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THE ADSORPTION OF METAL CHELATE COMPLEXES
FROM ORGANIC ~~SOLUTIONS~~ ^{SOLVENTS}.

A thesis submitted for the Doctorate of Philosophy
at the University of London.

By

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SUMMARY.

The work described in this thesis was undertaken in order to determine the feasibility of using chelating agents of the 8-quinolinol type and column chromatography for the separation and analysis of metallic ores and alloys.

An investigation of the factors influencing the adsorption of the metal chelates showed that, with the exception of the copper and chromium chelates, they were irreversibly adsorbed from non-polar solvents onto polar adsorbents. Once adsorbed they could not be eluted by polar solvents.

Studies based on adsorption isotherms and kinetics of adsorption indicated that the adsorption was a two stage process. The initial coverage of the surface, which was apparently irreversible, and the subsequent multimolecular adsorption, which was partially reversible, both involved low activation energies. Calculation of the apparent entropies of activation from the experimentally determined activation energies and rate constants gave unexpectedly high values.

Analysis of the eluant for free ligand and investigation of the adsorbed material by X ray powder and infra red techniques gave no evidence of decomposition of the adsorbed material.

By measurement of heats of preferential

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adsorption it was determined that the heat evolved on adsorption was not as high as might be expected if a decomposition was taking place. Further experiments showed that the heat of preferential adsorption could be related directly to the elution of compounds, and that the copper, nickel, chromium, and iron, chelates of 8-quinolinethiol would be readily elutable from an alumina column by benzene. Chromatographic investigations confirmed that all four chelates could be eluted with almost complete separation.

These results, together with the knowledge of the factors determining the adsorption of the 8-quinolinol chelates, showed that, from a chromatographic point of view, chelating agents of the sulphur and nitrogen type are promising reagents for the separation of metals by adsorption chromatography.

General Introduction

The use of adsorption chromatography for the separation of metal chelates in organic solvents is one of the few chromatographic fields where the amount of published work is small.

The adsorption of the dithiozone chelates of certain metals on alumina has been studied by Erametsa (1), and sodium diethyldithiocarbamate has been used for the separation of pairs of the transition metals using alumina and chloroform/benzene mixtures (2). Berg and McIntyre (3), and Berg and Strassner (4) (5) carried out a series of investigations on the paper chromatographic separation of β di-ketone chelates. They report that separations sufficient for identification were obtained but no quantitative analytical uses were reported.

The separation of copper, aluminium, iron, cobalt, and nickel, on silica gel by the use of their 8-quinolinol chelates in chloroform-alcohol solutions was reported by Hilliard and Feiser (6). A very promising degree of separation was achieved, with apparently quantitative recovery, but no analytical applications were made of the results of this investigation.

The use of alumina columns for the quantitative separation and subsequent analysis of the 2-methyl-8-quinolinol chelates of chromium and copper was reported by Blair and Pantony (7) (8). No further interest in this separation system is evident from the literature, and, bearing in mind the separations reported by Hilliard and Freiser (6), the present work was undertaken in order to discover if the technique could be extended to other metal quinolinol chelates.

Since some of the difficulties involved were known (9), it was clear that a more fundamental study of the factors influencing the adsorption of the 8-quinolinol chelates was an essential part of the work. Accordingly, the adsorption isotherms were constructed, and the kinetics of adsorption extensively investigated, in order to obtain data to explain the very strong adsorption of these compounds on alumina.

The relationship between molecular constitution and chromatographic behaviour has been dealt with in several books (10-14), mainly from an empirical point of view, but there is little known about the exact relation between adsorption energy and chromatographic behaviour. The kinetics of adsorption and desorption are obviously of great

importance, and, while the kinetics of zone migration have come under close scrutiny, e.g. (15), the use of kinetics of adsorption in mechanistic studies of chromatographic adsorption is an almost neglected field.

The main objective in this work was to develop a chromatographic system for the separation and subsequent analysis of metal chelate compounds, and so a method of developing the required system that was more soundly based than the empirical rules of elutability was required. Recently there have been several theoretical treatments of chromatography advanced (15, 16, 17), but the problem in applying these theoretical treatments to the particular systems studied is that there is a great lack of data, e.g. viscosity of the solution in the vicinity of the adsorbent, surface tension at the solid liquid interface, etc., which is required to enable the equations to be solved with any degree of reliability. Accordingly, it was decided to try and apply measurements of heat of preferential adsorption to the characterisation of the adsorption system. In the elution adsorption chromatographic systems studied, the essential step is the replacement of solvent

molecules on the surface by solute molecules during adsorption, and vice versa during desorption, and so the heat change during adsorption, which is a function of the changes in free energy and entropy, may be used as a measure of the order of elution. The lower the heat of preferential adsorption the more likely the substance is to elute (18).

The following sections therefore deal with:

- Section I Qualitative description of the
 chromatographic behaviour of
 3-quinolinol and similar chelates.
- Section II a) Adsorption isotherms
 b) Kinetics Studies
 c) Thermal changes during adsorption

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SECTION I

CHROMATOGRAPHIC BEHAVIOUR OF
2-METHYL-8-QUINOLINOL AND CERTAIN
OTHER RELATED CHELATES

CHAPTER I

CHROMATOGRAPHIC ADSORPTION OF
2-METHYL-8-QUINOLINOL CHELATES

The chromatographic separation of metal chelates should provide a useful addition to solvent extraction or precipitation for the analysis of a wide variety of metals. This is particularly true when a chelating agent based on the 8-quinolinol nucleus is used, since it will form stable, highly coloured, complexes, soluble in organic solvents, with a large number of metals.

Blair and Pantony (7, 8) successfully separated chromium and copper from each other, and both from a large number of other metals by the use of an alumina/benzene + chloroform system.

In the present work, the adsorption chromatographic behaviour of many 2-methyl-8-quinolinol chelates has been investigated with particular reference to the characteristics of the chelate, the adsorbent surface, and the solvent system, with a view to extending the technique to other elements.

Choice of chelating agent,adsorbent, and solvent system

In view of this intention, the system chosen was that which had been found most promising,

viz alumina, 2-methyl-8-quinolinol, and a solvent system based largely on benzene + chloroform mixtures. Very early in the work a standard adsorption system was adopted as a reference for comparative studies and to give some continuity to the adsorption data.

The adsorbent chosen was Peter Spence 'Type H' alumina (120-150 mesh), which had been well washed in a Soxhlet filter, dried, sieved, activated at 400°C for 3 hours, and cooled under vacuum. The alumina thus prepared was of Brockman activity (19) I to II and, provided that the activation conditions were closely reproduced, was quite repeatable.

The solvent system was May and Baker R' grade sulphur free benzene. Chloroform was not used owing to its sensitivity to light, and also the alcohol which is frequently added and which is not reproducibly the claimed 1% proportion.

The 2-methyl-8-quinolinol chelates were chosen as the main chelates for investigation because, apart from two desirable differences, they were chemically very similar to the parent 8-quinolinol chelates. The two differences were that the reagent did not remove aluminium from an alumina column; and the 2-methyl-8-quinolinol chelates are appreciably more soluble in organic solvents than the 8-quinolinol chelates.

Chemical similarity to the parent compound was also desirable as it was intended that the effect of other substituents be investigated.

Preparation of 2-methyl-8-quinolinol

The reagent was prepared by the Skraup condensation of σ -aminophenol and crotonaldehyde according to the method of Merritt and Walker (20) modified by Blair and Pantony (9), with the further modification that the quantity of σ -nitrophenol was reduced to 0.25 Mole.

Preparation of metal 2-methyl-8-quinolinol chelates

The metal chelates were all prepared by precipitation from an aqueous 10^{-2} M solution by the standard gravimetric procedures (21).

The chelates formed in this way were completely soluble in benzene, so only organic impurities should be present. Only on rare occasions was the presence of excess reagent noticed chromatographically, and could be simply removed by re-precipitating the complexes from an acetone water mixture:-

The chelate was dissolved in acetone and double distilled water added until precipitation just occurred. The precipitate was re-dissolved by the addition of acetone. Recrystallisation was effected by bubbling a stream of air through a warm, approximately 50°C solution, which caused steady

evaporation of the acetone. At no time was there any evidence of heterogeneity of the chelates prepared in this manner.

Attempts were also made to purify the chelates by recrystallisation from absolute alcohol, but this method was abandoned when it was noticed that the ferric chelate decomposed on standing to give a reddish brown precipitate. A sample of this precipitate was washed with fresh alcohol, in which it was insoluble, and examined by infra red spectroscopy. The spectrum indicated that the material was inorganic in character, and subsequent analysis for iron indicated that the material was probably Fe_2O_3 .

This decomposition in alcohol is a possible explanation for the two iron bands reported by Hilliard and Freiser (6) during chromatographic elution of 8-quinolinol chelates with alcohol + chloroform mixtures.

Adsorption of 2-methyl-8-quinolinol

chelates on alumina from benzene

The initial study of the chelates was an investigation of their adsorptions on alumina from benzene in order to provide a reference for comparing the effects of various parameters involved in the adsorption process. The behaviour of the chelates

of a large number of metals was investigated, although for later studies a lesser number of representative chelates were chosen.

Using the standard alumina/benzene system the following metals were studied, copper, nickel, iron, cerium, uranium, cobalt, gallium, zinc, and chromium.

All the chelates were strongly adsorbed and prolonged elution with benzene caused, at the most, the band to widen, except in the case of chromium where slight elution occurred. Elution with a dilute solution, 0.5% of reagent in benzene caused the elution of copper as reported by Blair and Pantony (8), but while other bands spread slightly no true elution occurred. It is interesting to note that while the band contains 1×10^{-6} moles of copper chelate a 1×10^{-2} M reagent solution is required to start the elution of the copper band with an R_f value of 1.0. If the reagent solution is less than 1×10^{-3} M the copper chelate is not eluted as a sharp band, but slowly leaches from the column. If the reagent is very dilute i.e. 10^{-4} M or less the copper chelate band is spread, but a visible quantity of chelate is left covering the whole column.

CHAPTER 12

The Influence of solvent and adsorbent
on the adsorption of metal chelates

One of the primary variables in an adsorption system is obviously the activity of the adsorbent. This was investigated for its effect on both the adsorption and desorption processes. A series of adsorbents of varying Brockman activity (19) were prepared by taking the standard alumina and equilibrating samples with atmospheres of known humidities.

Salt (saturated soln)	Relative Humidity	Brockman Activity
Zinc Chloride	10%	IIb
Calcium Chloride	32%	III
Potassium Carbonate	44%	IV
Sodium Dichromate	52%	V
Sodium Chloride/Sucrose	70%	<V

Variation in the activity of the alumina had but slight effect. If a high flow rate was used the chelates were adsorbed as broad diffuse bands on the least active aluminas. This was suspected to be owing to streaming since, when low flow rates were used, the adsorption was identical in character to that obtained with the more active aluminas.

Elution with deactivating solvents, particularly water-containing solvents, had a much more marked effect on the elution. The solvents used were solutions of water in methyl ethyl ketone. This solvent was chosen as it did not have any eluting effect on the chelates itself and solution of 10% V/V water in methyl ethyl ketone could be made.

A series of solutions containing 1%, 2%, 5%, 8% and 10% water in methyl ethyl ketone were prepared and their eluting power investigated.

All these solutions had some effect on the desorption of the chelates. With the low concentrations of water, the initial effect was to cause some of the adsorbed chelate to move down the column on the solvent front. As the front descended the column, chelate was gradually lost by adsorption on the alumina. Prolonged elution with these solutions caused spreading of the band until eventually the column blocked owing to the swelling of the alumina, which always happened with the aqueous solutions.

The more concentrated water mixtures exhibited the same movement of the adsorbed material but enhanced to the point that substantial amounts of chelate were eluted with the solvent front.

Prolonged elution led to the recovery of 80% to 90% of the chelates of chromium, copper, nickel, and iron, which were the only chelates extensively investigated.

When 2-methyl-8-quinolinol was added to the water-methyl ethyl ketone mixtures further improvement of recovery was obtained; to the extent that less eluant was needed to reach the stage where no further detectable recovery of chelate was occurring, but, except in the case of copper, it was never possible to obtain quantitative recovery.

Since the elution of the chelates was such a time consuming process, more of a leaching process than a true elution, the approach was abandoned as a practicable means of separation.

Adsorption, desorption and solvent polarity

The water containing solutions could effect the adsorption either by altering the chemical composition of the alumina, or by replacing the adsorbed chelate molecule by a more polar molecule. If replacement of the solvent by a water molecule is sufficient to cause elution, then other solvents of a more polar nature than benzene might be expected to cause elution of the chelates.

A series of solvents were chosen in order to determine the effect of solvent polarity on the chelate

adsorption, both before adsorption had occurred and after the chelates had been adsorbed from benzene.

Solvent	Dielectric Constant	General remarks on Chelate Solubility
Formamide	109	Soluble but decomposition occurs
Dimethylformamide	36.7	Soluble, colour change, decomposition ?
Nitrobenzene	35	Soluble
Methanol	32	Soluble
Ethanol	24	Soluble also decomposition
Acetone	21	Very Soluble
Pyridine	12	Soluble, some decomposition
Ethyl Acetate	6	Soluble
Chloroform	4.8	Very soluble, stable
Benzene	2.3	Soluble and stable
1:4 Dioxane	2.2	Soluble

When the solvent was used to pre-treat the adsorbents, or was used as the solvent for adsorption of the chelates, it was found that the

width of the adsorbent band increased approximately in the order of increasing dielectric constant. There were some variations owing to different solubilities, and pyridine exhibited a greater effect than its relative position in the dielectric constant order would suggest.

However, after adsorption from benzene had taken place, the effect of dielectric constant was less marked. The adsorption band could be spread, and some elution obtained, by prolonged elution with chloroform, acetone, or alcohol; but the majority of the chelate remained firmly adsorbed on the alumina. Recovery of the metal was possible with dimethylformamide, and formamide, and also acetic acid, and formic acid, but in all cases the chelate complex had been extensively decomposed.

As an example of the effect of dielectric constant, chromium 2-methyl-8-quinolinol is not adsorbed on alumina from (1 + 1) benzene/chloroform. Indeed this is used as the basis for a method of quantitative analysis for chromium in complex mixtures (7). However, once adsorbed on alumina from benzene, the chelate cannot be recovered quantitatively by elution with this mixture, or any solvent with a higher dielectric constant. This apparent total irreversibility once the adsorption

has been allowed to occur is highly characteristic of these systems and its significance is discussed in more detail in conjunction with the kinetics studies.

The adsorbent surface and chelate adsorption

One of the fundamental variables in adsorption chromatography is the nature of the adsorbent surface. Since most of the adsorbents are of variable composition, and many are hydroxide/oxide mixtures, it is difficult to classify them by a chemical analysis. Also, as adsorption is usually confined to the 'exterior' surface of the particles, although some diffusion into porous materials can occur, it is the atoms and bonds exposed on the adsorbent surface that are important rather than the overall composition. Several methods are available for estimating the adsorbent activity which may depend on chromatographic behaviour (19, 22), measurement of the distribution of acid sites, (23), or the heat preferential adsorption of a standard substance on various adsorbents (18).

In this work, a rapid comparison of a series of adsorbents was carried out by determining the adsorption isotherms of the copper chelate on the various adsorbents. This method had the advantage of enabling the adsorbents to be compared not only

for adsorbent activity, but also enabled the type of site necessary for adsorption of the chelates to be discovered.

The series of adsorbents chosen were:-

- a) acid washed alumina, b) Type 'H' alumina,
- c) 'sodium washed' alumina, d) silica alumina,
- e) aluminium washed silica gel, and f) silica gel.

The adsorbents were prepared as follows:-

- a) acid washed alumina : Peter Spence type 'H' alumina, 120 to 150 mesh, was stirred with (1 + 1) acetic acid for 30 mins. The slurry was filtered on sintered glass and washed thoroughly with deionized water. Finally the alumina was extracted in a Soxhlet apparatus with deionized water for two hours, dried at 110°C in an air oven, and activated under the standard conditions.
- b) Type 'H' alumina : No treatment was given, the alumina used was the same as for the standard adsorption investigations.
- c) Sodium-washed alumina : Type 'H' alumina was suspended in a 5% solution of sodium hydroxide for 30 mins. The alumina was then filtered, rinsed with water, dried in an air-oven, re-sieved, and activated under the standard conditions.
- d) Silica/Alumina : This was a commercial catalyst ground to the required mesh size and activated under standard conditions. It contained 55% Al_2O_3 .

e) Aluminium-washed silica gel : This material was kindly donated by B P Research Station, Sunbury.

It was claimed to be entirely Bronsted acid in character.

f) silica gel : The material used was Hopkin and Williams M.F.C. silica gel sieved to 120 to 150 mesh. This was activated in the same manner as the aluminas.

These materials were compared by constructing the Freundlich adsorption isotherm for the adsorption of the copper chelate. As pointed out in the next section this isotherm is far from ideal in explaining adsorption processes, but in the present case, where the competition from the solvent is low, it may be applied.

The copper chelate was chosen since preliminary work on the adsorption isotherms had indicated that the adsorption of the chelate was simpler than that of the other chelates.

As can be seen from Fig. 1 the slopes of the isotherms are in all cases but one very similar. On the other hand, there is a definite progression in the quantity adsorbed per gram of adsorbent at a fixed equilibrium concentration, which correlates with the increasing Bronsted acid character of the surface. Alumina and silica/alumina show a high degree of

Lewis acid character (23, 24). The exception - the sodium washed alumina - may show ion exchange properties (25).

The presence of Bronsted acid sites, or proton donating sites, as distinct from Lewis acid or electron accepting sites, was further proved necessary for adsorption by investigating the adsorption of the 2-methyl-8-quinolinol chelates on other materials. These materials, reagent (fused) alumina, cellulose, calcium carbonate, boric acid, titanium dioxide, (rutile), sodium dihydrogen phosphate, and sodium orthophosphate, were ground to 200 mesh and oven dried at a temperature necessary to remove surface moisture but not decompose the materials. Using four different chelates, those of copper, chromium, iron, and nickel, it was found that some adsorption occurred in the case of cellulose, boric acid, and sodium dihydrogen phosphate, all possessing hydroxyl groups, when the chelates were added in benzene solution. No retention was noticed with any of the other, hydroxyl free, adsorbents.

