_3 = 0.73$ $K_4 = 0.0105$ (Ref. 210.)

TABLE B.2.3. Distribution of the chlorocomplexes of Fe(III)
as a function of chloride ion concentration

LiCl*(M)	Fe ³⁺ (%)	FeCl ²⁺ (%)	FeCl ₂ ⁺ (%)	FeCl ₃ (%)	FeCl ₄ ⁻ (%)
0.5	63.3	0.8	2.0	33.1	0.7
1.0	15.7	0.4	2.2	77.9	3.8
1.5	3.9	0.2	1.5	87.4	7.0
2.0	1.2	0.1	1.0	87.2	10.5
2.5	0.4	-	0.7	84.4	14.5
3.0	0.1	-	0.5	80.2	19.2
4.0	-	-	0.2	68.8	31.0
5.0	-	-	0.1	54.7	45.2
6.0	-	-	-	40.0	60.1
7.0	-	-	-	26.7	73.2
8.0	-	-	-	16.6	83.4
9.0	-	-	-	10.1	89.9
10.0	-	-	-	6.1	93.8

(*) Effective chloride activities presented in Table B.2.7.

$K_1 = 0.033$ $K_2 = 0.224$ $K_3 = 10$ $K_4 = 0.616$ (Ref. 214)

TABLE B.2.4. Distribution of the chlorocomplexes of Fe(III)
as a function of chloride ion concentration

LiCl* (M)	Fe ³⁺ (%)	FeCl ²⁺ (%)	FeCl ₂ ⁺ (%)	FeCl ₃ (%)	FeCl ₄ ⁻ (%)
0.5	97.1	-	2.7	0.2	-
1.0	87.0	-	10.9	1.7	0.3
1.5	68.5	-	23.4	6.1	2.0
2.0	45.1	-	34.6	13.6	6.8
2.5	24.8	-	38.5	21.4	15.2
3.0	11.5	-	34.7	27.0	26.8
4.0	1.7	-	18.9	27.7	51.6
5.0	0.2	-	7.8	20.8	71.2
6.0	-	-	2.8	13.4	83.8
7.0	-	-	0.9	8.0	91.1
8.0	-	-	0.3	4.6	95.1
9.0	-	-	0.1	2.7	97.3
10.0	-	-	-	1.6	98.4

(*) Effective chloride activities presented in Table B.2.7.

$K_1 = 0.001$ $K_2 = 0.2$ $K_3 = 0.04$ $K_4 = 0.0102$ (Ref. 212)

TABLE B.2.5. Distribution of the chlorocomplexes of Fe(III)
as a function of chloride ion concentration

HCl* (M)	Fe ³⁺ (%)	FeCl ²⁺ (%)	FeCl ₂ ⁺ (%)	FeCl ₃ (%)	FeCl ₄ ⁻ (%)
0.5	39.0	60.0	0.3	0.7	-
1.0	21.9	73.1	0.7	4.2	0.1
1.5	13.0	73.2	1.1	12.1	0.5
2.0	7.4	64.2	1.5	25.1	1.7
2.5	3.9	49.3	1.7	41.0	4.0
3.0	1.9	33.2	1.7	55.6	7.7
4.0	0.3	11.2	1.1	69.1	18.3
5.0	-	3.1	0.5	64.7	31.6
6.0	-	0.7	0.2	51.8	47.2
7.0	-	0.2	0.1	38.6	61.0
8.0	-	-	-	26.3	73.6
9.0	-	-	-	17.4	82.5
10.0	-	-	-	12.2	87.8

(*)Effective chloride activities presented in Table B.2.8.

$K_1 = 4.02$ $K_2 = 0.045$ $K_3 = 0.339$ $K_4 = 0.0105$ (Ref. 215)

TABLE B.2.6. Distribution of the chlorocomplexes of Fe(III)
as a function of chloride ion concentration

HCl* (M)	Fe ³⁺ (%)	FeCl ²⁺ (%)	FeCl ₂ ⁺ (%)	FeCl ₃ (%)	FeCl ₄ ⁻ (%)
0.5	51.0	48.6	0.1	0.2	-
1.0	29.0	68.5	0.5	2.0	-
1.5	16.9	74.4	0.9	7.6	0.3
2.0	9.4	68.9	1.4	19.2	1.1
2.5	4.7	54.0	1.7	36.4	3.2
3.0	2.1	35.7	1.7	53.5	7.0
4.0	0.3	10.9	1.1	69.2	18.6
5.0	-	2.7	0.5	63.6	33.2
6.0	-	0.6	0.2	50.4	48.8
7.0	-	0.1	0.1	36.2	63.5
8.0	-	-	-	24.3	75.6
9.0	-	-	-	15.5	84.5
10.0	-	-	-	9.6	90.4

(*) Effective chloride activities presented in Table B.2.9.

(Equation 3.6.10)

$$K_1 = 4.02 \quad K_2 = 0.045 \quad K_3 = 0.339 \quad K_4 = 0.0105 \quad (\text{Ref. 215})$$

TABLE B.2.7. Activity of LiCl¹⁶⁹

LiCl (M)	LiCl (m)	γ_{LiCl}	a_{Cl}	$\log a_{\text{Cl}}$
0.5	0.506	0.739	0.374	-0.427
1.0	1.022	0.776	0.791	-0.102
1.5	1.548	0.845	1.306	0.116
2.0	2.087	0.938	1.959	0.292
2.5	2.636	1.058	2.786	0.445
3.0	3.198	1.217	3.890	0.590
4.0	4.361	1.675	7.311	0.864
5.0	5.58	2.40	13.397	1.127
6.0	6.86	3.56	24.434	1.388
7.0	8.20	5.43	44.463	1.648
8.0	9.62	8.48	81.470	1.911
9.0	11.11	12.93	143.880	2.158
10.0	12.69	19.4	246.037	2.391

TABLE B.2.8. Activity of HCl¹⁶⁹

HCl (M)	HCl (m)	γ_{HCl}	a_{Cl}	$\log a_{\text{Cl}}$
0.5	0.506	0.757	0.383	-0.416
1.0	1.022	0.812	0.830	-0.081
1.5	1.549	0.906	1.403	0.147
2.0	2.085	1.033	2.153	0.333
2.5	2.637	1.193	3.141	0.497
3.0	3.198	1.395	4.457	0.649
4.0	4.358	1.962	8.570	0.933
5.0	5.57	2.83	15.776	1.198
6.0	6.84	4.30	29.444	1.469
7.0	8.18	6.23	50.933	1.707
8.0	9.59	9.42	90.365	1.956
9.0	11.08	13.8	153.109	2.185
10.0	12.67	20.3	233.346	2.368

TABLE B.2.9. Activity of HCl calculated from equation
 (3.6.10), $\log \gamma_{\text{Cl}} = -0.42 + 0.18 (\text{Cl})$

HCl (M)	HCl (m) *	γ_{HCl}	a_{Cl}	$\log a_{\text{Cl}}$
0.5	0.506	0.468	0.237	-0.625
1.0	1.022	0.575	0.588	-0.231
1.5	1.549	0.708	1.097	0.040
2.0	2.085	0.871	1.816	0.259
2.5	2.637	1.072	2.827	0.451
3.0	3.198	1.318	4.215	0.625
4.0	4.358	1.995	8.694	0.939
5.0	5.57	3.020	16.821	1.226
6.0	6.84	4.571	31.266	1.495
7.0	8.18	6.918	56.589	1.753
8.0	9.59	10.471	100.417	2.002
9.0	11.08	15.849	175.607	2.245
10.0	12.67	23.988	303.938	2.483