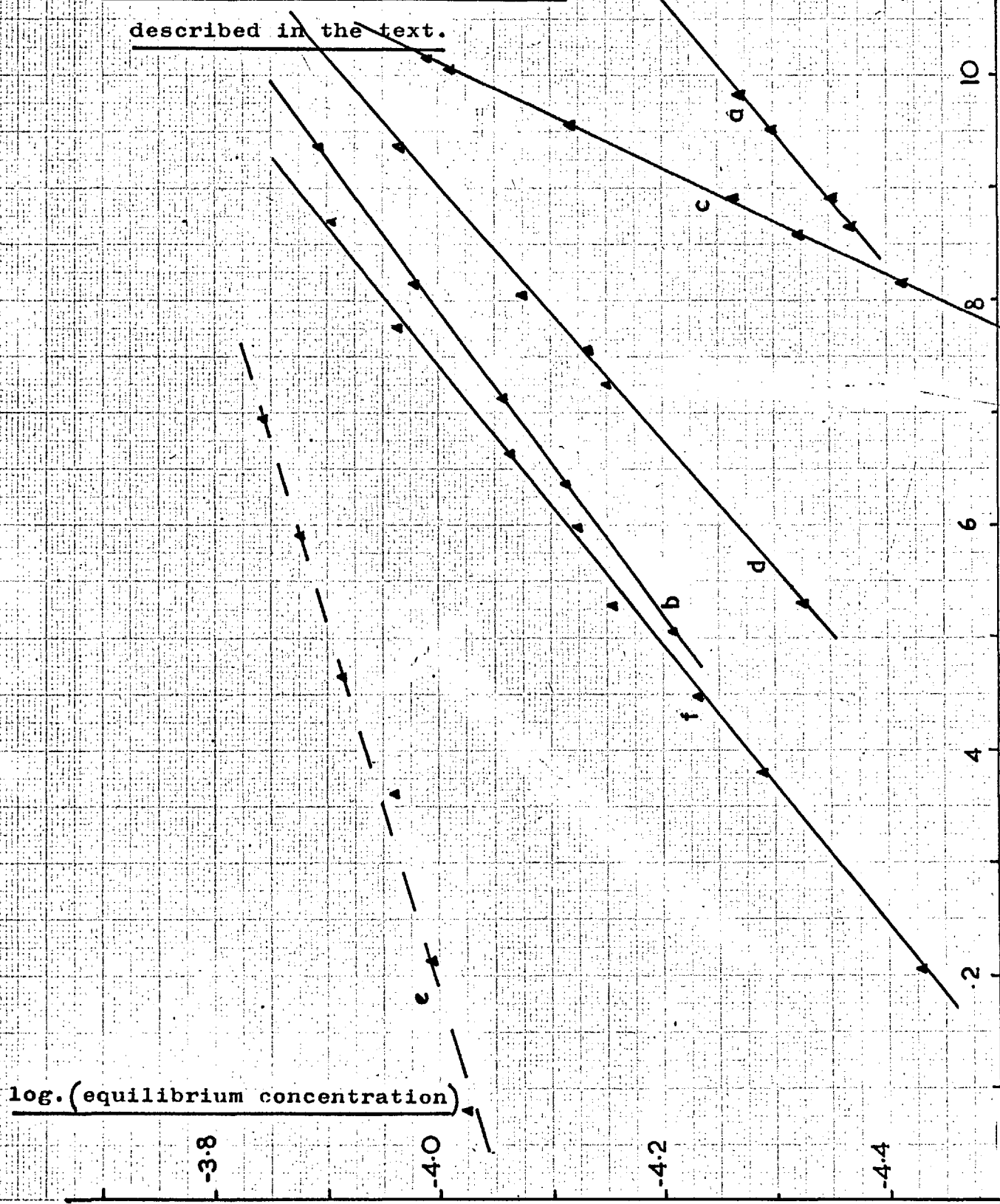
This evidence indicated that a hydroxyl group on the surface was necessary for adsorption, but raised the problem of the very great difference in adsorption characteristics between the parent reagent, eluted R_f 0.9 from benzene, and the

chelates, $R_f = 0$ in benzene. Many organic materials are separated by adsorption chromatography on silica gel and alumina, and in the case of aromatic molecules, it is postulated (26) that the adsorption is by surface hydroxyl bonding to the Π electrons. A polar grouping such as the hydroxyl group on the reagent would be expected to be an active site for adsorption purposes by proton donation to the surface forming a hydrogen bond (27, 28, 29). In the case of the metal chelates this obviously cannot occur and so some other mechanism of adsorption must be postulated.

FIG 1 25a
Adsorption of copper
2-methyl-8-quinolinol
on various adsorbents.

$\log(x_m)$
millimoles
per mg.

a,b,etc. refer to the adsorbents
described in the text.



CHAPTER 3

Adsorption of β -diketone
and aetioporphyrin chelates

In order to determine whether the chelate ring incorporating the metal atom was the most active site for adsorption, the chromatographic behaviour of two other types of chelate was investigated, and compared with the behaviour of the parent reagent, and the 2-methyl-8-quinolinol chelates.

The chelates chosen were a) of the β -diketone type, 2-thenoyltrifluoroacetone chelates were used, and b) chelates of aetioporphyrin (1).

With the β -diketone chelates, the formation of the chelate ring will have a greater effect on the electron distribution in the molecule than is the case with the 8-quinolinol chelates. On the other hand the aetioporphyrin molecule is such that the chelate ring structure is shielded by the ligand molecule, and, although there is a high degree of mesomerism enabling substituents to relay their electron withdrawing or donating capacities to the co-ordinating atoms, it is the structure of the reagent rather than the chelate ring that determines the structure and electron distribution in the chelate.

Therefore, it may be argued that if the chelate ring structure plays an important part in the adsorption process, then the chromatographic behaviour of the β -diketone chelates will be quite different from the behaviour

of the parent reagent, whereas the metalloporphyrins should be similar to the parent-aetioporphyrin.

Initially the acetylacetonone chelates of Fe (III), Cr (III), Cu (II), and Ni (II), were prepared, but since it was difficult to ensure that the chelates were not contaminated with reagent, the chelates of 2-thenoyltrifluoroacetone were prepared. These chelates were readily re-crystallised from chloroform and were used for all the subsequent chromatographic investigations. As the substituents, particularly the thenoyl group could affect the adsorption behaviour, the same acetylacetonone chelates were checked to see that their behaviour was similar to that of the thenoyltrifluoroacetone chelates.

The chelates were prepared according to the method of Berg and McIntyre (3), i.e. the reagent was added as a 10% solution in ethyl alcohol to a 10^{-2} M solution of metal ion buffered to pH 7.5 with sodium acetate. The complexes of copper (II), nickel (II), iron (III), and cobalt (II), precipitated immediately, that of chromium (III) was slow to form, 30 minutes at 65°C were required before an appreciable quantity of the solid was formed.

All of the chelates except that of chromium were strongly adsorbed on Type 'H' alumina from (1 + 1) benzene-chloroform solutions. The chromium complex was the least strongly adsorbed, - with high flow

rates (10 ml per minute) and a short column (5 cm) the majority of the chelate passed straight through the column. When the flow was slowed to 1 to 2 ml per minute the chromium chelate was adsorbed, indicating that the rate of adsorption was important, (cf. section II rate of adsorption of chromium 2-methyl-8-quinolinol on silica gel from benzene-chloroform mixtures). Continued elution with the solvent mixture served only to spread the adsorbed chelate bands without any movement of the band as a whole.

Most of the work carried out on 2-methyl-8-quinolinol chelates and their behaviour with various solvents was repeated with the β -diketone chelates with the following results:

As with the 2-methyl-8-quinolinol chelates hydroxyl containing adsorbents were necessary to retain the chelates on the column. The chromium chelate was again the least strongly adsorbed, it was not adsorbed on alumina from chloroform whereas all the other chelates were retained.

Elution with methylethylketone -water mixtures, causing in situ deactivation of the column, caused removal of the chelates from the alumina leaving some slight staining at the top of the column.

The copper chelate did not show the same sensitivity to solutions of the reagent as did the 2-methyl-8-quinolinol chelate.

Elution of the chelates, with some separation, was possible with 10% ethyl alcohol in chloroform. The bands were diffuse and a high degree of tailing was evident.

The parent reagent, 2-thienoyltrifluoroacetone, reacted with alumina to give some aluminium chelate in the eluant, but in contrast to the metal complexes was not adsorbed on silica gel even from (1 + 1) petroleum ether-benzene.

Adsorption of metalloporphyrin chelates

The chelates available for study were those of copper, nickel, and vanadium (vanadyl), together with a small quantity of the parent reagent aetioporphyrin I.

The three metal chelates were not adsorbed on alumina or on silica gel from benzene solution, neither was the parent reagent. All four compounds were adsorbed from 5% benzene in petroleum ether on to silica gel and eluted with 20% benzene in petroleum ether. With the metal chelates some staining was noticed at the top of the column, but since this did not re-occur when the eluted chelates were recovered and chromatographed it was assumed

that the initial chelate sample contained impurities.

The porphyrin derivatives appeared promising as far as possibilities of separation were concerned, but for other reasons, discussed below, they are not considered to be of great use from an analytical point of view.

Little further work was carried out on the porphyrin derivatives, but it was sufficient to indicate that qualitative separation of the three metal chelates could be achieved by elution with 20% benzene in petroleum ether from a silica gel column in the order copper, nickel, vanadyl.

Evaluation of data on β -diketone
and aetioporphyrin chelates

From the chromatographic data it appears that the aetioporphyrin chelates are the most 'organic' like in their behaviour, they show a reversible adsorption pattern basically similar to that of the parent reagent, but with differences according to the chelated metal. However, the porphyrin molecule can only accommodate four of the co-ordinate valencies of the metal, so many metals will be left with 'unsatisfied' bonding capabilities which may give rise to the formation of chelates incorporating solvent molecules under suitable conditions; for example, if alcohol or

pyridine were incorporated in the eluant mixture (30, 31, 32, 33).

A second difficulty that might arise is the formation of a bond between an electron-donating oxygen atom on the adsorbent surface and the partially chelated metal atom. Both of these difficulties could be tolerated, and perhaps overcome by deliberately forming a mixed ligand chelate, if the porphyrins were sufficiently attractive from an analytical point of view. However, the difficulty in quantitatively forming the porphyrin derivatives of a number of metals in an analytically acceptable time seems to be far from satisfactory solution, in spite of the advances made by Dempsey et al (34) and Lowe and Phillips (35).

Chromatographically, there is little to choose between the β -diketone chelates and the 2-methyl-8-quinolinol chelates. Both types are strongly adsorbed, the 2-methyl-8-quinolinol complexes more so than those of the β -diketone type.

The β -diketone chelates could be eluted by alcoholic solutions and also by in situ deactivation of the column, but not quantitatively. Further work might lead to the discovery of a solvent system where the degree of tailing was lessened, but other factors also cause the β -diketone to be less attractive

analytically. On alumina columns some decomposition definitely occurred, it was frequently possible, especially when the iron chelate was being studied, to identify the aluminium chelate in the eluant. On silica gel it appeared that some decomposition occurred if the chelates were allowed to remain on the column for any length of time. Also, although 2-thienoyltrifluoroacetone has been extensively used for the analysis of metals by solvent extraction procedures (36, 37, 38), there is ample evidence that many β -diketone chelates may readily accept up to two extra ligands (39). In solvent extraction systems this is unlikely to be a serious problem since two mutually saturated phases are used. In a chromatographic system, on the other hand, the composition of the eluant is variable and it would be difficult to ensure that the β -diketone chelate was entirely in one form. During the chromatographic investigations it was noticed that the position of the adsorption maximum varied with the composition of the eluant, indicating that adducts were being formed, and spectrophotometry was therefore unreliable as a quantitative tool.

Therefore it was decided to continue with the 8-quinolinol system, although the adsorption was extremely strong, because many of the 8-quinolinol

derivatives formed metal chelates readily and quantitatively, secondary complex formation was not a problem with these chelates, and the basic 8-quinolinol skeleton afforded many possibilities of altering the electron distribution over the molecule by the substitution of mesomeric and inductive groups. Substitution in the 5 and 7 positions in particular will have a direct effect on the oxygen in the 8 position, and hence on the chelate ring.

Further investigations were carried out as to the nature of the adsorption process, and from these results it was possible to predict the changes necessary in the adsorption system in order to achieve chromatographic separations.

For ease of presentation the rest of the chromatographic work is grouped in this section although the studies in Section II largely proceeded and partly ran concurrent with the work.

CHAPTER 4

The Chromatographic Behaviour of
Certain Substituted 8-quinolinol chelates

Preliminary studies of the adsorption of 2-methyl-8-quinolinol chelates by adsorption isotherm and kinetics studies indicated that the adsorption was not a simple process. Apparently there was a rapid initial adsorption of chelate that was irremovable from the surface, followed by a further adsorption that was less irreversible. This postulated mechanism, and the evidence for it, is discussed in Section II.

From a chromatographic point of view, the major problem was to weaken the initial adsorption sufficiently to make it reversible. The investigations with graded polarity solvents, and the comparison work carried out with thenoyltrifluoroacetone and aetioporphyrin chelates had indicated that the chelate ring area of the molecule had a definite bearing on the adsorption on alumina and silica gel. Also, since the adsorption was apparently to Bronsted acid type sites, it was the ability of the chelate ring or some part of it, to act as a centre of electron density that caused the strong adsorption. If this were so, substituents of an inductive or mesomeric

character that withdrew electrons from the nucleus would be expected to reduce the strength of the adsorption.

A series of 5, and 5:7 substituted 2-methyl-8-quinolinol compounds were prepared, 5:7 dibromo-, 5:7 di-iodo-, 5 iodo, and 5:7 di-nitro- 2-methyl-8-quinolinol. Attempts were made to prepare the 5-bromo- derivative, but not enough was isolated to prepare sufficient chelate for chromatographic purposes.

The halogen substituted derivatives were prepared by direct halogenation from 2-methyl-8-quinolinol by the appropriate method (40, 41). The 5:7 di-nitro was prepared by direct nitration (42). The yields of the preparations, particularly of the 5-iodo derivative were poor, but this was because large amounts of product were lost in the purification procedures since the quality of the final product was of more importance than the yield.

The metal chelates were formed by adding with vigorous stirring a 5% solution of the reagent in dioxane to a warm, 60°C, weakly acid pH 4-5, $10^{-2}M$ solution of the metal ion. The precipitates were filtered hot, washed with 10% dioxane in water and dried. It was found difficult to avoid co-precipitation of the reagent, and although the

dioxane-water wash reduced the amount of contamination, this method of precipitation was never completely satisfactory. Later some improvement was effected by precipitating the chelates from homogeneous solution (42).

The solubilities of the halogen substituted chelates were substantially smaller than those of the analogous 2-methyl-8-quinolinol chelates. The 5:7 di-iodo and 5:7 di-nitro chelates were at the best only sparingly soluble in benzene and chloroform, and some difficulty was experienced with precipitation in the chromatographic columns.

In chromatographic behaviour the 5-iodo-substituted chelates were similar to the unsubstituted 2-methyl-8-quinolinol chelates. The adsorption from benzene was strong, although there were some indications that the adsorption bond was wider for the same quantity of chelate.

With the di-halogen substituted derivatives the initial adsorption bond was three to five times as wide as for the same quantity of chelate. The 5:7 di-nitro chelates showed even weaker adsorption, although incipient precipitation made comparisons difficult. Prolonged elution with benzene caused the bands to spread, but, as in the case of the unsubstituted chelates, no movement of the band was

observed.

Once the chelates were adsorbed, however, the same effect as with the 2-methyl-8-quinolinol chelates were noticed i.e. the great difficulty in removing the adsorbed chelate from the column. Investigations were carried out to discover whether it was possible to use a higher dielectric constant solvent and pass the chelates through the column with no adsorption. If this could be done, then the polarity of the solvent could be slowly decreased, by the addition of benzene, for example, until adsorption was just occurring. The solubility of the chelates was a hindrance in this respect, precipitation frequently occurred particularly when alcohol was used as a solvent. It was never possible to prevent the adsorption of the chelates entirely, and, although pyridine enabled the bulk of the chelate to pass through the column, the adsorbent was still visibly coated with adsorbed complex.

Although unsuccessful in enabling chromatographic separations to be carried out, the halogen substituted chelates provided confirmation for two important points. The electron distribution in the molecule was important for the adsorption of the chelates. Also, as the substituents used were in the ortho and para positions relative to the

chelating oxygen atom it was likely that the point of attachment to the surface was the oxygen atom or the oxygen to metal bond.

This hypothesis was further confirmed by studying the chromatographic behaviour of the 6-chloro and 6-nitro derivatives of 2-methyl-8-quinolinol. In this case the substituents are in the meta position to the oxygen atom and so although they can exert an electron withdrawing effect on the nucleus this will be limited to the delocalised electrons and will not affect the 8 position to any great extent. Any difference in chromatographic behaviour would therefore be attributable merely to changes in solubility, especially in the 6-chloro compound. 6-chloro-2-methyl-8-quinolinol was prepared according to Schock's method (44) and 6-nitro-3-quinolinol was prepared by modification of the standard 2-methyl-8-quinolinol preparation (20) using 5-nitro-2-aminophenol in place of 2-aminophenol.

The chromatographic behaviour of the metal chelates of these derivatives was essentially similar to that of the 2-methyl-8-quinolinol chelates, with some minor differences attributable to different solubilities. The adsorption of the 6-nitro chelates was apparently stronger, probably

because of the reduced solubility. This apparent adsorption may not have been classical adsorption. The solubility of the 6-nitro compound was so low that precipitation on the adsorbent is very likely to have occurred.