*Data from Reference 169

TABLE B.3.1. Density and viscosity of HCl solutions²²⁵

HCl (M)	density (gm/cm ³)	viscosity (cS)
0.553	1.0098	1.021
0.975	1.0172	1.035
1.402	1.0246	1.051
1.982	1.0345	1.073
2.424	1.0420	1.091
2.872	1.0494	1.109
4.098	1.0695	1.161
5.047	1.0847	1.204
6.022	1.1000	1.251
7.361	1.1205	1.326
8.745	1.1411	1.423
10.173	1.1614	1.551

TABLE B.3.2. Density and viscosity of LiCl solutions²²⁵

LiCl (M)	density (gm/cm ³)	viscosity (cS)
0.476	1.0099	1.062
0.964	1.0233	1.122
1.462	1.0330	1.187
1.971	1.0463	1.257
2.490	1.0578	1.336
3.021	1.0675	1.426
4.117	1.0910	1.637
5.260	1.1150	1.909
5.850	1.1274	2.076
6.452	1.1399	2.281
7.069	1.1527	2.537
7.699	1.1658	2.846
8.343	1.1791	3.210

APPENDIX C

Extract from a typical computer output for the curve fitting programme (MINITAB).

- C.1. Effect of stirring speed on mass transfer coefficient (isotopic transfer).
- C.2. Effect of temperature on mass transfer rate (isotopic transfer).
- C.3. Effect of aqueous chloride concentration on mass transfer coefficient (isotopic transfer).
- C.4. Effect of TOAHCl concentration on mass transfer coefficient (isotopic transfer).
- C.5. Effect of stirring conditions on initial mass transfer rate.
- C.6. Effect of aqueous chloride concentration and stirring speed on initial extraction rate.
- C.7. Effect of aqueous Fe(III) concentration on initial extraction rate.
- C.8. Effect of TOAHCl concentration on initial extraction rate.
- C.9. Effect of temperature on initial extraction rate.
- C.10. Effect of interfacial area on initial extraction rate.
- C.11. Experimental results for extraction experiments at 4 M chloride.
- C.12. Experimental results for extraction experiments at 7 M chloride.
- C.13. Effect of chloride concentration on initial extraction rate (constant stirring speed).
- C.14. Effect of chloride concentration on initial extraction rate (constant Reynolds number).
- C.15. Experimental results for stripping experiments.
- C.16. Equilibrium distribution ratio of iron as a function of TOAHCl concentration.
- C.17. Equilibrium distribution ratio of iron as a function of chloride concentration.
- C.18. Determination of Cl/Fe ratio. (1 M aqueous Cl^-).
- C.19. Determination of Cl/Fe ratio (3 M aqueous Cl^-).
- C.20. Determination of Cl/Fe ratio (5 M aqueous Cl^-).
- C.21. Determination of Cl/Fe ratio (7 M aqueous Cl^-).

81/01/28. 18.14.49.
 I.C.C.C. NETWORK OPERATING SYSTEM. NOS 1.1-430.11A
 USER NUMBER: UMCJ088
 PASSWORD
 ■■■■■■■■
 TERMINAL: 53,TTY
 RECOVER/ SYSTEM:LIBFILE(MINITAB)
 /MINITAB.
 *** MINITAB II ***
 ?

RUN E-6

? NOTE J. C. SILVA CASSA
 ?

? NOTE
 ? NOTE
 ?
 ? NOTE
 ? NOTE

FITTING SECOND DEGREE POLYNOMIAL TO KINETIC DATA

?
 ? SET C1
 ? 0 5 10 15 20 25 30 35 40 45 50 55 60
 ?

? SET C2
 ? 0.0 4.3 8.7 12.7 16.3 20.0 23.4 27.0 30.2 33.7 36.5 39.2 43.0
 ?

? DEFINE 0.145 INTO K1
 ? MULT C2 BY K1,C3
 ? OMIT ROW WITH 0 IN C1,CORR. ROWS C2-C3,PUT IN C4,C5,C6
 ? DIVIDE C6 BY C4,C7
 ?

PRINT C4-C7				
COLUMN	C4	C5	C6	C7
COUNT	12	12	12	12
ROW				
1	5.	4.3000	.62350	.124700
2	10.	8.7000	1.26150	.126150
3	15.	12.7000	1.84150	.122767
4	20.	16.3000	2.36350	.118175
5	25.	20.0000	2.90000	.116000
6	30.	23.4000	3.39300	.113100
7	35.	27.0000	3.91500	.111857
8	40.	30.2000	4.37900	.109475
9	45.	33.7000	4.88650	.108589
10	50.	36.5000	5.29250	.105850
11	55.	39.2000	5.68400	.103345
12	60.	43.0000	6.23500	.103917

?
 ? NOTE C4=TIME(MIN) C5=ABS X 10+2 C6=CONC (GM/L) × 10³
 ? NOTE C7=CONC/TIME

?

NOBRIEF

?

REGRESS Y IN C7 ON 1 PRED IN C4, ST RES IN C8, PRED Y IN C9

THE REGRESSION EQUATION IS
 $Y = .128 - .0004 X1$

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	.127775	.000903	141.46
X1	C4	-.0004343	.0000245	-17.69

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
 $S = .00147$
 WITH (12- 2) = 10 DEGREES OF FREEDOM

R-SQUARED = 96.9 PERCENT
 R-SQUARED = 96.6 PERCENT, ADJUSTED FOR D.F.

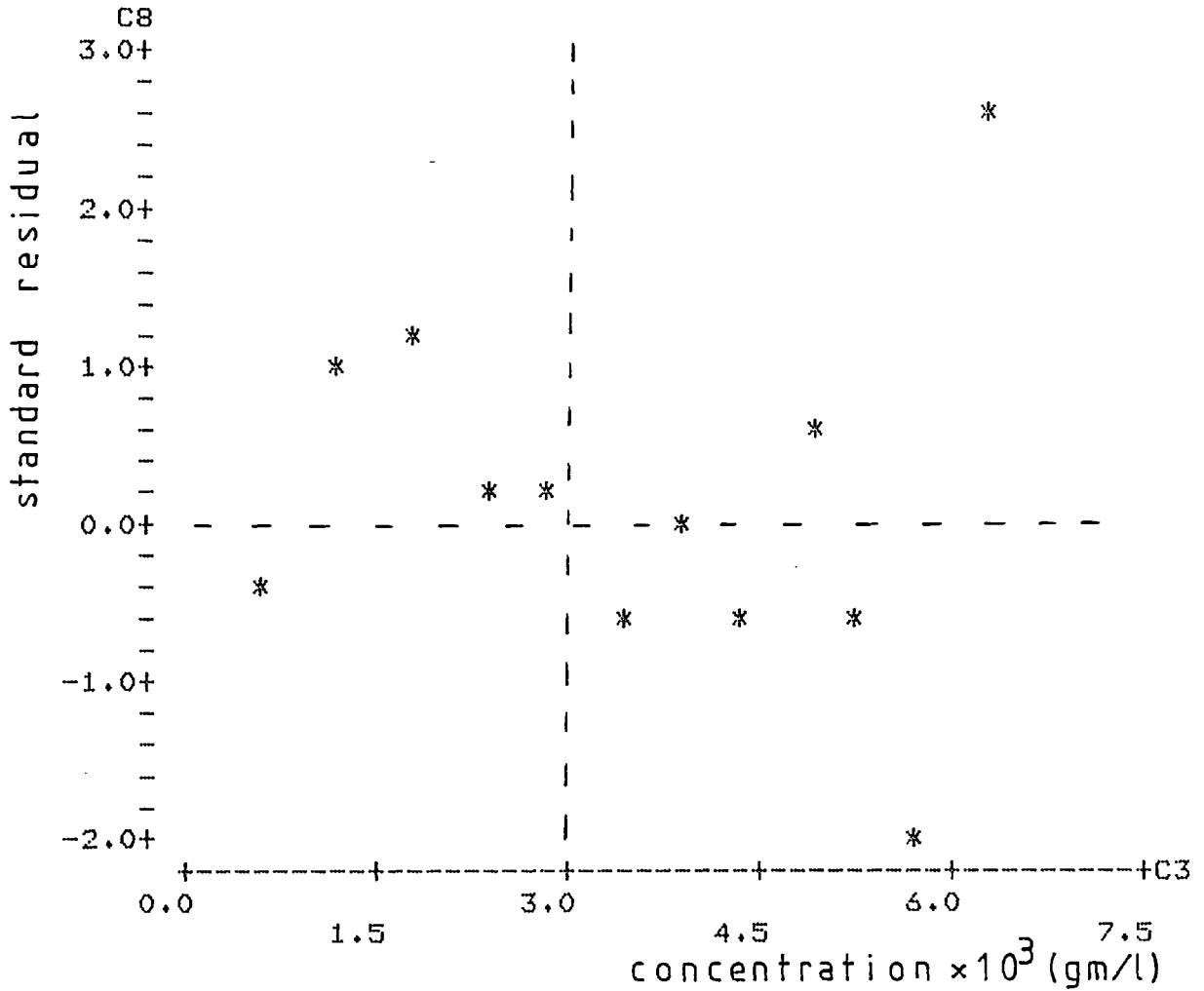
ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	.00067425	.00067425
RESIDUAL	10	.00002154	.00000215
TOTAL	11	.00069579	

ROW	X1 C4	Y C7	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
1	5.0	.12470	.12560	.00080	-.00090	-.73
2	10.0	.12615	.12343	.00070	.00272	2.10R
3	15.0	.12277	.12126	.00060	.00151	1.13
4	20.0	.11818	.11909	.00052	-.00091	-.67
5	25.0	.11600	.11692	.00046	-.00092	-.66
6	30.0	.11310	.11475	.00043	-.00165	-1.17
7	35.0	.11186	.11257	.00043	-.00072	-.51
8	40.0	.10948	.11040	.00046	-.00093	-.67
9	45.0	.10859	.10823	.00052	.00036	.26
10	50.0	.10585	.10606	.00060	-.00021	-.16
11	55.0	.10335	.10389	.00070	-.00054	-.42
12	60.0	.10392	.10172	.00080	.00220	1.78

R DENOTES AN OBS. WITH A LARGE ST. RES.

NOTE PLOTTING RESIDUALS
? PLOT C8 VS C3



? NOTE PLOTTING NORMAL SCORES
? NSCORES OF C8 PUT IN C12
? PLOT C12 VS C8

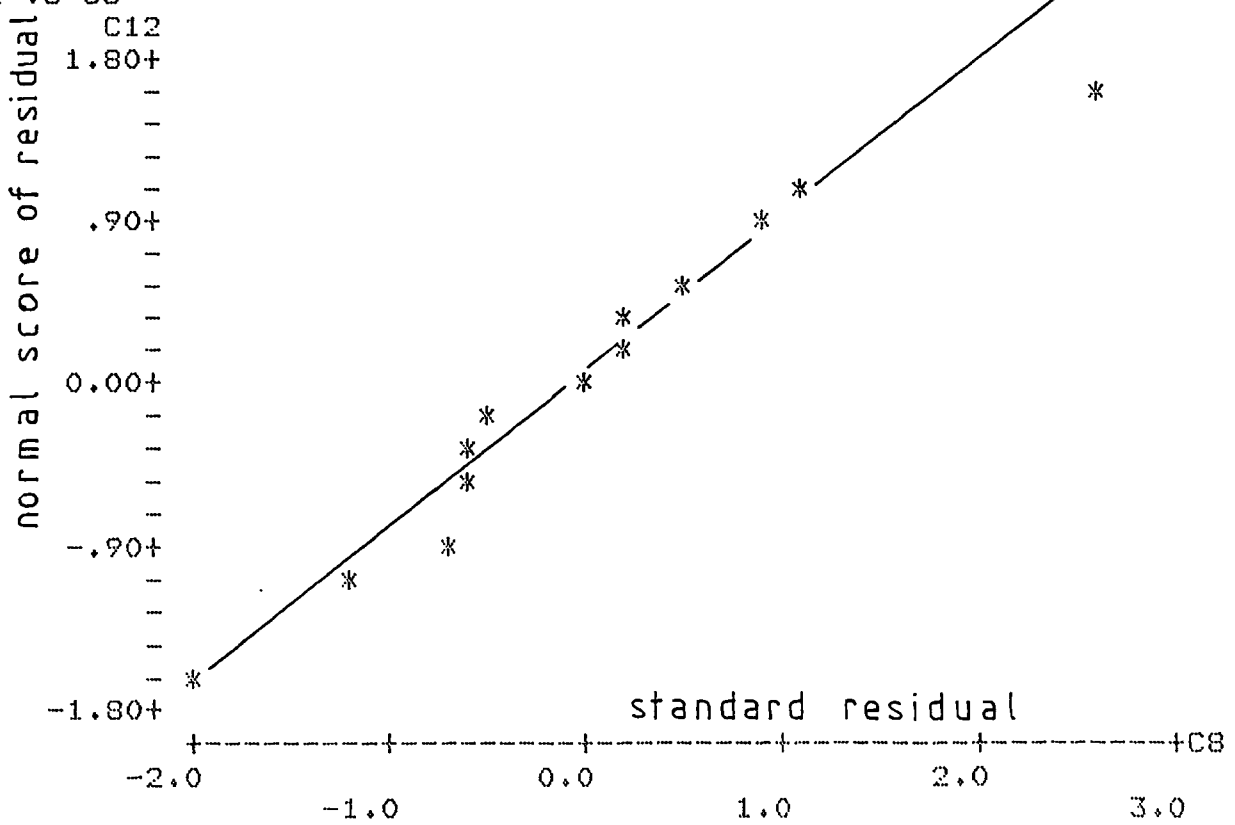
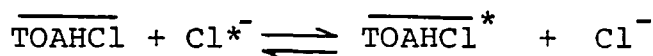


TABLE C.1. Effect of stirring speed on mass transfer coefficient (isotopic transfer)

System:



Transfer:

aqueous $\longrightarrow$ organic

Conditions:

TOAHCl = 0.025 M

HCl = 1 M

$\text{Cl}^{36} = 5 \mu\text{Ci}/500 \text{ ml}$

O=A = 480 ml

Interfacial area = 30 cm^2

Stirring speed A = 0 (contra-rotating stirrers)

Temp = 25°C

Sampling:

0, 5, 10, 15, 20, 25, 30, 40, 50, 60 minutes

Fitted equation:

$$(\text{Cl}^{36}) = a_1 t + a_2 t^2 \quad (\text{Cl}^-) = \text{gmol/l} \times 10^3$$