CHAPTER 5

The Chromatographic Adsorption
of 8-quinolinethiol chelates

Reference to known data on intramolecular hydrogen bonding (45, 46) indicated that the most likely bond to form from the surface hydroxyl group was to the oxygen atom of the chelate. Therefore, it may be predicted that substitution of a chelating atom in the 8-position of the quinoline nucleus which was reluctant to partake in hydrogen bonding, but would still enable metal chelate formation to take place, would lead to a reagent whose chelates would exhibit chromatographic behaviour radically different from that of the 8-quinolinol chelates.

The obvious reagent to satisfy these conditions was 8-quinolinethiol, whose use as an analytical absorptiometric reagent has been the subject of several papers (47, 48, 49, 50, 51). It has also been studied as a gravimetric reagent (52).

For the initial investigation of 8-quinolinethiol, a quantity of the reagent was kindly supplied by Dr. J.A.W. Dalziel of Chelsea College of Technology. Later, when further quantities of the reagent and chelates were required the compound was prepared by the method of Lee (53). As the

reagent and its dihydrate are readily oxidized by ~~air~~, the benzoyl derivative which is quite stable to air, was prepared. Working quantities were kept as the sodium salt, which, if dry, is stable for several months (52).

The metal chelates were prepared according to the gravimetric procedures of Dalziel and Kealy (52). The chelates were filtered and dried under vacuum at 50°C, and then stored in stoppered tubes until required. The chelates were found to be stable to air oxidation as no impurities could be detected chromatographically after a period of six months. Benzene solutions of the dry chelates were stable for several days, no significant change in optical density was noticed over a period of a week, which was the longest period any solution was kept. Infra red investigations of the solid failed to show the presence of a sulphur to sulphur bond - the reagent on oxidation forms a disulphide (52). It has been reported (54) that solutions of the chelates in dioxane-water are readily oxidized.

The chelates were sparingly soluble in organic solvents, the nickel chelate in particular. The chelates are reportedly more soluble in bromobenzene, and bromoform (55), but no work has been done in these solvents. The limiting solubility of the nickel chelate was of the order of 10^{-5} M in hot benzene. The chromium, copper, and

iron, chelates showed adequate solubility ranging from 10^{-4} M to $>10^{-3}$ M.

The chromatographic investigations were limited by the careful choice of solvents necessary to avoid decomposing the chelates. Basic or aqueous solvents cause extensive decomposition in a matter of minutes. However, the chelates were quite stable in petroleum ether, benzene, chloroform, ethyl-acetate, ethyl, and methyl alcohols and n-butyl alcohol.

The chromatographic behaviour of the chelates were investigated on both silica gel, and alumina, in the limited range of solvents available, and, as expected, this behaviour differed markedly from that of the 2-methyl-8-quinolinol chelates.

Initial studies using silica gel as adsorbent showed that the chelates attained a state of dynamic equilibrium. All the chelates investigated, copper, chromium, nickel, iron, palladium, platinum, and mercury, are reversibly adsorbed on alumina from benzene, and may be eluted chromatographically with the same solvent.

Since the behaviour of these chelates appeared very promising, the chelates of nickel, iron, copper, and chromium, were chosen for further study. On silica gel all the complexes are adsorbed and may be eluted with benzene-chloroform mixtures. The

nickel chelate may be eluted with an R_f value of 0.7 by 5% chloroform in benzene. The chromium chelate is also elutable with an R_f value of 0.2. Both of these chelates elute as sharp bands with little or no tailing, so quantitative separation and recovery is readily obtainable. The copper and iron chelates showed a tendency to decompose on the column. The iron chelates eluted with an R_f value of 0.7 to 0.8, but only 60% was recovered. A green stain at the top of the column indicated decomposition.

On alumina, the chelates were quite stable, and all four chelates could be eluted by benzene with the following results:

Chelate	R_f value	Recovery (mean of 3 results)
Nickel	0.6	Quantitative
Copper	0.4	95%
Iron	0.7	97%
Chromium	0.1	Quantitative

Attempted Separations of 8-quinolinethiol chelates

All three chelates, nickel, iron, and copper, could be separated clearly from the chromium chelate. Attempts to separate nickel, iron, and copper, from each other were not successful, owing to the spreading of the iron band. The chelates may be eluted with higher R_f values by increasing

the di-electric constant of the eluant but this is at the expense of the degree of separation. This is as expected since increasing the di-electric constant will displace the equilibrium between the adsorbed chelate and the chelate in solution in favour of the solution, and so increase the possibility of band spreading owing to longitudinal diffusion (56), and nonequilibrium (57).

Ideally, the adsorption of the chelates should be carried out from petroleum ether/benzene mixtures, which increase the adsorption, and then eluted with increasing quantities of benzene.

The copper and iron chelates are separable in this manner, enabling the chelates of iron, copper, and chromium to be separated. Unfortunately, the solubility of the nickel chelate is so low that precipitation occurs in the column with this solvent system.

SECTION II

Physico - chemical studies of the
adsorption of 2-methyl-8-quinolinol chelates
on silica gel and alumina

CHAPTER 6

ADSORPTION ISOTHERMS

A study of the adsorption isotherms of the 2-methyl-8-quinolinol chelates is of prime importance, since a knowledge of the adsorption behaviour is not only of great help in mechanistic interpretations of the adsorption process, but may also be of use in predicting eluant concentration profiles and order of elution (58, 59).

In the case of the metal chelates studied, it was not possible to elute the chelates, so the interpretation of the isotherms has been confined to the mechanics of the adsorption, classification of the isotherms, and suggestions as to the orientation of the adsorbed molecules.

The isotherms were constructed by equilibrating benzene solutions of the metal chelate of known concentration with the solid adsorbent and measuring the 'equilibrium' concentration. This in itself was a difficult procedure, and, until it was realised that the kinetics of adsorption, described fully in the next chapter, affected the adsorption over many hours, the results obtained were very poor.

Later, however, by equilibrating the adsorbent and adsorbate solution for a time arbitrarily chosen as six hours, consistent results were obtained,

although a few spurious results were still obtained.

Experimental details and results

The isotherms shown, figs 2-5, are the composite results of two groups of results carried out on the same samples of adsorbent but with slightly different experimental conditions.

In the initial studies the isotherms were determined by equilibrating 50 ml. samples of the adsorbate solutions with 0.1g of adsorbent.

This was carried out in a ground-glass stoppered 150 ml. conical flask which was immersed in a water-bath at 25°C for six hours with periodic agitation. The initial and final concentrations were determined spectrophotometrically after suitable dilution and all points were determined in triplicate. Owing to the adsorbents being of a heterogeneous nature, and of the small sample size, points where the three values of the equilibrium concentration had a coefficient of variation of more than 5% were repeated. The coefficient of variation, 100 x standard deviation was used in order to allow mean value higher absolute errors with very high equilibrium concentrations where large dilution factors were necessary. The graphical points are the arithmetic mean of the accepted points.

The second group of results which were necessary to complete the isotherms, particularly in the lower equilibrium concentration regions, were determined by equilibrating 10 ml. samples of the adsorbate solutions with 0.07g of adsorbent in glass vials fitted with closely fitting polypropylene stoppers. The vials were kept in constant movement on a 'rolamix' machine in a room in which the temperature was controlled to ~~25.2~~ 25.2°C. This batch of results showed a higher degree of precision, indicating that variation in temperature affected the precision of the results less than evaporation of solvent and non-exposure of some of the adsorbent to the solution, which may be expected to be more serious in the first group of results.

Interpretation of the Adsorption Isotherms

Adsorption isotherms, particularly those of adsorption from solution, raise many problems in interpretation owing to the uncertainty of the nature of the adsorbent phase. However, it is possible to make certain deductions concerning the adsorption mechanism and the nature of the adsorbed phase from a study of the shape of the isotherms (60).

The isotherms shown in figs. 3-5 may be classified as type L3 according to Giles' classification (60), although aspects of high affinity are shown. In this case, dilute solutions are completely adsorbed and concentrations in the adsorbent may be appreciably higher than those in the solution.

The exception, fig. 2, the isotherm for the adsorption of copper, 2-methyl-8-quinolinol, belongs to the 'S' class of isotherms. In this case, as the equilibrium concentration of the solute is increased the adsorption apparently becomes easier, in contrast to the expected reduction in the number of sites available for adsorption. Giles et al (60) suggest that this type of 'co-operative' adsorption occurs when three conditions are fulfilled:- the solute molecule a) is monofunctional, b) has moderate intermolecular attraction, causing it to pack

vertically in a regular array in the adsorbed layer, and c) meets strong competition for adsorbate sites from molecules of the solvent or from another adsorbed species.

In this particular situation conditions a) and b) do not appear to be satisfied, and so a further explanation taking due account of the similarities and differences between the chelates is necessary.

The copper chelate is essentially similar to the other chelates, and so the mechanism of adsorption may be expected to be similar to that of the other chelates, it is extremely difficult to see how the point of attachment of the copper chelate could be the 4 or 5 position necessary for end-on orientation of the planar chelate. However, the copper chelate is unique among the chelates studied in that it readily forms a dihydrate. In fact precipitation from aqueous solution leads to the formation of $\text{Cu}(\text{C}_{10}\text{H}_8\text{NO})_2 \cdot 2\text{H}_2\text{O}$ (21). On drying at 110°C , the brown dihydrate readily changes to the green anhydrous chelate. During the determination of the adsorption isotherms saturated solutions of the chelate were prepared and it was noticed that the initial green precipitate readily turned brown if left exposed to air indicating ready re-conversion to the dihydrate.

Formation of the dihydrate may lead to a form of co-operative adsorption and hence an isotherm of the 'S' type in the following manner. Initially, there can be competition for hydrogen bonding sites between the metal chelate and traces of firmly bound water, either left in the activation procedure or adsorbed from the atmosphere during exposure while weighing. This competition may be reduced, and adsorption promoted, by some of the chelate molecules associating with the water to form the chelate dihydrate either before, or during, adsorption. A similar mechanism has been proposed for the adsorption of methanol on cellulose (61). The other metal chelates cannot form such a dihydrate and no such enhancement of the adsorption may be expected. A study of the behaviour of the cobalt chelate would be interesting as this metal forms an anhydrous chelate and also a monohydrate.

This proposed mechanism for the adsorption of the copper chelate also explains the larger quantity of chelate adsorbed at the point of saturation of the surface relative to that obtained with the other chelates (Table 1).

The most significant difference between the L Type of isotherm and the S type is that the former show a point of inflexion, or, as in the case of the chromium chelate on alumina, a plateau, followed by

a further rise in the amount adsorbed with increasing equilibrium concentration.

If it is assumed that the adsorbate phase consists entirely of the solute, as it is in this case where the solvent has a very much lower affinity for the adsorbent than does the solute, then it may be assumed that this point corresponds to Brunauer's point B (62). Thus, this point represents the condition in which all possible adsorption sites on the original surface are filled, and adsorption must now only take place on new surfaces.

This completion of a 'monolayer' on the surface has frequently been used as the basis of surface area determinations (63, 64, 65), but the assumption that this point implies the complete coverage of the surface with a close packed layer of single molecules is not completely justifiable in solution, and the use of the BET isotherm equation (62) to describe mathematically the adsorption isotherm is in most cases completely unjustifiable theoretically (66).

The rise in the isotherm after the attainment of 'monolayer' coverage is attributed to adsorption on a fresh surface that has developed during the adsorption process (61). There are several possible ways in which this may occur, a) on part of the original surface, exposed by re-orientation of the adsorbed layer, as is noticed with the adsorption of

phenol from water on to graphite (67), b) penetration of the solute into new regions of the adsorbate (61), c) the formation of condensed layers on top of the first monolayer, as with phenyl-azo-2-naphthol on graphite (67), water on alumina (68), and d) successive adsorption on different types of site (60, 69, 70).

Recently it has been proposed that a rise not leading to a limiting value of adsorption is indicative of incipient crystallisation of the solute (71).

With the metal chelates it is not possible to state categorically which of these mechanisms takes place. However, from the kinetic studies it appears that the adsorption takes place in two successive steps showing different affinities for the metal chelate, while within each stage the adsorption takes place on an apparently 'homogenous' surface. This strongly suggests that the second adsorption step takes place on top of chelate already adsorbed rather than on further areas of the original surface. In this latter case the adsorption would be expected to become increasingly difficult as adsorption was forced to take place on more remote areas of the surface. Furthermore, X-ray powder studies of the adsorbed material (cf Chapt. 9) suggest that crystallisation of the solute in the vicinity of the adsorbent is possible.

Calculation of apparent surface areas

Although it is not possible to obtain surface areas by adsorption from solution which compare exactly with surface area measurements obtained by gas adsorption, β nitrophenol adsorption from benzene appears to give results which are reasonably reliable. Table I shows the quantity adsorbed per gram and the calculated surface areas for the adsorption of the metal chelates and β nitrophenol on silica gel and alumina. The batches of adsorbent used for the adsorption isotherms and kinetics were of a smaller size (<200 mesh) than those used for the chromatographic studies.

The areas of the metal chelate molecules were taken as the smallest rectangle which would enclose a projection of a model of the chelate and are open to errors of 10% to 20%. The area taken for β nitrophenol is that quoted by Giles (61).

As can be seen from the table, the apparent surface areas agree quite well with the areas calculated from β -nitrophenol adsorption, except those calculated from the adsorption of the chromium chelate which indicate 50% to 60% coverage. It is difficult to explain why this is so, possibly, the inner orbital character of this chelate reduces the availability of electrons for hydrogen bonding

so sites of higher 'affinity' for electron pairs are necessary to bring about the adsorption. This would reduce the number of sites available on the surface.

TABLE 2

Apparent surface areas of silica and alumina

Adsorbate	Adsorbent	Estimated Adsorbate Area	Quantity and Adsorbed/g	Apparent Surface Area
nitrophenol	Silica gel	15A ^{o2}	1.1x10 ⁻⁴ moles	108.4x10 ³ cm ² per g.
	Alumina	15A ^{o2}	1.0x10 ⁻⁴ moles	90.4x10 ³ cm ² per g.
Copper 2-methyl-8-quinolinol	Silica gel	150A ^{o2}	1.4 10 ⁻⁵ moles	133 cm ² per g.
	Alumina	150A ^{o2}	1.0 10 ⁻⁵ moles	94 cm ² per g.
Nickel 2-methyl-8-quinolinol	Silica Gel	135A ^{o2}	1.1x10 ⁻⁵ moles	89.7x10 ³ cm ² per g.
	Alumina	135A ^{o2}	0.9x10 ⁻⁵ moles	73.3x10 ³ cm ² per g.
Ferric 2-methyl-8-quinolinol	Silica Gel	130A ^{o2}	1.3x10 ⁻⁵ moles	102x10 ³ cm ² per g.
	Alumina	130A ^{o2}	0.9x10 ⁻⁵ moles	70.6x10 ³ cm ² per g.
Chromium 2-methyl-8-quinolinol	Silica Gel	130A ^{o2}	0.8x10 ⁻⁵ moles	65.5x10 ³ cm ² per g.
	Alumina	130A ^{o2}	0.7x10 ⁻⁵ moles	62.7x10 ³ cm ² per g.

FIG 2

Adsorption of copper 2-methyl-8-quinolinol

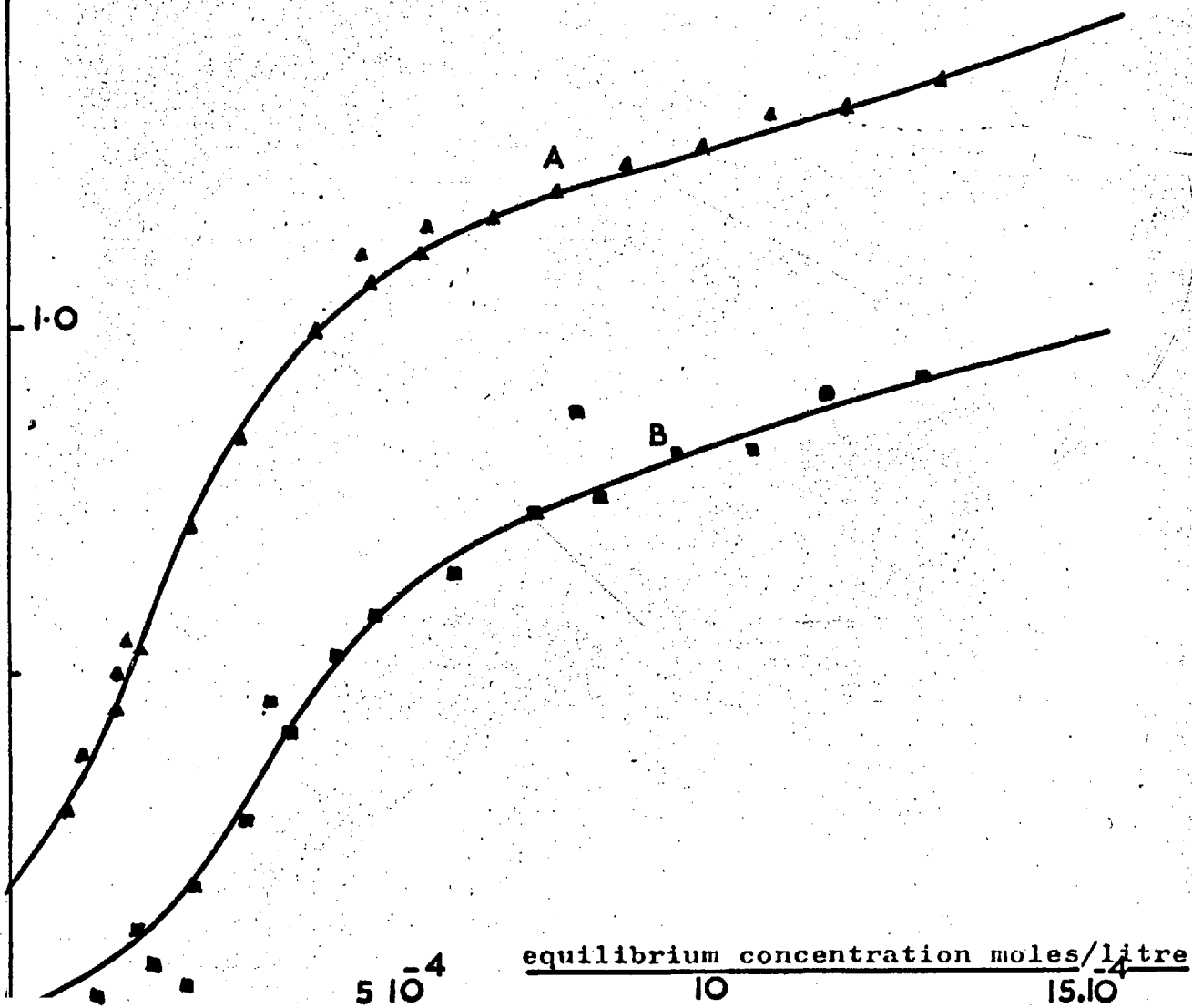
from benzene 55

A. On silica gel.

B. On alumina.

amount adsorbed

$2.0 \cdot 10^{-5}$ moles per gram.