$t = \text{min}$

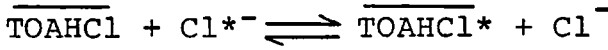
Run	stirring speed (rpm)	a_1	a_2	T-ratio* (a_1)	$R \times 10^3$ ($\frac{\text{gmol}}{\text{l} \times \text{min}}$)	$R \times 10^3$ (cm/sec)
MT-1	150	0.180	-0.0006	33.35	0.180	1.920
MT-2	200	0.219	-0.0007	25.54	0.219	2.336
MT-3	250	0.253	-0.0009	54.80	0.253	2.697
MT-4	250	0.256	-0.0010	45.39	0.256	2.734
MT-5	300	0.318	-0.0014	92.35	0.318	3.392
MT-6	350	0.386	-0.0016	41.95	0.386	4.117

(*) T-ratio = $a_1/\text{ST. DEV.}$

$R_c^2 \geq 0.95$ (R_c = correlation coefficient)

TABLE C.2. Effect of temperature on mass transfer rate
(isotopic transfer)

System:



Transfer:

aqueous $\longrightarrow$ organic

Conditions:

TOAHCl = 0.025 M
HCl = 1 M
 $\text{Cl}^{36} = 5 \mu\text{Ci}/500 \text{ ml}$
O=A = 480 ml

Interfacial area = 30 cm²

Stirring speed = 250 rpm (aq. = org.)
Contra-rotating stirrers

Sampling:

0, 5, 10, 15, 20, 25, 30, 40, 50, 60 minutes

Fitted equation:

$$(\text{Cl}^{36}) = a_1 t + a_2 t^2 \quad (\text{Cl}^{36}) = \text{gmol/l} \times 10^3$$

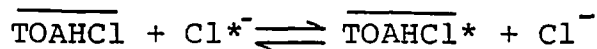
t = min

Run	T(°C)	a ₁	a ₂	T-ratio* (a ₁)	Rx10 ³ ($\frac{\text{gmol}}{\text{l} \times \text{min}}$)	Rate Constant x 10 ³ (min ⁻¹)
MT-7	15	0.248	-0.0008	62.32	0.248	9.92
MT-3	25	0.253	-0.0009	54.80	0.253	10.12
MT-4	25	0.256	-0.0010	45.39	0.256	10.24
MT-8	35	0.259	-0.0010	39.16	0.259	10.36

(*) T-ratio = a₁/ST. DEV.
 $R_c^2 \geq 0.95$

TABLE C.3. Effect of aqueous chloride concentration on mass transfer coefficient (isotopic transfer)

System:



Transfer:

aqueous $\longrightarrow$ organic

Conditions:

$\text{TOAHCl} = 0.025 \text{ M}$

$\text{Cl}^- = 1 \text{ M HCl} + x \text{ M LiCl}$

$\text{Cl}^{36} = 5\text{--}10 \text{ } \mu\text{Ci}/500 \text{ ml}$

$\text{O}=\text{A} = 480 \text{ ml}$

Interfacial area = 30 cm^2

Stirring speed = 250 rpm (aq. = org)

Temperature = 25°C

Contra-rotating stirrers

Sampling:

0, 5, 10, 15, 20, 25, 30, 40, 50, 60 minutes

Fitted equation:

$$(\text{Cl}^-) = a_1 t + a_2 t^2 \quad (\text{Cl}^-) = \text{gmol/l} \times 10^3$$

$t = \text{min}$

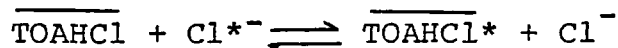
Run	$\text{Cl}^-(\text{M})$	a_1	a_2	T-ratio*	$\text{Rx}10^3$ $\left(\frac{\text{gmol}}{\text{l} \times \text{min}}\right)$	$\text{Rx}10^3$ (cm/sec)
MT-3	1	0.253	-0.0009	54.90	0.253	2.697
MT-4	1	0.256	-0.0010	45.39	0.256	2.736
MT-9	3	0.235	-0.00013	42.76	0.235	2.507
MT-10	5	0.212	-0.0008	33.65	0.212	2.261
MT-11	7	0.164	-0.0005	28.52	0.164	1.749

(*) T-ratio = $a_1/\text{ST. DEV.}$

$$R_c^2 \gg 0.95$$

TABLE C.4. Effect of TOAHCl concentration on mass transfer coefficient (isotopic transfer)

System:



Transfer:

aqueous $\longrightarrow$ organic

Conditions:

HCl = 1M

$\text{Cl}^{36} = 5 \mu\text{Ci}/500 \text{ ml}$

O=A = 480 ml

Interfacial area = 30 cm^2

Stirring speed = 250 rpm (aq. = org.)

Contra-rotating stirrers

Temp = 25°C

Sampling:

0, 5, 10, 15, 20, 25, 30, 40, 50, 60 minutes

Fitted equation:

$$(\text{Cl}^-) = a_1 t + a_2 t^2 \quad (\text{Cl}^-) = \text{gmol/l} \times 10^3$$

$t = \text{min}$

Run	TOAHCl (M)	a_1	a_2	T-ratio* (a_1)	$R \times 10^3$ $\left(\frac{\text{gmol}}{\text{l} \times \text{min}}\right)$	$R \times 10^3$ (cm/sec)
MT-12	0.010	0.103	-0.0004	38.92	0.103	2.747
MT-3	0.025	0.253	-0.0009	54.80	0.253	2.697
MT-4	0.025	0.256	-0.0010	45.39	0.256	2.734
MT-13	0.050	0.490	-0.0018	58.42	0.490	2.613
MT-14	0.100	1.072	-0.0033	66.81	1.072	2.859

(*) T-ratio = $a_1/\text{ST. DEV.}$

$$R_c^2 \geq 0.95$$

TABLE C.5. Effect of stirring conditions on initial mass transfer rate

Conditions: EXTRACTION - Fe(III) = 0.0025 M, TOAHCl = 0.025 M, HCl = 1 M
STRIPPING - Fe(III) = 0.00174 M, TOAHCl = 0.01 M, HCl = 1 M
25°C, Int. area = 30 cm², phase volume O=A = 480 ml (extraction), O=A = 500 ml (stripping)

			$\vec{R} \times 10^8 \text{ (gmol/cm}^2 \cdot \text{min)}$						
direction of stirrers	Baffles	stirring conditions (rpm)	stirring speed (rpm)						
			100	150	200	250	300	350	400
<u>EXTRACTION</u>									
Contra-R	Yes	O=A	3.18	4.24	7.76	(7.65 7.88)	7.57	7.81	9.85
Co-R	Yes	O=A	3.06	4.16	7.93	7.79	7.92	7.62	9.64
Contra-R	No	O=A	6.35	8.17	9.35	17.86	-	-	-
Co-R	No	O=A	7.25	8.98	13.38	-	-	-	-
Contra-R	Yes	O=250 A=variable	4.14	5.79	7.63	7.80	7.75	7.48	8.60
Contra-R	Yes	A=250 O=variable	7.27	7.68	7.85	7.94	7.80	7.71	8.19
<u>STRIPPING</u>									
Contra-R	Yes	O=A	10.06	12.52	15.19	(15.88 15.52)	15.92	15.12	18.69

TABLE C.6. Effect of aqueous chloride concentration and stirring speed on initial extraction rate

Conditions: 25°C, Interfacial area = 30 cm², phase volume O=A = 480 ml
Stirring speed: O = 250 rpm, A at constant Re = 2680
Contra-rotating stirrers

	$\vec{R} \times 10^8 \text{ (gmol/cm}^2 \text{ min)}$								
	Stirring Speed (rpm)								
Cl ⁻	100	200	300	350	400	450	500	550	600
1	18.93	23.45	28.61	-	36.19	-	-	-	-
4	10.16	16.34	24.76	24.53	23.86	23.25	32.40	-	-
7	6.68	10.92	15.34	-	22.06	-	29.81	31.60	30.37
9	4.75	8.39	12.95	-	17.69	-	22.49	-	30.95

Additional experimental conditions:

At 1 M Cl⁻ - Fe(III) = 0.05 M, TOAHCl = 0.1 M

At 4, 7, 9 M Cl⁻ - Fe(III) = 0.001 M, TOAHCl = 0.01 M

TABLE C.7. Effect of aqueous Fe(III) concentration on initial extraction rate

Conditions: HCl = 1 M TOAHCl = 0.01 M Temp = 25°C
 Interfacial area = 30 cm² Phase volume: A=O = 480 ml
 Contra-rotating stirrers A=O = 250 rpm

Fitted equation: $Fe = a_1 t + a_2 t^2$ $Fe = \text{gm/l} \times 10^3$ $t = \text{min}$
 $R_c^2 \geq 0.95$ d.f. ≥ 10

Run	Duration (min)	Fe (III) Mx10 ³	a ₁	a ₂ x 10 ⁴	T-ratio (a ₁)	R x 10 ³ gm 1.min	$\vec{R}$ x 10 ⁸ gmol cm ² .min
E-1	60	0.5	0.0284	-1.35	49.30	0.0284	0.814
E-2	120	1.0	0.0573	-2.06	113.96	0.0573	1.642
E-3	60	1.0	0.0595	-2.75	104.18	0.0595	1.705
E-4	60	1.5	0.0889	-3.60	113.80	0.0889	2.547
E-5	60	2.0	0.118	-4.21	123.97	0.118	3.381
E-6	60	2.21	0.128	-4.34	141.46	0.128	3.668
E-7	60	2.21	0.133	-4.58	100.05	0.133	3.811
E-8	60	2.5	0.147	-4.86	126.82	0.147	4.212
E-9	60	2.5	0.149	-5.36	112.40	0.149	4.269
E-10	60	3.0	0.174	-8.02	117.59	0.174	4.986
E-11	60	4.0	0.239	-11.33	138.84	0.239	6.848
E-12	60	5.0	0.292	-13.59	145.21	0.292	8.367

TABLE C.8. Effect of TOAHCl concentration on initial extraction rate

Conditions: HCl = 1 M Fe(III) = 0.0025 M Temp = 25°C

Interfacial area = 30 cm² Phase volume A=O = 480 ml

Contra-rotating stirrers A=O = 250 rpm

Fitted equation: $Fe = a_1 t + a_2 t^2$ $Fe = \text{gm/l} \times 10^3$ $t = \text{min}$
 $R^2 \geq 0.95$ d.f. ≥ 10

Run	Duration (min)	TOAHCl Mx10 ²	a ₁	a ₂ x 10 ⁴	T-ratio (a ₁)	$R \times 10^3$ gm 1. min	$\bar{R} \times 10^8$ gmol cm ² .min
E-13	60	0.2	0.0342	-1.27	41.79	0.0342	0.980
E-14	60	0.5	0.0833	-3.14	50.56	0.0833	2.387
E-8	60	1.0	0.147	-4.86	126.82	0.147	4.212
E-9	60	1.0	0.149	-5.36	112.40	0.149	4.269
E-15	60	1.5	0.188	-8.79	83.94	0.188	5.387
E-16	60	2.0	0.236	-11.60	114.31	0.236	6.762
E-17	60	2.5	0.267	-13.34	96.16	0.267	7.650
E-18	60	2.5	0.275	-13.23	118.98	0.275	7.880
E-19	60	5.0	0.408	-17.80	104.56	0.408	11.691
E-20	50	10.0	0.561	-21.75	130.58	0.561	16.074

TABLE C.9. Effect of temperature on initial extraction rate

Conditions: HCl = 1 M Fe(III) = 0.0025 M TOAHCl = 0.025 M
 Interfacial area = 30 cm² Phase volume A=O = 480 ml
 Contra-rotating stirrers A=O = 250 rpm

Fitted equation: $Fe = a_1 t + a_2 t^2$ $Fe = \text{gm/l} \times 10^3$ $t = \text{min}$
 $R^2 \geq 0.95$ d.f. ≥ 10

Run	Duration (min)	T (°C)	a ₁	a ₂ x 10 ⁴	T-ratio (a ₁)	$R \times 10^3$ $\frac{\text{gm}}{1. \text{ min}}$	$\bar{R} \times 10^8$ $\frac{\text{gmol}}{\text{cm}^2 \cdot \text{min}}$
E-21	60	15.2	0.119	-9.94	88.70	0.119	3.410
E-22	60	20.4	0.192	-11.98	103.37	0.192	5.501
E-17	60	25.0	0.267	-13.34	96.16	0.267	7.650
E-18	60	25.0	0.275	-13.23	118.98	0.275	7.880
E-23	60	30.1	0.400	-19.07	122.38	0.400	11.461
E-24	40	36.0	0.642	-24.85	145.87	0.642	18.395

TABLE C.10. Effect of interfacial area on initial extraction rate

Conditions: HCl = 1 M TOAHCl = 0.025 M Fe(III) = 0.0025 M

Temp = 25°C Phase volume A=O = 480 ml

Contra-rotating stirrers A=O = 250 rpm

Fitted equation: $Fe = a_1 t + a_2 t^2$ $Fe = \text{gm/l} \times 10^3$ $t = \text{min}$
 $R^2 \geq 0.95$ d.f. ≥ 10

Run	Duration (min)	Area (cm ²)	a_1	$a_2 \times 10^4$	T-ratio (a_1)	$R \times 10^3$ gm 1. min	$\vec{R} \times 10^8$ gmol cm ² .min
E-25	60	20	0.168	-7.53	116.78	0.168	7.320
E-26	60	25	0.231	-11.27	103.42	0.231	7.943
E-17	60	30	0.267	-13.34	96.16	0.267	7.650
E-18	60	30	0.275	-13.23	118.98	0.275	7.880
E-27	60	35	0.310	-14.85	83.14	0.310	7.614
E-28	60	40	0.368	-16.43	68.96	0.368	7.908

TABLE C.11. Experimental results for extraction experiments at 4 M chloride

Conditions: Fe(III), TOAHCl, Temperature and Interfacial area, as indicated

Contra-rotating stirrers O = 250 rpm. A = 375 rpm

Phase volume A=O = 480 ml

Fitted equation: $Fe = a_1 t + a_2 t^2$, $Fe = \text{gm/l} \times 10^3$, $t = \text{min}$, $R^2 \geq 0.95$ d.f. ≥ 10

Run	Duration (min)	Fe(III) (Mx10 ²)	TOAHCl (Mx10 ²)	T (°C)	Area (cm ²)	a ₁	a ₂ x 10 ³	T-ratio (a ₁)	R x 10 ³ $\frac{\text{gm}}{\text{l.min}}$	$\vec{R} \times 10^8$ $\frac{\text{gmol}}{\text{cm}^2 \cdot \text{min}}$
E-29	60	0.5	1.0	25	30	0.426	-2.08	68.30	0.426	12.206
E-30	30	1.0	1.0	25	30	0.812	-3.91	41.37	0.812	23.266
E-31	30	1.0	1.0	25	30	0.859	-3.45	54.69	0.859	24.613
E-32	20	1.5	1.0	25	30	1.203*	-	-	1.203	34.470
E-33	15	2.0	1.0	25	30	1.761*	-	-	1.761	50.458
E-34	10	2.5	1.0	25	30	2.015*	-	-	2.015	57.736
E-35	60	1.0	0.5	25	30	0.463	-2.14	42.40	0.463	13.266
E-36	20	1.0	1.5	25	30	1.182*	-	-	1.182	33.868
E-37	20	1.0	2.0	25	30	1.427*	-	-	1.427	40.888
E-38	15	1.0	2.5	25	30	1.694*	-	-	1.694	48.539
E-39	20	1.0	1.0	30	30	1.234*	-	-	1.234	35.358
E-40	60	1.0	1.0	15.3	30	0.375	-1.86	75.97	0.375	10.745
E-41	45	1.0	1.0	25	20	0.561	-2.26	68.85	0.561	24.111
E-42	20	1.0	1.0	25	40	1.274*	-	-	1.274	27.378