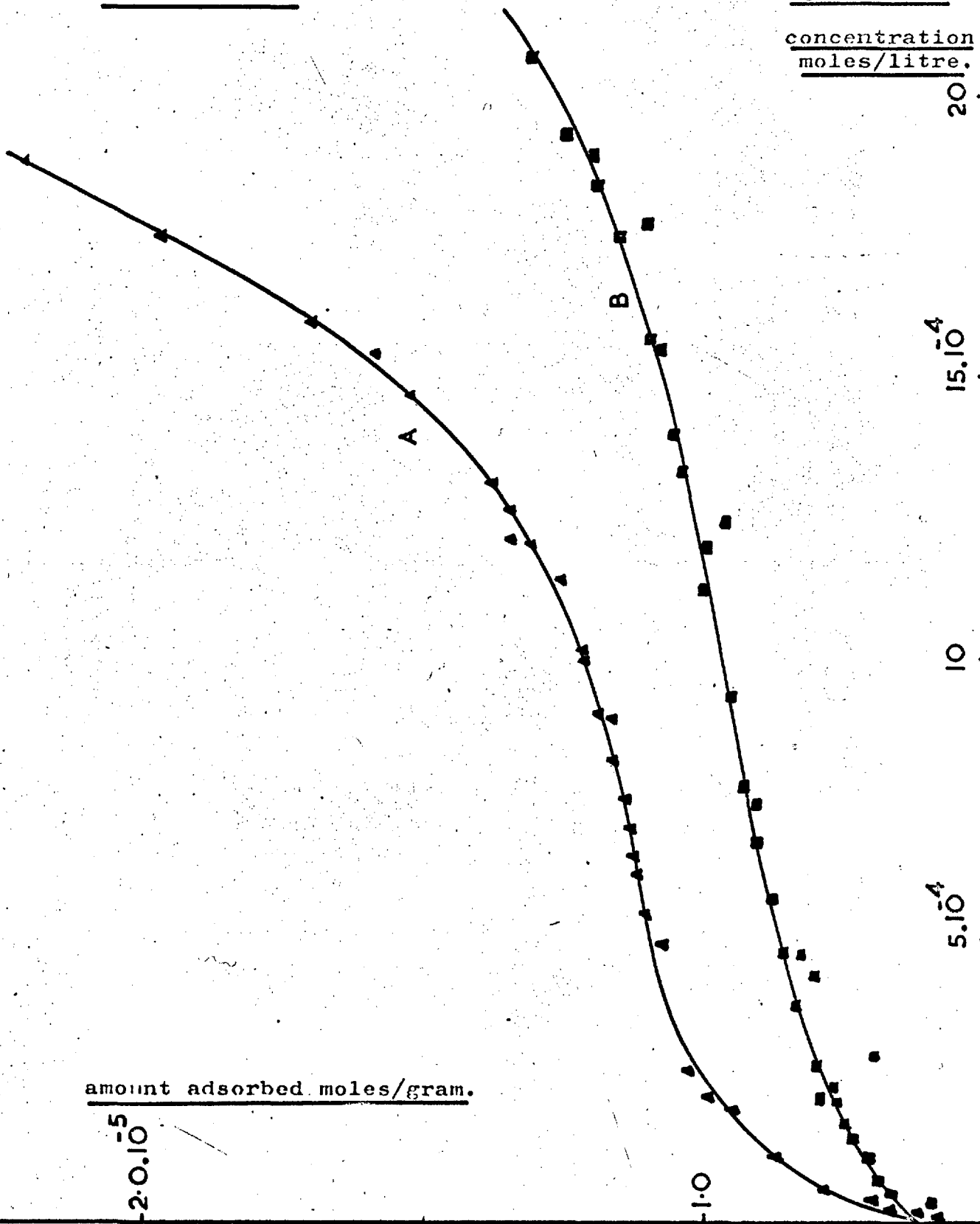
from benzene. 56

A. On silica gel.

B. On alumina.

FIG 3

Equilibrium
concentration
moles/litre.



amount adsorbed moles/gram.

2.0.10⁻⁵

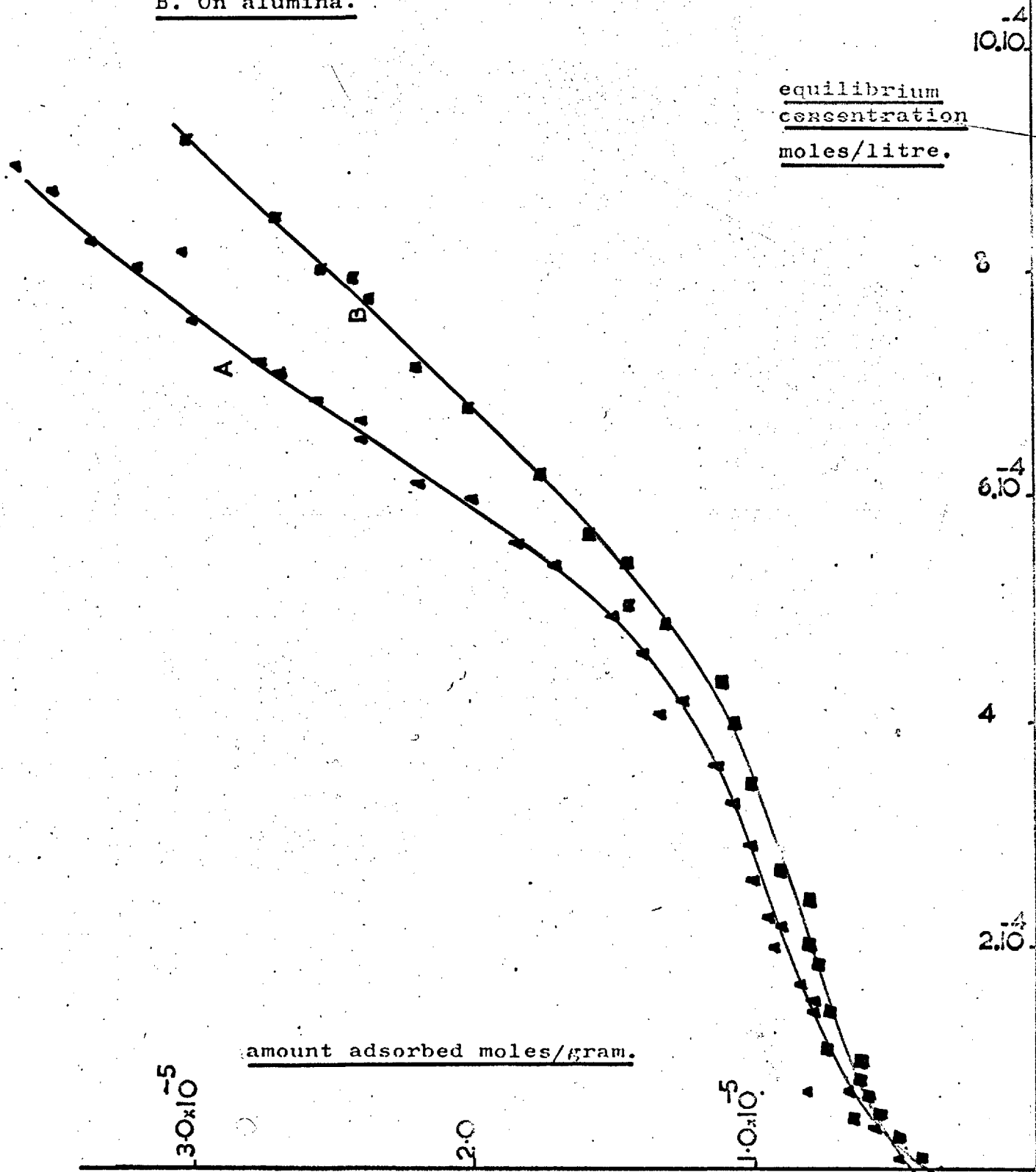
1.0

5.10⁻⁴

10

15.10⁻⁴

20

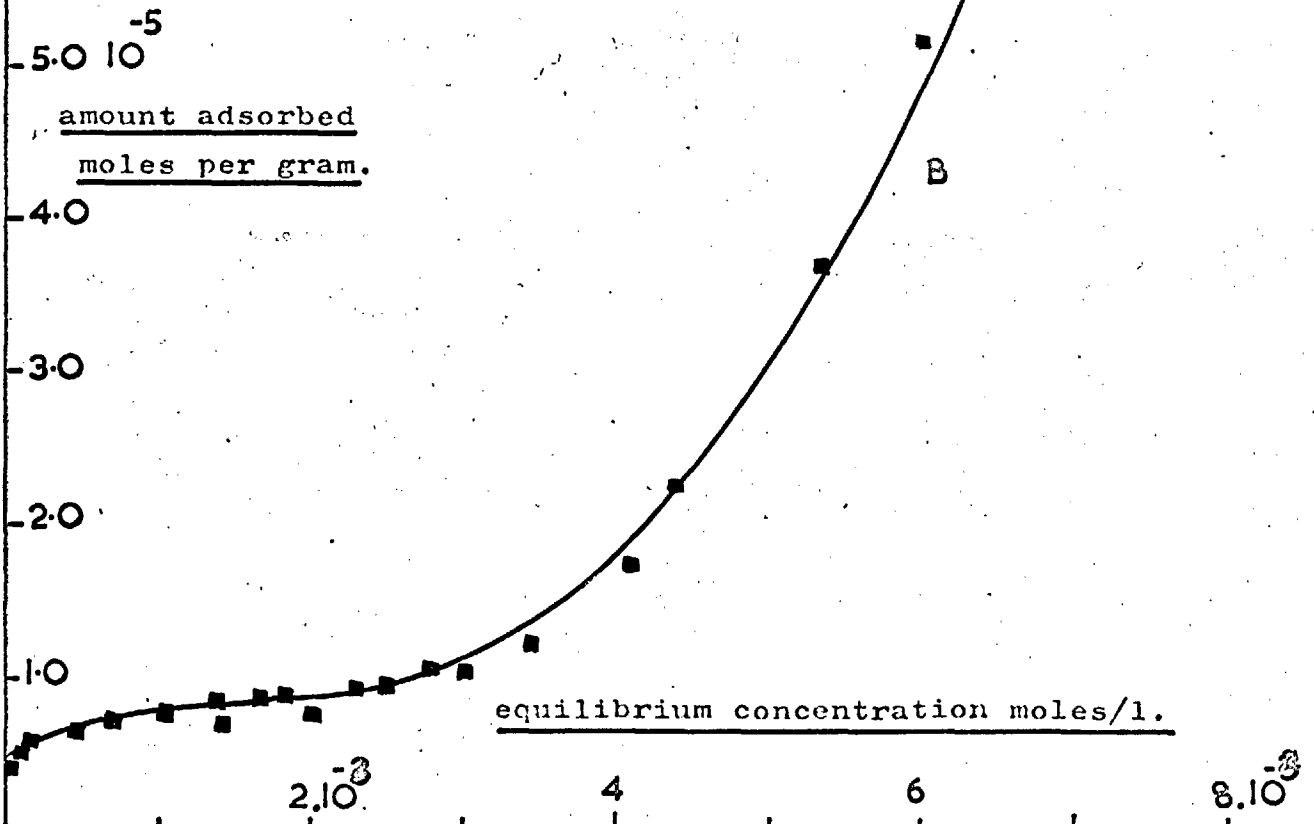
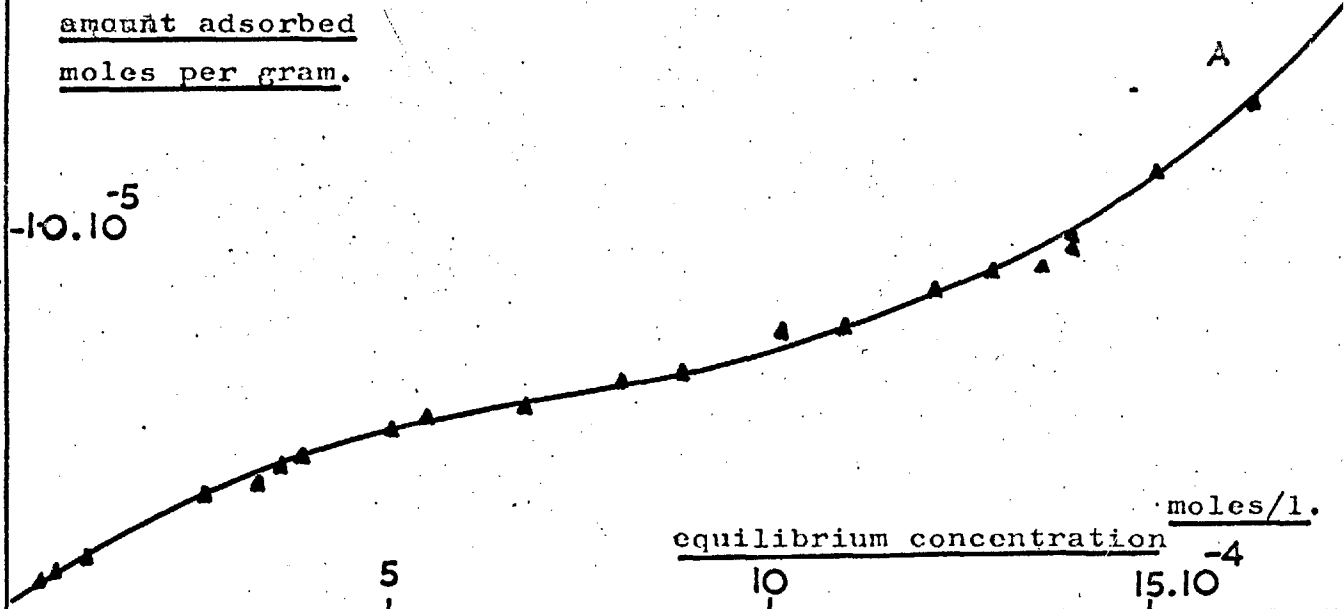
Adsorption of nickel 2-methyl-8-quinolinolfrom benzene.A. On silica gel.B. On alumina.FIG 4

Adsorption of chromium 2-methyl-8-quinolinol
from benzene

A. On silica gel.

B. On alumina

FIG 5



CHAPTER 7

KINETICS OF ADSORPTION

As stated in the previous chapter, the kinetics of adsorption appeared to control the adsorption over long periods of time. Accordingly, kinetic investigations were carried out in order to discover the basis of this time dependence.

The initial experiments were carried out on a batchwise basis. Standard volumes of chelate solution were equilibrated with accurately weighed adsorbent samples for measured periods of time. Fig. 6 shows a plot of quantity adsorbed per gram of adsorbent against time, and indicates an apparent rate change when $0.35 \cdot 10^{-5}$ moles of chelate had been adsorbed. Surface area measurements determined by p-nitrophenol adsorption from benzene on the sample of alumina gave an area of $(30.05 + 1.2) \times 10^3 \text{ cm}^2/\text{g}$. Geometric calculations of the expected surface area from known sieve sizes give $5 \times 10^3 \text{ cm}^2/\text{g}$ as the estimated area. Obviously, owing to the nature of the material and methods of measurements, close agreement between the measured area and estimated area cannot be expected.

The quantity adsorbed at the apparent rate change, 0.35×10^{-5} moles, corresponds to a fractional coverage of 0.9, whereas the maximum quantity adsorbed,

0.45×10^{-5} moles, corresponds to a fractional coverage of 1.4. This indicates that there could be different factors controlling the adsorption in the two stages 1) up to 'monolayer' coverage and 2) during 'multilayer' coverage.

The batchwise kinetics studies having provided some interesting results it was thought desirable to devise an improved method of determining the concentration - time relationships during adsorption. The major requirements for obtaining reliable values for rate constants were: a) the solute concentration should be monitored continuously, and b) stirring or agitation sufficient to keep silica gel or alumina evenly dispersed in the chelate solution, c) good temperature control.

The experimental assembly finally chosen was based on a Unicam SP600 spectrophotometer which was the only one that could be readily adapted for kinetics purposes. The choice of instrument was largely governed by the stirring requirements which would have to be very vigorous in order to keep the solid adsorbent dispersed in the solvent. Agitation by vibration was not feasible, and the use of a gas jet would raise evaporation problems. Accordingly, a simple glass de Witt stirrer was chosen as the most suitable means of stirring, and the Unicam as the most suitable

instrument available, as it was the only one in which the cell carriage position was fixed relative to the instrument lid (see Fig. 21). The cells were contained in a thermostatted cell carriage which was maintained at the desired temperature by water circulated from a water bath the temperature of which could be controlled to $\pm 0.1^{\circ}\text{C}$.

Evaporation of the solvent was minimised by covering the top of the cell carriage with a neoprene sheet and choosing cells such that they were a close fit to the sheet.

The choice of particle size for the adsorbent required the balancing of two competing factors: the necessity for a large surface area to provide measurable quantities of adsorbed chelate, and the necessity for the adsorbent to settle quickly when the stirring was stopped for the purpose of making optical density measurements on a completely clear solution. Samples of particle size 75 to 90 μ (BS sieve size 170 - 200 mesh) were found to give the optimum results.

Use of a glass stirrer inserted an obstruction in the light path which hindered measurement of the solute concentration. Initially compensation was made by calibrating the optical density against solute concentration with the stirrer in position in a marked

orientation. The wave length chosen for the measurement of solute concentration was such that the interference of the stirrer was minimised. In later measurements it was found possible to re-arrange the stirrer guide and drive to enable the stirrer to be raised out of the light path. All of the kinetics results shown, except for the adsorption of chromium 2-methyl-8-quinolinol on alumina from benzene - chloroform mixtures were determined by the latter method.

Throughout the kinetic determinations the stirrer speed was maintained at 500 rpm which was found sufficient to keep the adsorbent suitably dispersed. The cells used were of 4 cm path length in order to allow the use of $10 \text{ ml of a } 10^{-4} \text{ M}$ solution. This raised problems in measuring the concentration spectrophotometrically (owing to very high optical densities), and so optical density measurements were made away from the peak absorption in regions, determined separately for each chelate, where the extinction coefficient was low enough for optical density measurements of the solution to be made.

Treatment of experimental results:

The kinetics of adsorption processes are extremely difficult to explain in many cases, and literature surveys lead to the conclusion that this is a field in which there is a great need for research. In the

field of gaseous adsorption much less attention has been paid to the kinetics of the adsorption processes than to the state of the equilibrium ultimately attained. The most widely used kinetics equation for gas adsorption is the Elovich equation (72):-
 $q = a \ln(bt + 1)$, where q is the quantity adsorbed in time t : a and b are proportionality constants specific to a particular system. A similar equation may be devised theoretically (73) by assuming that the activation energy necessary for adsorption increases linearly with surface coverage. The validity of many of the proposed models of adsorption processes (74, 75, 76) must however be considered dubious as the authors' intentions appeared to be to justify a posteriori this equation.

Recently it has been suggested that this equation is at best a general solution which will only give very approximate solutions to adsorption processes (77).

The kinetics of adsorption from solution is an even more neglected field. In most cases investigations have been designed to determine the times necessary for equilibration and the fitting of rate data even to empirical equations is rare.

For the systems in which the kinetics of adsorption have been studied, fatty acids on silica gel, (78) polymers on charcoal, (79) and sodium

dodecylbenzenesulphonate on cotton (80), it appears that the rate of adsorption is a function of the distance from equilibrium.

$$\frac{da}{dt} = f(a_a - a_t) \quad - (1)$$

where a_a = amount adsorbed at equilibrium

a_t = amount adsorbed at time t.

In the particular form used by Swearingen and Dickinson (77) for fatty acids from aqueous solutions on to silica gel the equation becomes:

$$kt = 2.303 \log\left(\frac{a_a}{a_a - a_t}\right)$$

where k is the rate constant.

However, the adsorption isotherms obtained from these systems are all of the most simple type where the amount adsorbed increases with increasing equilibrium concentration until a limiting value, corresponding to complete coverage of the surface is reached. Further increase in the equilibrium concentration does not bring about further adsorption.

Obviously with this type of system the number of sites available for adsorption decreases as the surface coverage increases, and hence the probability of a molecule with sufficient energy for adsorption striking an adsorption site, and thus the rate constant, must be proportional to the number of free sites remaining.

With multimolecular adsorption taking place, it

is more difficult, new adsorption sites are being produced as the coverage of the initial surface increases. Hence as the probability of adsorption on the initial surface approaches zero, so the probability of adsorption on the 'new' surface approaches a maximum.

This would seem to indicate that equation (1) cannot be applied to a multistage system, unless the adsorption takes place in successive stages on the same surface.

This is a very unlikely occurrence which will be limited to a few special cases where the adsorbate is first adsorbed in a parallel orientation, and then, on completion of a monolayer, re-orientates to a perpendicular orientation, e.g. the adsorption of polystyrene from methyl ethyl ketone on to charcoal in the presence of water (81). With most multimolecular adsorption processes, the adsorption of the multilayer takes place on an adsorption site with different characteristics to those of the initial surface sites, and thus the activation energies required, and the rate constants, will differ from the rate constants for adsorption on the initial surface.

In the case of the metal chelate adsorption, the quantity adsorbed in the multilayer does not reach a limiting value, at least over the concentration

range investigated, and quantities of the order of five times the monolayer value may be adsorbed, and so it is impossible to give any meaning to the amount adsorbed at infinite time. It is not possible to obtain a_{∞} from the adsorption isotherm with a known equilibrium concentration in the liquid phase because, as was pointed out in the last chapter, the isotherms determined show the state of adsorption after six hours whereas it is known that adsorption, particularly of the iron chelate, is incomplete after eighteen hours, especially when equilibrium concentrations greater than are necessary to form the 'monolayer' are used.

Accordingly, it must be concluded that none of the published kinetic equations used to date for adsorption processes is applicable to more than a narrow range of systems, and that each particular system must be interpreted according to its characteristics.

Most reaction processes in chromatography follow a rate law that is first order with respect to solute concentration, and as a simplification, the total process of adsorption may be thought of as consisting of two steps:-

a) diffusion through the solution to the surface of the adsorbent and b) adsorption at the surface.

One of these two steps will be rate determining, and unless the adsorption is a chemisorption process it is expected that the rate of adsorption is much faster than the rate of the diffusion processes (32).

Therefore the rate equation may be expressed as:

$$- \frac{dc}{dt} = f [ck] \quad \text{where } c = \text{solute concentration} \\ k = \text{rate constant}$$

Bearing in mind the probable 1st order dependence of the adsorption a solute concentration, the rate equation may be expressed in the form:

$$- \frac{(N_0 - N)}{t} = k (N_0 - N) \quad \text{where } N_0 = \text{orig no. of moles per unit volume} \\ N = \text{no. of moles adsorbed per unit volume}$$

This may be integrated from $t = 0$ to $t = a$ giving:

$$k = \frac{2.303}{t} \log \left(\frac{N_0}{N_0 - N} \right)$$

Therefore if the adsorption process is of first order a plot of $\log (N_0 - N)$ versus time should be a straight line of slope $-\frac{2.303}{k}$

The kinetics results were therefore plotted in this manner, with interesting results; as suspected from the batchwise kinetics, a single rate constant was not sufficient to describe the adsorption from a clean surface to a multimolecular surface, and, by fitting the experimental data to 1st and higher order equations,

it was found that the data could best be fitted by assuming two successive first order reactions, one up to 'monolayer' coverage and the second for the formation of the multilayers. The experimental data is presented in Figs. (8 - 20) as $\ln(N_0 - N)$ versus time. The rate constants, and quantities adsorbed at the intersection of the two lines, are tabulated at the end of the chapter.

By application of the Arrhenius' equation:

$\ln k = \frac{-E}{RT} + \text{constant}$, the energy term, E , may be evaluated for each rate process provided that E , the activation energy as it is usually called, is not temperature dependent. In the present work the temperature range covered is so small that any temperature dependence of E would probably be insignificant.

Significance of E

In adsorption processes, the activation energy term is usually referred to as the 'activation energy of adsorption', but its significance depends on which stage in the many processes leading to adsorption is the formation of the activated complex. If the surface is involved in this stage, as the terminology suggests, then, owing to its heterogeneous nature, the simple rate equations must be modified. The surface may be thought of as a finite number of sites which

are not necessarily identical and which require varying activation energies for adsorption to occur.

Qualitatively, it may be expected that the frequency of collision between an adsorbate molecule, with or without the required activation energy, and the surface site, will decrease with increasing surface coverage, provided that the solution concentration remains reasonably constant, and also, since at any time the proportion of molecules having the required activation energy will be greater the lower the activation energy is, the activation energy necessary for adsorption will increase with increasing surface coverage.

Consequently the normal first order rate equation of form:

$$-\frac{dc}{dt} = kc \quad \text{where } c \text{ - concentration}$$

$$k \text{ - rate constant}$$

$$= A \exp\left(\frac{-E}{RT}\right)$$

would have to be modified.

Taking that at time $t = 0$ $k = A_0 \exp\left(\frac{-E_0}{RT}\right)$ and at time t , corresponding to a fractional coverage of θ_e :

$$k = A_0 f (1 - \theta_e) \exp\left(\frac{-E_0 f^1 (1 + \theta_e)}{RT}\right)$$

Therefore the rate of loss of adsorbate from the solution, and hence the rate of adsorption will be

$$\text{given by: } -\frac{dc}{dt} = c \left[A_0 f (1 - \theta_e) \exp\left(\frac{-E_0 f^1 (1 + \theta_e)}{RT}\right) \right]$$

Obviously calculation of activation energies from this equation is impossible owing to lack of knowledge of the form of the two functions, and it must be concluded that there is a great need for research into the kinetics of adsorption from solution on to known surfaces where there is a possibility of calculating the probability of adsorption from the known geometric distribution of the adsorbent sites.

Fortunately, in the case of the metal chelates the surface appears to have but a limited effect. To a good approximation the rate of adsorption is independent of surface coverage. This implies that the activation step involves the solution, either in the bulk phase or the 'stagnant' layer adjacent to the surface rather than the surface itself. As may be seen from Tables 2 - 3 the activation energies are low, implying that the adsorption is probably by a diffusion controlled mechanism. This is supported by the change in rate constant with the change in rate of stirring. Fig. 22 shows the adsorption of ferric 2-methyl-8-quinolinol onto silica gel from benzene. The 'low stirring' was the minimum stirring speed necessary for keeping the silica gel dispersed, the high stirring the maximum stirring speed possible with the apparatus.

Entropy of Activation

Knowing the activation energy, the entropy of activation may be calculated as follows:-

The specific reaction constants i.e. the rate constant k_r is related to the free energy of activation $\Delta G^{o\pm}$ by

$$k_r = \frac{kT}{h} \exp \left(\frac{-\Delta G^{o\pm}}{RT} \right) \quad \text{where } k = \text{Boltzmann's constant}$$

$$h = \text{Planck's constant}$$

$$\text{But } \Delta G^{o\pm} = \Delta H^{o\pm} - T\Delta S^{o\pm}$$

$$\text{Therefore } k_r = \frac{kT}{h} \exp \left(\frac{\Delta S^{o\pm}}{R} \right) \exp \left(\frac{-\Delta H^{o\pm}}{RT} \right)$$

Taking logarithms

$$\log k_r = \log \left(\frac{kT}{h} \right) + \frac{\Delta S^{o\pm}}{R} \log e - \frac{\Delta H^{o\pm}}{RT} \log e$$

$$\text{But } k_r = A \exp \left(\frac{-E_a}{RT} \right)$$

$$\text{Therefore } \frac{\ln k_r}{T} = \frac{E_a}{RT^2} = \frac{\Delta H^{o\pm} + RT}{RT^2}$$

$$E_a = \Delta H^{o\pm} + RT$$

Specimen Calculations

Calculation of Rate Constants

The slope of the semilogarithmic plot of time vs log (solute concentration) is related to the rate constant as follows:-

$$-\frac{2.303}{k} = \left(\frac{\text{time}_2 - \text{time}_1}{\log c_2 - \log c_1} \right)$$

$$\text{Therefore } k = - \left(\frac{\log c_2 - \log c_1}{\text{time}_2 - \text{time}_1} \right) 2.303$$

For the adsorption of ferric 2-methyl-8-quinolinol on silica gel at 25°C

$$k = - \frac{[\log(7.00 \cdot 10^{-5}) - \log(7.90 \cdot 10^{-5})]}{[39.60]} \cdot 2.303$$

$$= \frac{5.07 \cdot 10^{-5} \text{ sec}^{-1}}{}$$

Calculation of activation energy:

From the Arrhenius equation:

$$\ln k = - \frac{E}{RT} + \text{constant}$$

The slope of a plot of $\ln k$ is $\frac{1}{T} = -\frac{E}{R}$

$$\text{Therefore Slope } \left(\frac{\log k}{\frac{1}{T}} \right) = \frac{-E}{2.303R}$$

For ferric 2-methyl-8-quinolinol:

$$\text{Slope} = - \frac{E}{2.303 R}$$

$$\text{Slope} = - \left[\frac{\log(1.21 \times 10^{-4}) - \log(3.54 \times 10^{-5})}{[0.03 \times 10^{-2}]} \right]$$

$$\text{Therefore } E = 2.30 \times 1.98 \times \text{slope}$$

$$= 8.1 \text{ kcal/mole}$$

The Entropy of Activation may be calculated from the equation:-

$$\log(kr) = \log\left(\frac{kT}{h}\right) + \frac{\log e}{R} \Delta S^{\ddagger} - \frac{\Delta H^{\ddagger}}{RT} \log e$$

For ferric 2-methyl-8-quinolinol

$$\Delta H^{\ddagger} = E_a - RT$$

$$= 8113 - 59 = 7523$$

$$\Delta H^{\ddagger} \log e = \frac{7523}{590} \times 0.4343 = 5.54$$

$$\text{Therefore } \log \Delta S^{\ddagger} = \left[\frac{7.253 + 4.250}{0.2186} \right] = - \underline{\underline{52.5 \text{ eu}}}$$

SUMMARY OF KINETICS RESULTS:

TABLE 3

Ferric 2-methyl-8-quinolinol on Silica Gel

Temperature	Rate Constant Stage 1	Rate Constant Stage 2	Quantity Adsorbed at Intercept
20°C	5.07×10^{-5} sec ⁻¹	1.56×10^{-5} sec ⁻¹	0.8×10^{-5} Moles/g
25°C	5.62×10^{-5} Sec ⁻¹	2.48×10^{-5} sec ⁻¹	0.7×10^{-5} Moles/g
30°C	8.81×10^{-5} sec ⁻¹	2.65×10^{-5} sec ⁻¹	0.6×10^{-5} Moles/g
35°C	1.00×10^{-4} sec ⁻¹	2.62×10^{-5} sec ⁻¹	1.1×10^{-5} Moles/g
40°C	1.29×10^{-4} sec ⁻¹	4.53×10^{-5} sec ⁻¹	0.85×10^{-5} Moles/g
45°C	1.50×10^{-4} sec ⁻¹	5.92×10^{-5} sec ⁻¹	0.6×10^{-5} Moles/g

Activation Energies: Stage I 8.1 Kcal mole⁻¹

Stage II 9.80 Kcal mole⁻¹

Quantity adsorbed at intercept $(0.78 \pm 0.19) \times 10^{-5}$ moles/g; which corresponds to a coverage factor of 0.64 by reference to the 'monolayer' value from the adsorption isotherm.

TABLE 4

Nickel 2-methyl-8-quinolinol on Silica Gel

Temperature	Rate Constant Stage 1	Rate Constant Stage 2	Quantity Adsorbed
20°C	6.82×10^{-5} sec	2.36×10^{-5} sec	1.3×10^{-5} moles/g
30°C	1.02×10^{-4} sec	3.60×10^{-5} sec	1.1×10^{-5} Moles/g
40°C	1.53×10^{-4} sec	5.49×10^{-5} sec	0.8×10^{-5} Moles/g

Activation Energies: Stage I 7.33 Kcal

Stage II 8.33 Kcal

Quantity adsorbed $(1.07 \pm 0.25) \times 10^{-5}$ moles/g;

which corresponds to a coverage factor of 0.97.

TABLE 5

Copper 2-methyl-8-quinolinol on Silica Gel

Temperature	Rate Constant	Rate Constant	Quantity Adsorbed at interception
10°C	3.44×10^{-5}		
25°C	6.80×10^{-5}		
35°C	1.05×10^{-4}	4.96×10^{-5}	0.41×10^{-5} moles/g
40°C	1.34×10^{-4}	6.20×10^{-5}	0.46×10^{-5} moles/g

Quantity adsorbed: $(0.425 \quad 0.02) \times 10^{-5}$ Moles/g

Activation Energy: $8.49 \text{ Kcal mole}^{-1}$

Quantity adsorbed corresponds to a coverage factor of 0.98. The silica gel used for the kinetics of adsorption of the copper and chromium chelates, except chromium 2-methyl-8-quinolinol at 25°C, had a surface area of $36.1 \times 10^3 \text{ cm}^2/\text{g}$ by *p*-nitrophenol adsorption.

TABLE 6

Chromium 2-methyl-3-quinololinol on Silica Gel

Temperature	Rate Constant Stage 1	Rate Constant Stage 2	Quantity adsorbed at intersection
25°C	9.42×10^{-5}	4.20×10^{-5}	1.1×10^{-5} moles/g
30°C	1.37×10^{-4}	5.81×10^{-5}	0.25×10^{-5} moles/g
35°C	1.47×10^{-4}	7.18×10^{-5}	0.25×10^{-5} moles/g
40°C	1.81×10^{-4}	9.29×10^{-5}	0.17×10^{-5} moles/g
45°C	2.26×10^{-4}	1.18×10^{-4}	0.18×10^{-5} moles/g

Activation Energy: Stage 1 $7.67 \text{ Kcal Mole}^{-1}$

Stage 2 $9.19 \text{ Kcal mole}^{-1}$

Quantity adsorbed $(0.21 \pm 0.04) \times 10^{-5}$ moles/g; corresponding to a coverage factor of 0.76.

TABLE 7

Entropies of Activation:

Cation	ΔS^\ddagger	
	Stage 1	Stage 2
Ferric III	- 52.5 e.u.	- 48.5 e.u.
Nickel II	- 54.5 e.u.	- 53.3 e.u.
Copper II	- 51.0 e.u.	
Chromium III	- 53.2 e.u.	- 49.4 e.u.

Discussion of results:

As may be seen from the calculated activation energies, and also the effect of stirring on the rate of adsorption, the adsorption process is probably diffusion controlled, although the second stage may be influenced by other factors.

The entropies of activation are extremely large and while the vigorous stirring will increase the randomness of the chelate molecules relative to the adsorbed area, and hence increase the entropy difference, the reason for the large entropy change must be sought in the nature of the activated complex.

From the nature of the system, adsorbent, solute, and solvent, the adsorption process cannot be a simple process similar to the adsorption of a gas on a solid. In this latter case, the adsorption site is vacant and thus the probability of adsorption is high.

With the chelate system, however, although the mobility of the chelate molecule is much lower than that of a simple gas molecule, adsorption with consequent loss of degrees of freedom will entail considerable re-arrangement of energy distribution throughout the complex molecule. As a further complication, the adsorption site will be occupied by a solvent molecule and thus the activated complex will

probably involve the adsorption site, the solvent molecule, and the solute molecule. If it is postulated that for reaction to occur, i.e. for the formation of activated complex, there are stringent requirements for the orientation and juxtaposition of the chelate molecule, the adsorbed solvent molecule, being replaced, and the adsorption site, it becomes clear that only a small fraction of collisions involving molecules with the required energy will lead to reaction, and so for a particular activation energy unexpectedly low rate constants will be obtained.