(*) Slope calculated graphically from the concentration-time profile

TABLE C.12. Experimental results for extraction experiments at 7 M chloride

Conditions: Fe(III), TOAHCl, Temperature and Interfacial area as indicated
 Contra-rotating stirrers O = 250 rpm A = 550 rpm
 Phase volume A=O = 480 ml

Fitted equation: $Fe = a_1t + a_2t^2$, $Fe = \text{gm/l} \times 10^3$, $t = \text{min}$, $R^2 \geq 0.95$, d.f. ≥ 10

Run	Duration (min)	Fe(III) (Mx10 ³)	TOAHCl (Mx10 ²)	T (°C)	Area (cm ²)	a ₁	a ₂ x 10 ³	T-ratio (a ₁)	R x 10 ³ $\frac{\text{gm}}{1.\text{min}}$	$\vec{R} \times 10^8$ $\frac{\text{gmol}}{\text{cm}^2.\text{min}}$
E-44	50	0.5	1.0	25	30	0.469	-2.31	59.75	0.469	13.438
E-45	25	1.0	1.0	25	30	1.053	-3.84	46.22	1.053	30.172
E-46	25	1.0	1.0	25	30	0.991	-3.66	33.80	0.991	28.395
E-47	15	1.5	1.0	25	30	1.796*	-	-	1.796	51.461
E-48	10	2.0	1.0	25	30	2.047*	-	-	2.047	58.653
E-49	10	2.5	1.0	25	30	2.951*	-	-	2.951	84.556
E-50	45	1.0	0.5	25	30	0.583	-2.61	34.49	0.583	16.705
E-51	15	1.0	1.5	25	30	1.485*	-	-	1.485	42.550
E-52	15	1.0	2.0	25	30	1.820*	-	-	1.820	52.149
E-53	10	1.0	2.5	25	30	2.094*	-	-	2.094	60.000
E-54	10	1.0	1.0	34.6	30	2.293*	-	-	2.293	65.702
E-55	50	1.0	1.0	15.2	30	0.472	-2.49	39.56	0.472	13.524
E-56	40	1.0	1.0	25	20	0.621	-2.85	20.38	0.621	26.691
E-57	20	1.0	1.0	25	40	1.326*	-	-	1.326	28.496

(*) Slope calculated graphically from the concentration-time profile

TABLE C.13. Effect of chloride concentration on initial extraction rate (constant stirring speed)

Conditions: TOAHCl = 0.01 M Fe(III) = 0.0010 M Temp = 25°C
 Interfacial area = 30 cm² Phase volume A=O = 480 ml
 Contra-rotating stirrers A=O = 250 rpm

Fitted equation: $Fe = a_1 t + a_2 t^2$ $Fe = \text{gm/l} \times 10^3$ $t = \text{min}$
 $R^2 \geq 0.95$ d.f. ≥ 10

Run	Duration (min)	Chloride (M)	a_1	$a_2 \times 10^4$	T-ratio (a_1)	$R \times 10^3$ <u>gm</u> 1.min	$\vec{R} \times 10^8$ <u>gmol</u> cm ² .min
E-2	120	1	0.0573	-2.06	113.96	0.0573	1.642
E-3	60	1	0.0595	-2.75	104.18	0.0595	1.705
E-59	60	2	0.246	-12.30	83.81	0.246	7.049
E-60	50	3	0.514	-23.06	74.50	0.514	14.728
E-61	30	4	0.756	-31.59	44.54	0.756	21.662
E-62	30	5	0.683	-26.34	52.32	0.683	19.570
E-63	50	7	0.469	-21.35	35.73	0.489	14.011
E-64	60	9	0.343	-18.73	20.38	0.343	9.828

TABLE C.14. Effect of chloride concentration on initial extraction rate (constant Reynolds number)

Conditions: TOAHCl = 0.01 M Fe(III) = 0.0010 M Temp = 25°C
 Interfacial area = 30 cm² Phase volume A=O = 480 ml
 Contra-rotating stirrers O = 250 rpm A (Re = 2680)
 Fitted equation: $Fe = a_1 t + a_2 t^2$ Fe = gm/l x 10³ t = min
 $R^2 \geq 0.95$ d.f. ≥ 10

Run	Duration (min)	Chloride (M)	a_1	$a_2 \times 10^4$	T-ratio (a_1)	$R \times 10^3$ gm lxmin	$\vec{R} \times 10^8$ gmol cm ² xmin
E-2	120	1	0.0573	-2.06	113.96	0.0573	1.642
E-3	60	1	0.0595	-2.75	104.18	0.0595	1.705
E-66	60	2	0.246	-12.20	94.80	0.246	7.049
E-67	45	3	0.529	-23.67	70.46	0.529	15.156
E-30	30	4	0.812	-39.19	41.37	0.812	23.266
E-31	30	4	0.859	-34.59	54.69	0.859	24.613
E-68	25	5	1.035	-36.34	35.86	1.035	29.656
E-69	25	6	0.983	-35.06	42.61	0.983	28.166
E-45	25	7	1.053	-38.42	46.22	1.053	30.172
E-46	25	7	0.991	-36.64	33.80	0.991	28.395

TABLE C.15. Experimental Results for stripping experiments

Condition: Fe(III), TOAHCl, Cl⁻, Temperature and Interfacial area, as indicated

Contra-rotating stirrers: O = 250 rpm, A at constant Re = 2680

Phase volume A=O = 500 ml

Fitted equation: $Fe = a_1 t + a_2 t^2$, $Fe = \text{gm/l} \times 10^3$, $t = \text{min}$, $R^2 \geq 0.95$ d.f. ≥ 10