Kinetics of Adsorption of Chromium 2-methyl-8-quinolinol
from mixed solvents

As had been reported by Blair and Pantony (7) it was found that the chromium chelate was not adsorbed on alumina from (1 + 1) benzene-chloroform. This behaviour was peculiar to the chromium chelate, and was complicated by the fact that once adsorbed from benzene the chelate, like the other chelates studied, could not be removed with benzene-chloroform mixtures. This indicated that in some way the benzene-chloroform mixture prevented adsorption taking place.

The results of the kinetic investigations are shown in Figs. 18 - 20. As may be seen from Fig. 20, increasing the percentage of chloroform in the solvent mixtures decreases the rate constant of the

first stage of the adsorption process to a much greater extent than that of the second stage. This indicates that the solvent mixture, in particular the chloroform molecule which will be adsorbed preferentially to the benzene, being more polar, is concerned in the process resulting in adsorption of the chelate on the adsorbent surface. The second stage of the adsorption process, which has a slightly higher activation energy, is much less dependent on the solvent composition. This reaction may be a process akin to the growth of precipitates, certainly the heats of preferential adsorption, (see next chapter), indicate that the energies involved in the second stage, are very much less than those in the initial stage, and that the 'multilayer' molecules may be held by Van der Waal forces rather than by chemical bonding.

The effect of the chloroform on the adsorption reaction cannot be explained quantitatively owing to lack of data. Qualitatively, it appears that the first addition of chloroform to the benzene solution has a greater effect than subsequent additions. This would suggest that the chloroform is adsorbed preferentially to the benzene and exhibits a blocking effect on the adsorption of the chelate.

The rates of adsorption of the chromium chelate on alumina and silica gel from benzene-chloroform mixtures were too low for determination of

activation energies with the apparatus used. With a system in which larger quantities may be used it would be interesting to investigate the variation of activation energy with solvent composition. Such studies may shed some light on the difference between silica gel and alumina as adsorbents for the chelate, and explain for instance why the use of 20% chloroform in benzene cuts the rate of adsorption of the chromium chelate to 15% of the rate of adsorption from benzene, while the corresponding decrease with silica gel is 45%.

Rate Constants of Adsorption of Chromium
2-methyl-8-quinolinol from mixed solvents.

(20% low stirring)

Percentage Chloroform	Alumina		Silica Gel	
	Stage 1		Stage 1	Stage 2
0%	3.46×10^{-5} sec ⁻¹		5.5×10^{-5} sec ⁻¹	2.0×10^{-5} sec ⁻¹
10%	1.14×10^{-5} sec ⁻¹			
20%	0.495×10^{-5} sec ⁻¹		1.2×10^{-5} sec ⁻¹	1.5×10^{-5} sec ⁻¹
40%	0.125×10^{-5} sec ⁻¹		0.65×10^{-5} sec ⁻¹	1.90×10^{-5} sec ⁻¹
60%			0.66×10^{-5} sec ⁻¹	1.98×10^{-5} sec ⁻¹
80%			0.46×10^{-5} sec ⁻¹	1.60×10^{-5} sec ⁻¹
100%			0.39×10^{-5} sec ⁻¹	1.27×10^{-5} sec ⁻¹

FIG 6

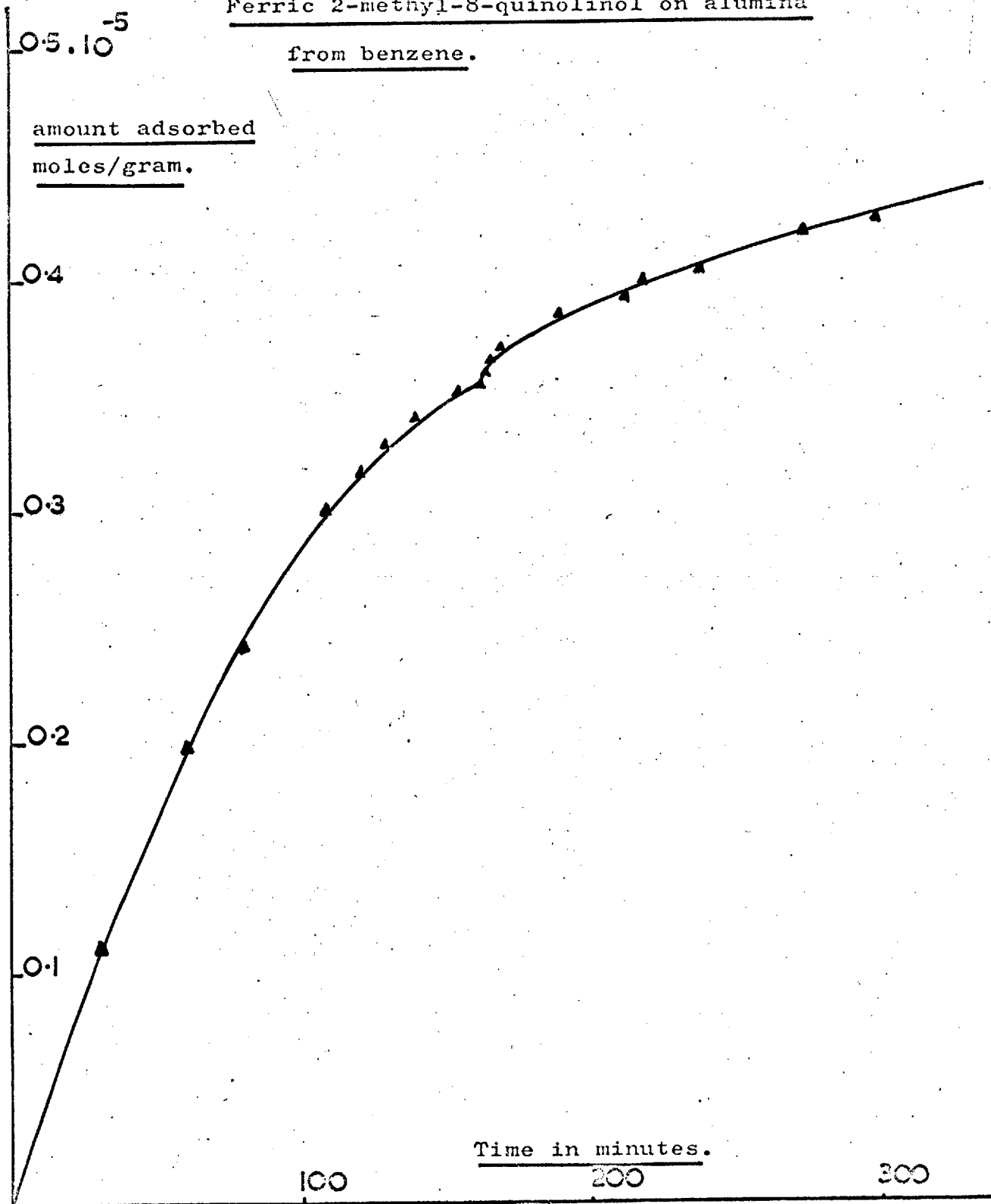
Batchwise Kinetics.Ferric 2-methyl-8-quinolinol on alumina
from benzene.

FIG 7 ⁸⁴ Kinetics of adsorption.

Ferric 2-methyl-8-quinolinol on silica gel
from benzene.

equil.
concentration
moles/l.

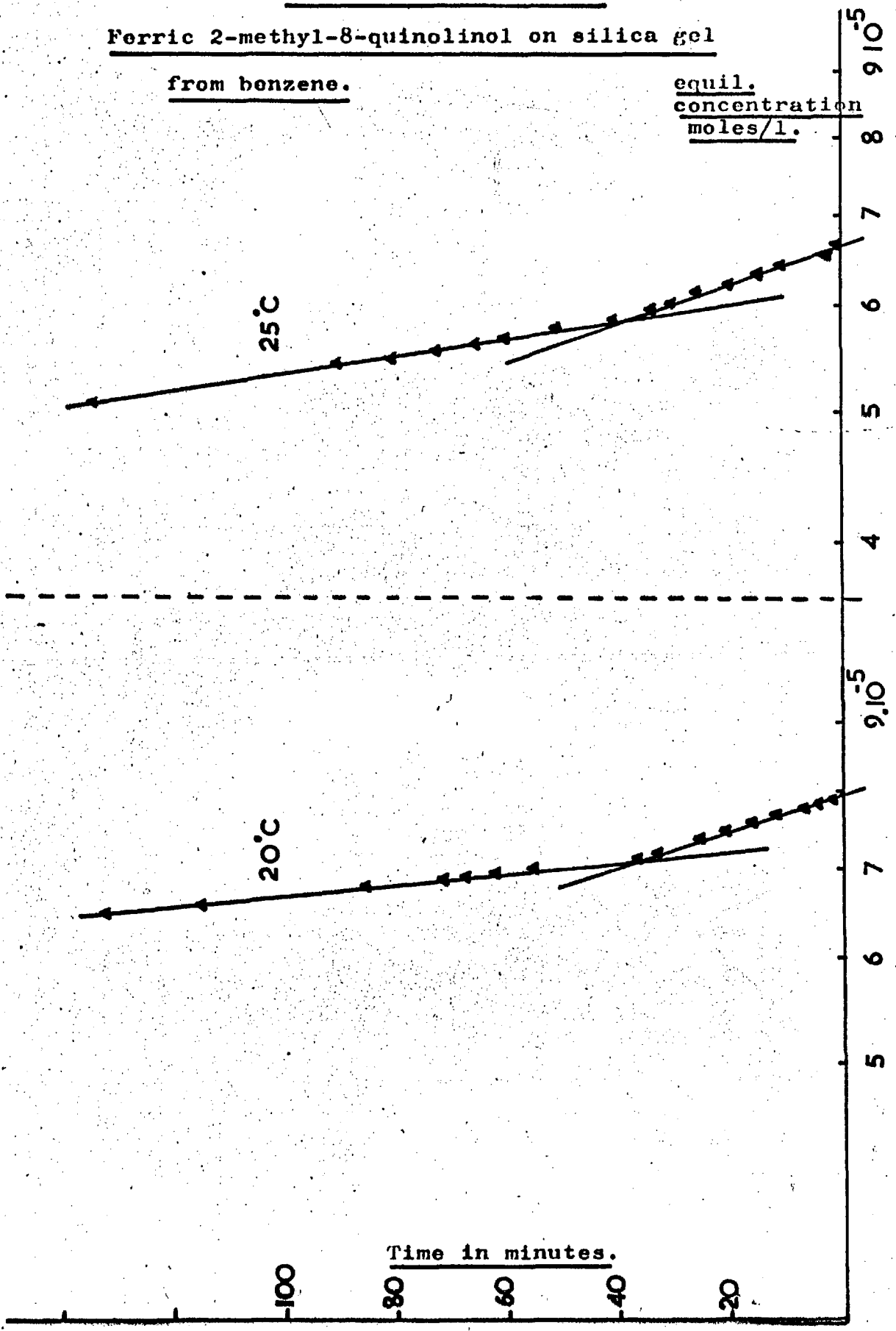


FIG 8 Kinetics of adsorption.

Ferric 2-methyl-8-quinolinol on silica gel
from benzene.

equilibrium
concentration
moles/litre.

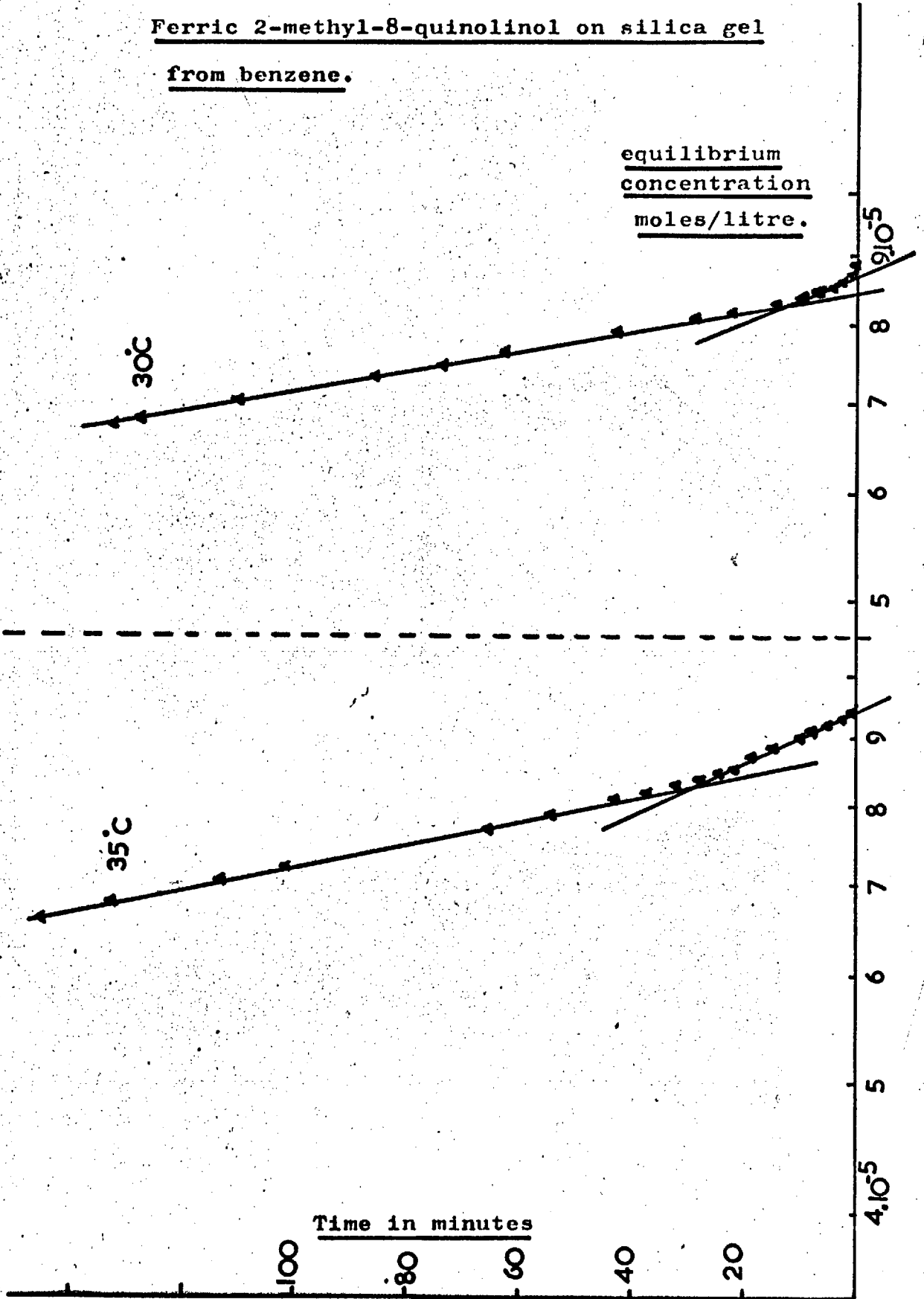
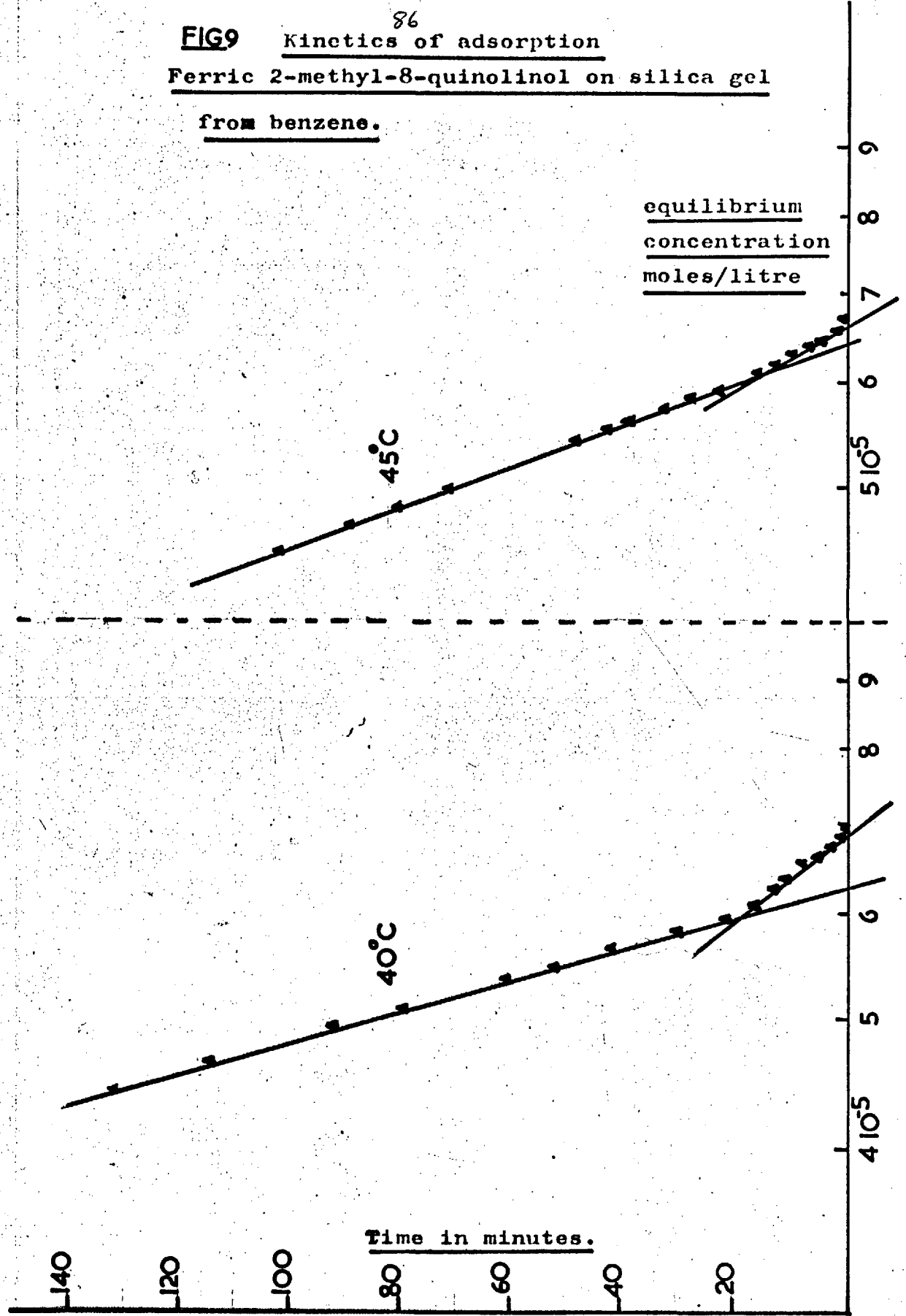
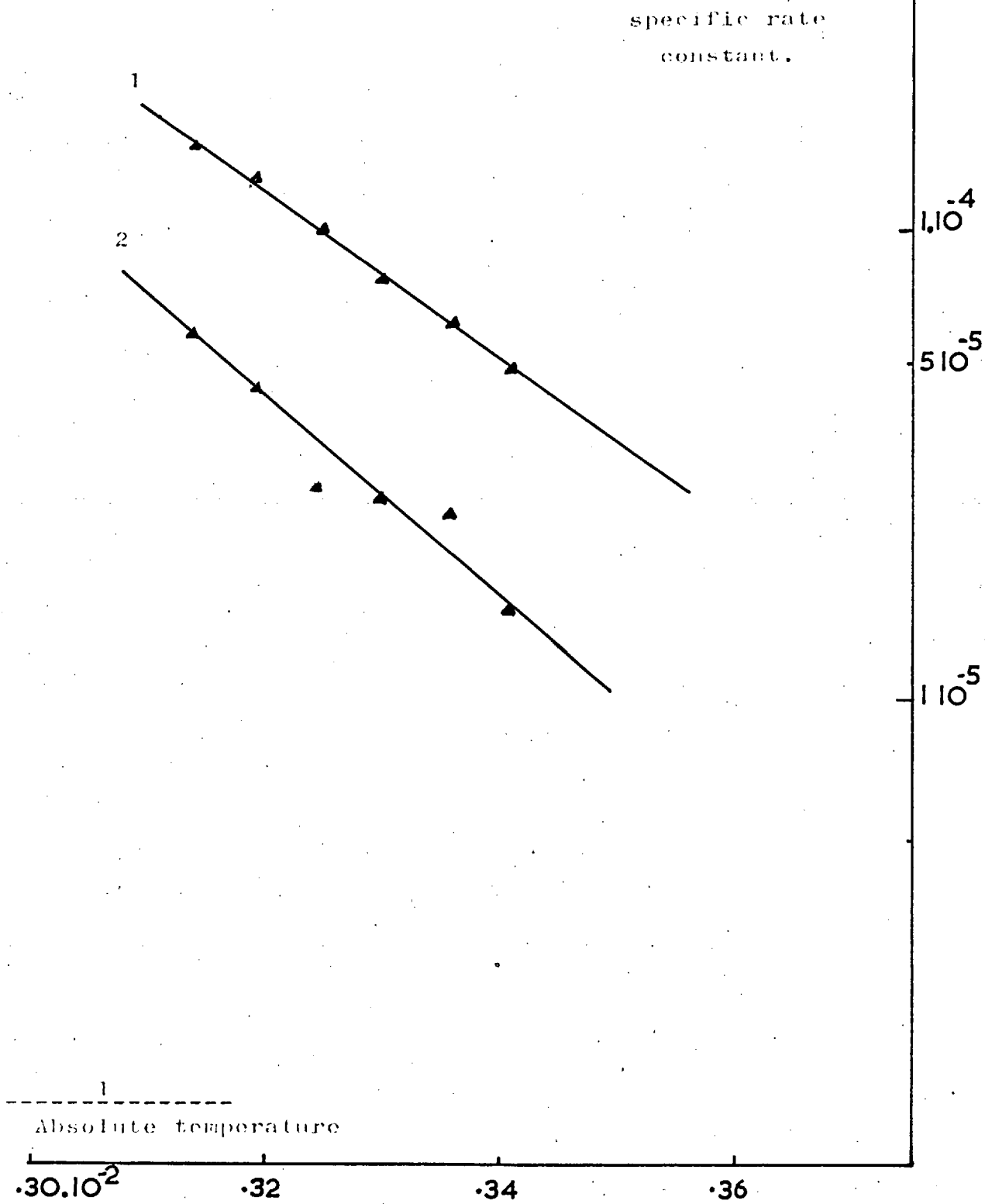


FIG9 Kinetics of adsorption
Ferric 2-methyl-8-quinolinol on silica gel
from benzene.



Ferric 2-methyl-8-quinolinol on silica gel.

Nickel 2-methyl-8-quinolinol on silica gel
from benzene. 88

Kinetics of adsorption.

FIG II

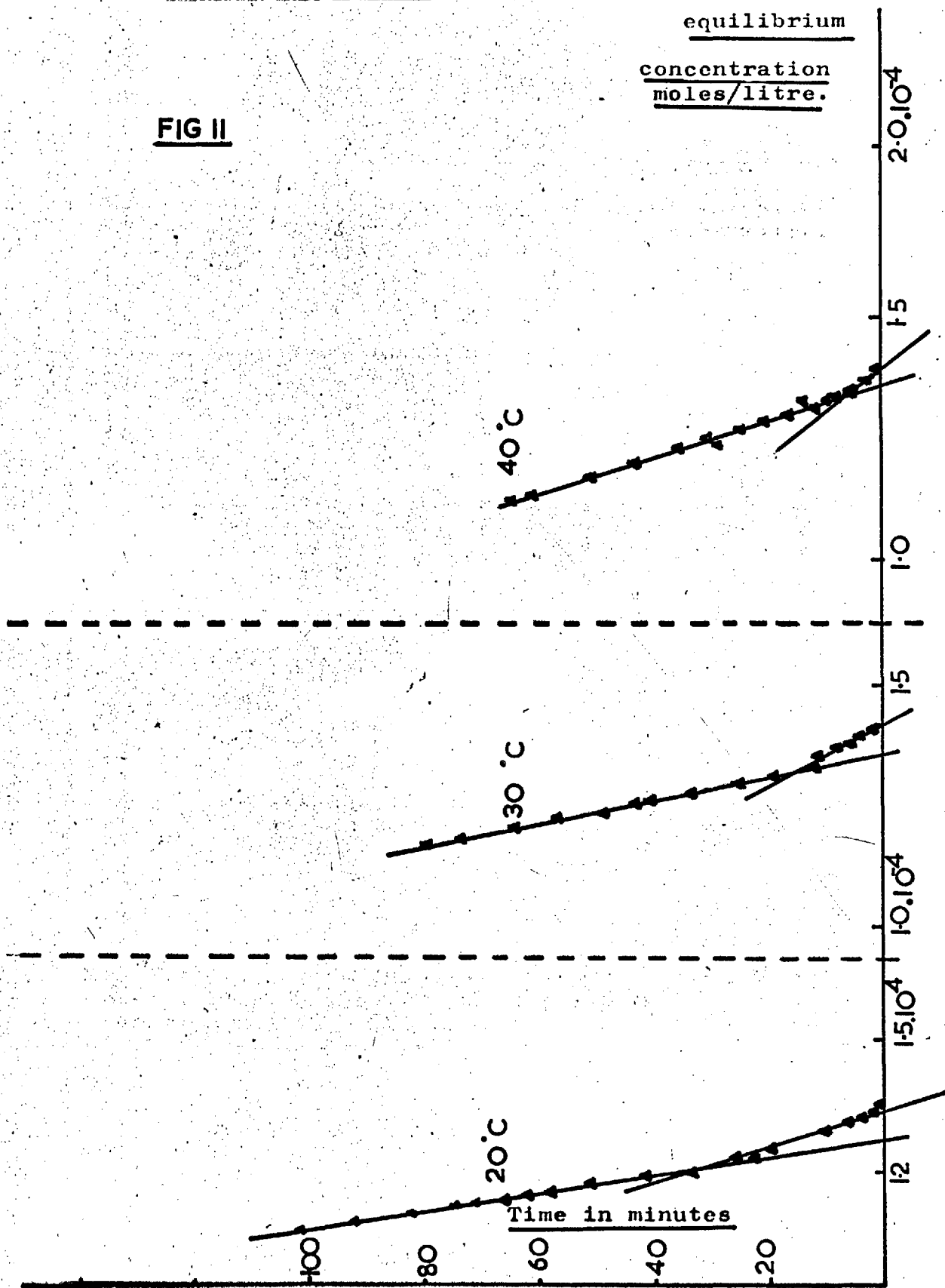
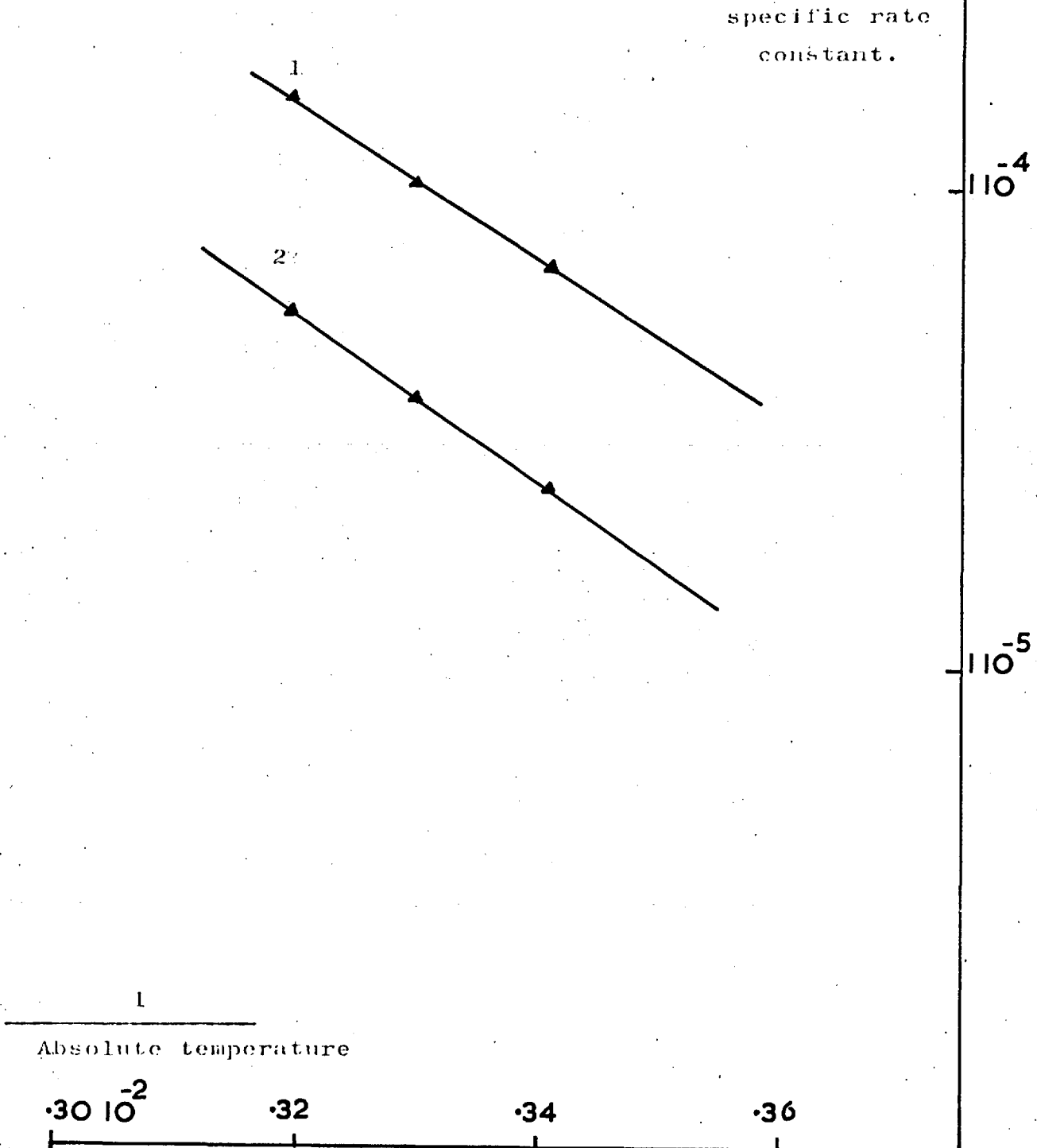


FIG. 12 Energy of Activation.Nickel 2-methyl-8-quinolinol on silica gel.

Kinetics of adsorption.

Copper 2-methyl-8-quinolinol on silica gel
from benzene.