Run	Duration (min)	Fe(III) (Mx10 ³)	TOAHCl (Mx10 ²)	Chloride (M)	T (°C)	Area (cm ²)	a ₁	a ₂ x 10 ⁴	T-ratio (a ₁)	R x 10 ³ <u>gm</u> 1.min	$\bar{R} \times 10^8$ <u>gmol</u> cm ² .min
S-1	60	0.174	1.0	1	25	30	0.0551	2.42	78.82	0.0551	1.645
S-2	60	0.348	1.0	1	25	30	0.103	4.27	120.02	0.103	3.074
S-3	60	0.870	1.0	1	25	30	0.276	12.69	90.58	0.276	8.238
S-4	60	1.392	1.0	1	25	30	0.469	17.13	71.52	0.469	13.998
S-5	50	1.740	1.0	1	25	30	0.532	22.19	54.60	0.532	15.879
S-6	50	1.740	1.0	1	25	30	0.520	20.51	60.35	0.520	15.521
S-7	60	1.740	2.0	1	25	30	0.257	14.95	87.36	0.257	7.671
S-8	60	1.740	3.0	1	25	30	0.175	9.22	93.51	0.175	5.223
S-9	60	1.740	5.0	1	25	30	0.096	3.72	51.95	0.096	2.865
S-10	60	1.740	10.0	1	25	30	0.044	2.51	31.34	0.044	1.313
S-11	50	1.740	1.0	2	25	30	0.557	25.57	34.60	0.557	16.625
S-12	50	1.740	1.0	3	25	30	0.506	33.73	39.21	0.506	15.103
S-13	50	1.740	1.0	4	25	30	0.526	42.04	31.47	0.526	15.700
S-14	50	1.740	1.0	4	25	30	0.488	39.68	43.75	0.488	14.565
S-15	30	1.740	1.0	1	35.8	30	0.741	35.30	30.27	0.741	22.117
S-16	60	1.740	1.0	1	14.7	30	0.368	15.52	93.11	0.368	10.984
S-17	60	1.740	1.0	1	25	20	0.338	17.56	68.54	0.338	15.133
S-18	30	1.740	1.0	1	25	40	0.697	25.15	41.96	0.697	15.603

TABLE C.16. Equilibrium distribution ratio of iron as a function of TOAHCl concentration

Fe(III) total = 2.5×10^{-4} M HCl = 1 M

TOAHCl M x 10^2	D	log D
0.5	0.0563	-1.25
1.0	0.187	-0.73
2.5	0.94	-0.03
5.0	2.81	0.45
10.0	10.46	1.02

TABLE C.17. Equilibrium distribution ratio of iron as a function of chloride concentration

Fe(III) total = 2.5×10^{-4} M TOAHCl = 0.01 M
Cl = 1 M HCl + x M LiCl

Cl ⁻ (M)	D	log D
1.0	0.187	-0.73
1.5	0.752	-0.12
2.0	2.28	0.36
2.5	5.42	0.73
3.0	10.38	1.02
4.0	74.18	1.87

TABLE C.18. Determination of Cl/Fe ratio.
Experiments with radioactive ^{36}Cl .
Extraction at 1 M aqueous Cl^- .

time (min)	Cl ($\text{M} \times 10^3$) isotopic transfer	Fe ($\text{M} \times 10^3$)	Cl ($\text{M} \times 10^3$) during Fe transfer	Cl/Fe ratio
5	1.83	0.324	2.84	3.12
10	3.48	0.610	5.35	3.06
15	5.31	0.844	7.77	2.92
20	6.90	1.064	10.23	3.13
25	8.39	1.350	12.57	3.09
30	9.62	1.480	13.97	2.94
40	12.15	1.869	18.19	3.23
50	14.47	2.389	21.81	3.07
60	16.57	2.490	23.64	2.84

Average Cl/Fe ratio = 3.04 ± 0.09

Experimental conditions:

TOAHCl = Fe = 0.025 M Cl = HCl 1 M ^{36}Cl = 5 C

25°C, Phase volume: A = O = 480 ml

Stirring speed: A = O = 250 rpm (contra-rotating)

Interfacial area = 30 cm²

TABLE C.19. Determination of Cl/Fe ratio.
Experiments with radioactive ^{36}Cl .
Extraction at 3 M aqueous Cl^- .

time (min)	Cl ($\text{M} \times 10^3$) isotopic transfer	Fe ($\text{M} \times 10^3$)	Cl ($\text{M} \times 10^3$) during Fe transfer	Cl/Fe ratio
2.5	0.94	0.549	2.80	3.39
5	1.79	1.085	5.81	3.14
10	3.51	2.170	9.87	2.94
15	5.26	3.189	14.99	3.05
20	6.73	3.948	19.46	3.22

Average Cl/Fe ratio = 3.15 ± 0.21

Experimental conditions:

TOAHCl = Fe = 0.025 Cl = 3 M ^{36}Cl = 5 C

25°C, Phase volume: A = O = 480 ml

Stirring speed: A = O = 250 rpm (contra-rotating)

Interfacial area = 30 cm^2

TABLE C.20. Determination of Cl/Fe ratio.
Experiments with radioactive ^{36}Cl .
Extraction at 5 M aqueous Cl^- .

Time (min)	Cl ($\text{M} \times 10^3$) isotopic transfer	Fe ($\text{M} \times 10^3$)	Cl ($\text{M} \times 10^3$) during Fe transfer	Cl/Fe ratio
2	0.72	0.732	3.14	3.31
4	1.53	1.464	6.03	3.07
6	2.10	2.249	9.04	3.09
8	2.71	2.955	12.65	3.36
10	3.58	3.791	15.76	3.21
12	4.29	4.105	16.39	2.95
14	4.60	4.608	18.95	3.12

Average Cl/Fe ratio = 3.16 ± 0.23

Experimental conditions:

TOAHCl = Fe = 0.025 M Cl = 5 M ^{36}Cl = 10 C

25°C , Phase volume: A = O = 480 ml

Stirring speed: A = O = 250 rpm (contra-rotating)

Interfacial area = 30 cm^2

TABLE C.21. Determination of Cl/Fe ratio.
Experiments with radioactive ^{36}Cl .
Extraction at 7 M aqueous Cl^- .

time (min)	Cl ($\text{M} \times 10^3$) isotopic transfer	Fe ($\text{M} \times 10^3$)	Cl ($\text{M} \times 10^3$) during Fe transfer	Cl/Fe ratio
2	0.65	0.313	1.80	3.69
4	1.51	0.620	3.92	3.89
6	1.99	0.993	5.22	3.25
8	3.31	1.256	6.95	2.90
10	3.67	1.566	9.24	3.56
12	5.34	1.880	11.75	3.41
14	5.58	2.193	14.26	3.96

Average Cl/Fe ratio = 3.52 ± 0.34

Experimental conditions:

$\text{TOAHCl} = \text{Fe} = 0.025 \text{ M}$ $\text{Cl}^- = 7 \text{ M}$ $^{36}\text{Cl} = 10 \text{ C}$

25°C , Phase volume: $A = O = 480 \text{ ml}$

Stirring speed: $A = O = 250 \text{ rpm}$ (contra-rotating)

Interfacial area = 30 cm^2

APPENDIX D

COMPUTER OUTPUT FOR REGRESSION ANALYSIS - RATE EQUATION
EVALUATION (Section 6.2.6.).

- D.1. Best full model (Extraction 1 M Cl^-).
- D.2. Best reduced model (Extraction 1 M Cl^-).
- D.3. Best full model (Stripping 1 M Cl^-).
- D.4. Best reduced model (Stripping 1 M Cl^-).
- D.5. Other reduced models (Stripping 1 M Cl^-).

$$\text{FITTED EQUATION: } \frac{(\text{Fe})}{(\text{R}) (\text{M1})} = \frac{1}{k_5^* \alpha_n} + \frac{k_7^*}{k_5^* \alpha_n} (\text{M1})$$

THE REGRESSION EQUATION IS
 $Y = 3.88 - .0034 X_1$

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
	--	3.8790	.0890	43.57
X1	C3	-.0034	.0107	-.32

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
 $S = .165$
 WITH (19- 2) = 17 DEGREES OF FREEDOM

R-SQUARED = .6 PERCENT
 R-SQUARED = -5.2 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	.0028	.0028
RESIDUAL	17	.4610	.0271
TOTAL	18	.4638	

ROW	X1 C3	Y C14	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
1	6.4	3.907	3.857	.040	.050	.31
2	6.4	3.873	3.857	.040	.016	.10
3	6.4	3.730	3.857	.040	-.127	-.79
4	6.4	3.746	3.857	.040	-.111	-.70
5	6.4	3.762	3.857	.040	-.095	-.59
6	6.4	3.832	3.857	.040	-.025	-.16
7	6.4	3.688	3.857	.040	-.169	-1.06
8	6.4	3.775	3.857	.040	-.082	-.51
9	6.4	3.725	3.857	.040	-.133	-.83
10	6.4	3.827	3.857	.040	-.030	-.19
11	6.4	3.715	3.857	.040	-.142	-.89
12	6.4	3.801	3.857	.040	-.056	-.35
13	1.7	4.413	3.873	.073	.540	3.66R
14	3.7	3.917	3.866	.055	.051	.33
15	8.5	3.945	3.850	.039	.095	.59
16	10.4	3.827	3.843	.048	-.017	-.11
17	12.0	3.925	3.838	.061	.087	.57
18	12.0	3.810	3.838	.061	-.027	-.18
19	18.7	3.990	3.815	.125	.176	1.63 X

R DENOTES AN OBS. WITH A LARGE ST. RES.

X DENOTES AN OBS. WHOSE X VALUE GIVES IT LARGE INFLUENCE.

TABLE D.1. COMPUTER OUTPUT FOR REGRESSION ANALYSIS.
 BEST FULL MODEL (EXTRACTION 1 M C1⁻).

FITTED EQUATION $R = k_5^* \alpha_n (\text{Fe}) (\text{M1})$

THE REGRESSION EQUATION IS
 $Y = + .259 X_1$

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
NOCONSTANT				
X1	C1	.25902	.00157	165.21

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
 $S = .144$
 WITH (19- 1) = 18 DEGREES OF FREEDOM

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	568.214	568.214
RESIDUAL	18	.375	.021
TOTAL	19	568.588	

ROW	X1 C1	Y C2	PRED. Y VALUE	ST. DEV. PRED. Y	RESIDUAL	ST. RES.
1	3.2	.814	.829	.005	-.015	-.10
2	6.4	1.642	1.658	.010	-.016	-.11
3	6.4	1.705	1.658	.010	.047	.33
4	9.5	2.547	2.461	.015	.086	.60
5	12.7	3.381	3.290	.020	.091	.64
6	14.1	3.668	3.652	.022	.016	.11
7	14.1	3.811	3.652	.022	.159	1.11
8	15.9	4.212	4.118	.025	.094	.66
9	15.9	4.269	4.118	.025	.151	1.06
10	19.1	4.986	4.947	.030	.039	.27
11	25.4	6.848	6.579	.040	.269	1.94
12	31.8	8.367	8.237	.050	.130	.96 X
13	4.3	.980	1.114	.007	-.134	-.93
14	9.3	2.387	2.409	.015	-.022	-.15
15	21.3	5.387	5.517	.033	-.130	-.93
16	25.9	6.762	6.709	.041	.053	.39
17	30.0	7.650	7.771	.047	-.121	-.88 X
18	30.0	7.880	7.771	.047	.109	.80 X
19	46.6	11.691	12.070	.073	-.379	-3.05RX

R DENOTES AN OBS. WITH A LARGE ST. RES.

X DENOTES AN OBS. WHOSE X VALUE GIVES IT LARGE INFLUENCE.

TABLE D.2. COMPUTER OUTPUT FOR REGRESSION ANALYSIS. BEST
 REDUCED MODEL (EXTRACTION 1 M C1⁻).

THE REGRESSION EQUATION IS
 $Y = .0079 + .0014 X1$

COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
---	.007921	.000614	12.91
X1 C3	.0013512	.0000474	28.54

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
 $S = .00105$
 WITH (10- 2) = 8 DEGREES OF FREEDOM

R-SQUARED = 99.0 PERCENT
 R-SQUARED = 98.9 PERCENT, ADJUSTED FOR D.F.

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	.00089792	.00089792
RESIDUAL	8	.00000882	.00000110
TOTAL	9	.00090675	

ROW	X1	Y	PRED. Y	ST.DEV.	RESIDUAL	ST.RES.
1	C3	C7	VALUE	PRED. Y	RESIDUAL	ST.RES.
1	6.4	.01663	.01651	.00040	.00012	.12
2	6.4	.01780	.01651	.00040	.00129	1.32
3	6.4	.01548	.01651	.00040	-.00104	-1.07
4	6.4	.01564	.01651	.00040	-.00088	-.90
5	6.4	.01723	.01651	.00040	.00071	.73
6	6.4	.01763	.01651	.00040	.00111	1.14
7	10.4	.02192	.02191	.00033	.00001	.01
8	13.5	.02462	.02620	.00035	-.00158	-1.60
9	18.7	.03255	.03314	.00050	-.00059	-.63
10	28.2	.04693	.04608	.00089	.00085	1.50 X

X DENOTES AN OBS. WHOSE X VALUE GIVES IT LARGE INFLUENCE.

TABLE D.3. COMPUTER OUTPUT FOR REGRESSION ANALYSIS. BEST FULL MODEL (STRIPPING 1 M CL⁻).

FITTED EQUATION: $R = k_6 \cdot \frac{Fe}{M}$

THE REGRESSION EQUATION IS
 $Y = + 92.3 X1$

COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
NOCONSTANT			
X1	92.25	1.52	60.61

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
 $S = .485$
 WITH (10- 1) = 9 DEGREES OF FREEDOM

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	863.006	863.006
RESIDUAL	9	2.115	.235
TOTAL	10	865.120	

ROW	X1	Y	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
1	.017	1.65	1.57	.03	.08	.17
2	.035	3.07	3.23	.05	-.16	-.33
3	.087	8.24	8.03	.13	.21	.46
4	.139	14.00	12.82	.21	1.18	2.70R
5	.174	15.88	16.05	.26	-.17	-.42 X
6	.174	15.52	16.05	.26	-.53	-1.31 X
7	.087	7.67	8.03	.13	-.36	-.76
8	.058	5.22	5.35	.09	-.13	-.27
9	.035	2.87	3.23	.05	-.36	-.74
10	.017	1.31	1.57	.03	-.26	-.53

R DENOTES AN OBS. WITH A LARGE ST. RES.

X DENOTES AN OBS. WHOSE X VALUE GIVES IT LARGE INFLUENCE.

TABLE D.4. COMPUTER OUTPUT FOR REGRESSION ANALYSIS. BEST REDUCED MODEL
 (STRIPPING 1 M CL).

FITTED EQUATION: $R = k_6 * \frac{\overline{Fe}}{M1}$

THE REGRESSION EQUATION IS
 $Y = + 55.2 X1$

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
NOCONSTANT				
X1	C7	55.18	2.87	19.20

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
 $S = 1.51$
 WITH (10- 1) = 9 DEGREES OF FREEDOM

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	844.44	844.44
RESIDUAL	9	20.62	2.29
TOTAL	10	865.06	

FITTED EQUATION: $R = k_6 * \frac{\overline{Fe}}{M_2}$

THE REGRESSION EQUATION IS
 $Y = + 17.3 X1$

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
NOCONSTANT				
X1	C8	17.263	.546	31.60

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
 $S = .927$
 WITH (10- 1) = 9 DEGREES OF FREEDOM

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	1	857.338	857.338
RESIDUAL	9	7.726	.858
TOTAL	10	865.064	

TABLE D.5. COMPUTER OUTPUT FOR REGRESSION ANALYSIS. OTHER REDUCED MODELS (STRIPPING 1 M Cl^-).

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