FIG 13

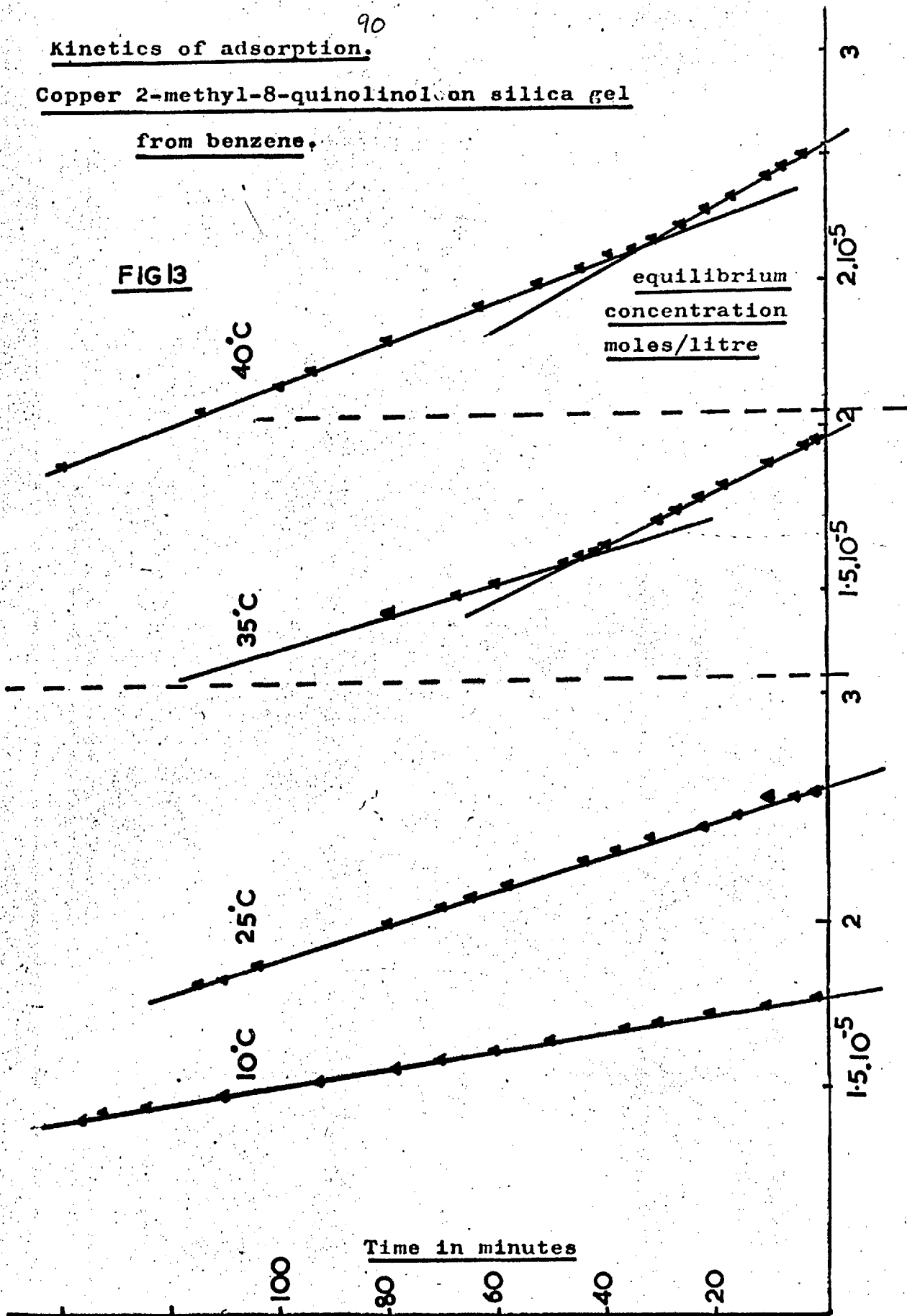
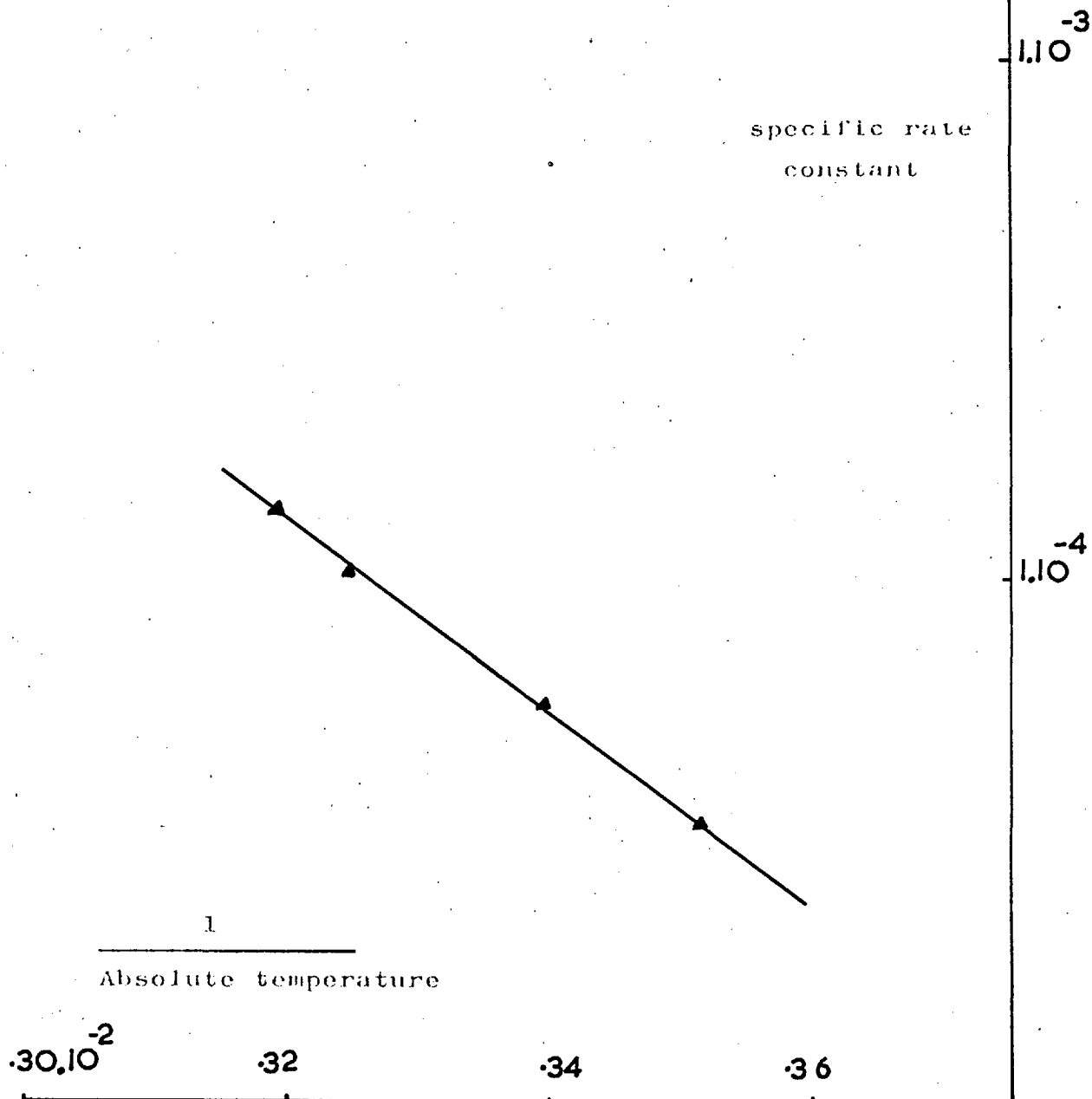
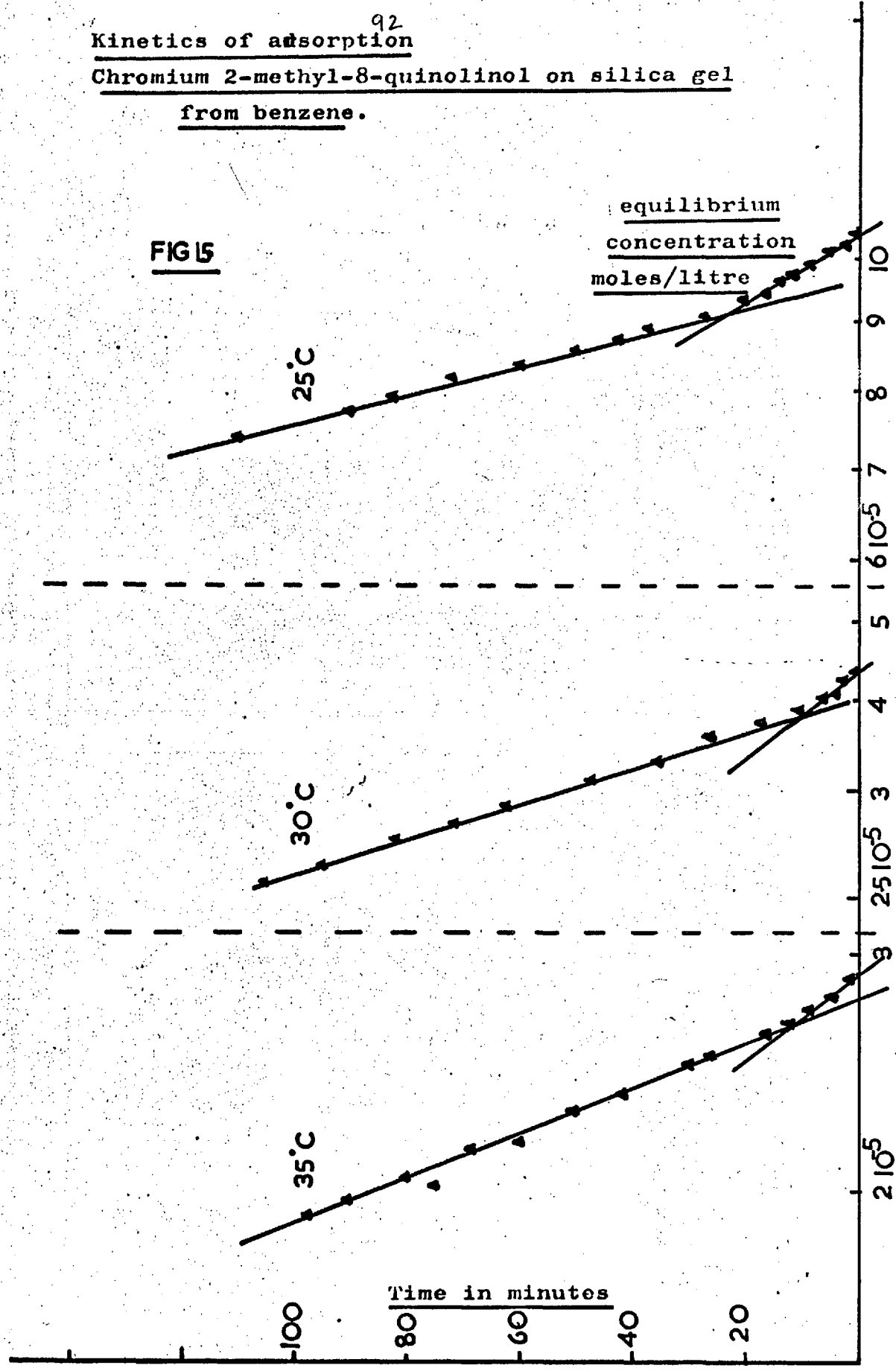


Fig 14. Energy of Activation.Copper 2-methyl-8-quinolinol on silica gel.

92
Kinetics of adsorption

Chromium 2-methyl-8-quinolinol on silica gel
from benzene.

FIG 15



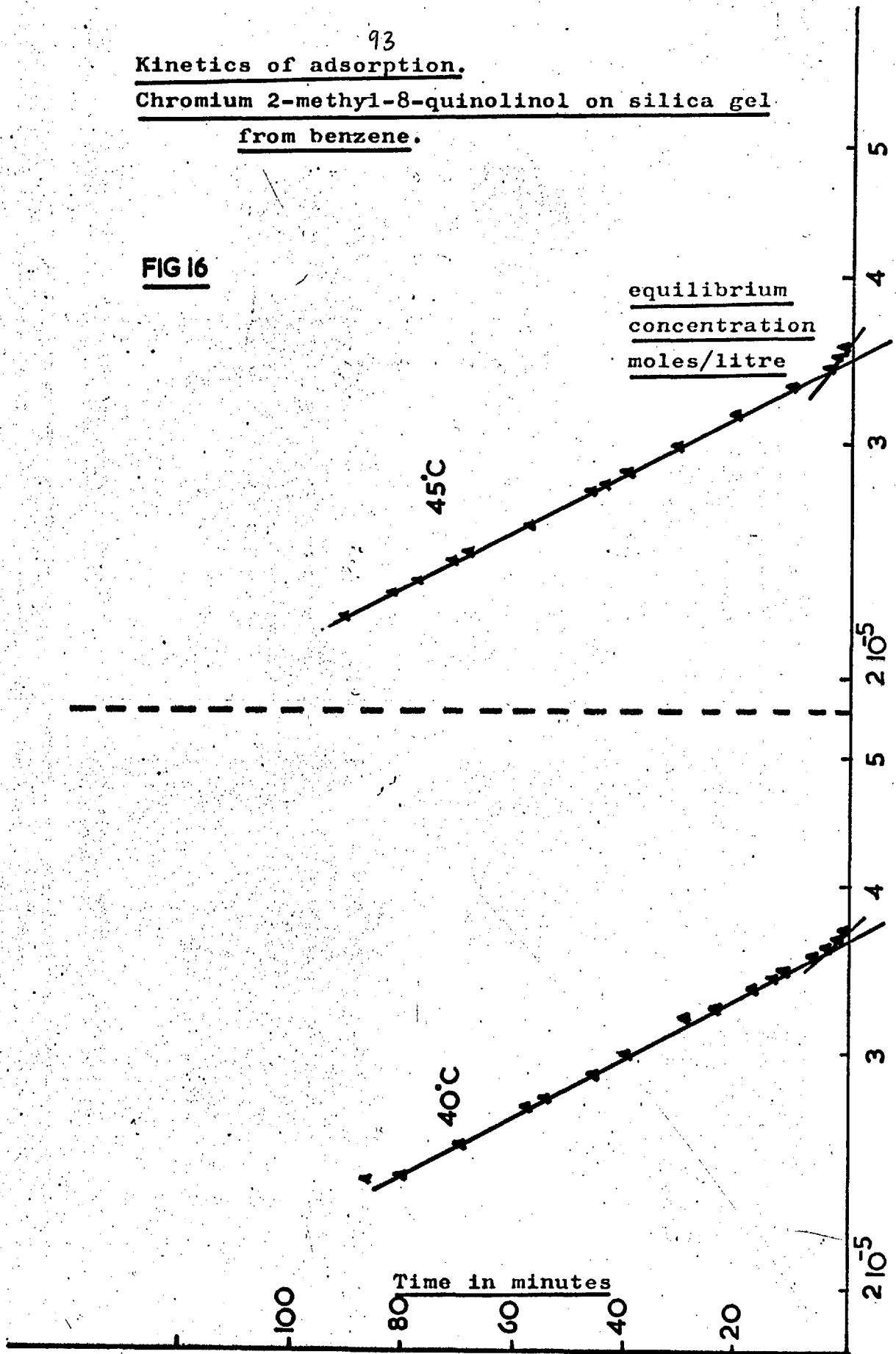
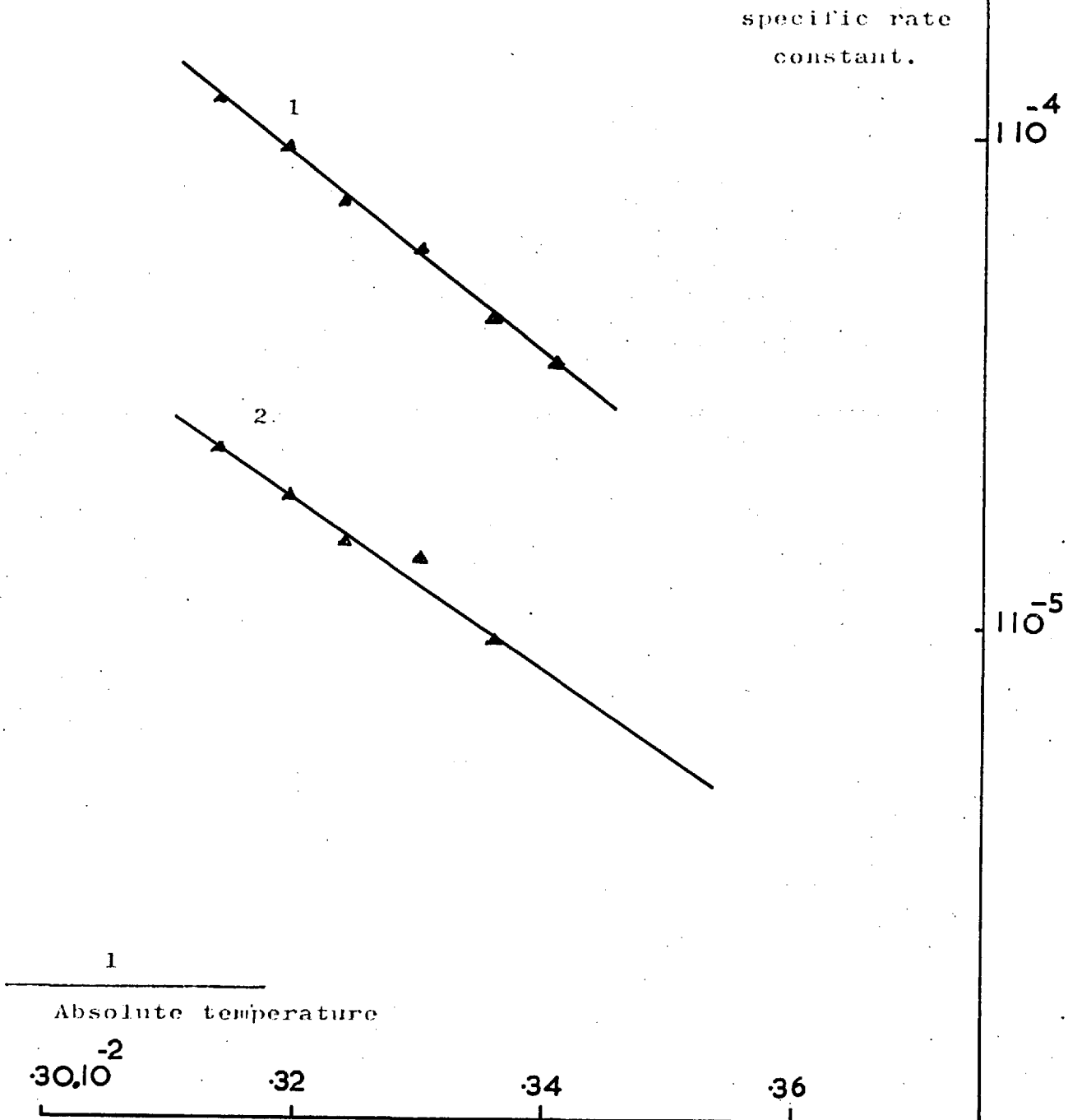
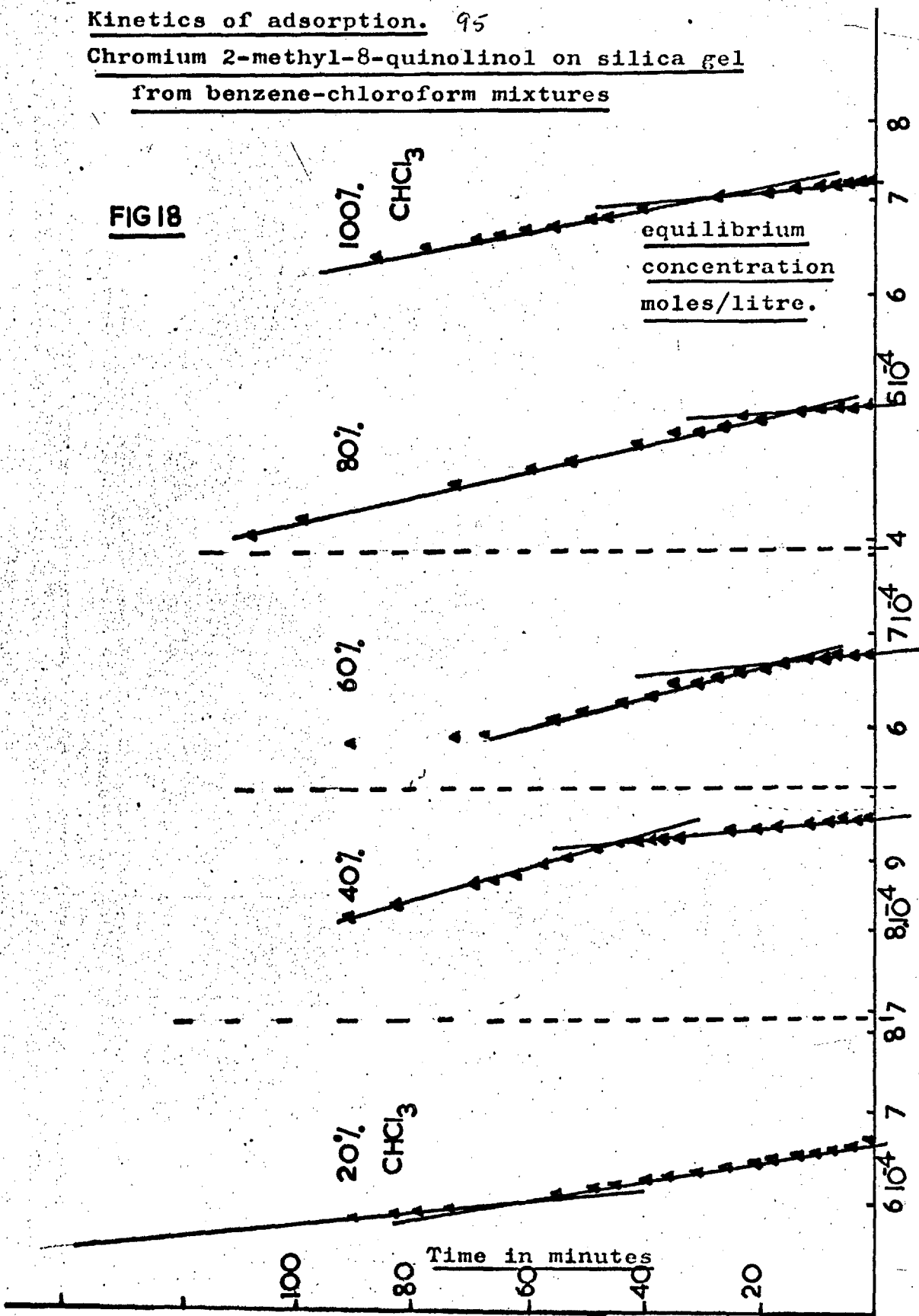
Kinetics of adsorption.Chromium 2-methyl-8-quinolinol on silica gel
from benzene.FIG 16

FIG.17 Energy of Activation.

Chromium 2-methyl-8-quinolinol on silica gel.

Chromium 2-methyl-8-quinolinol on silica gel
from benzene-chloroform mixtures

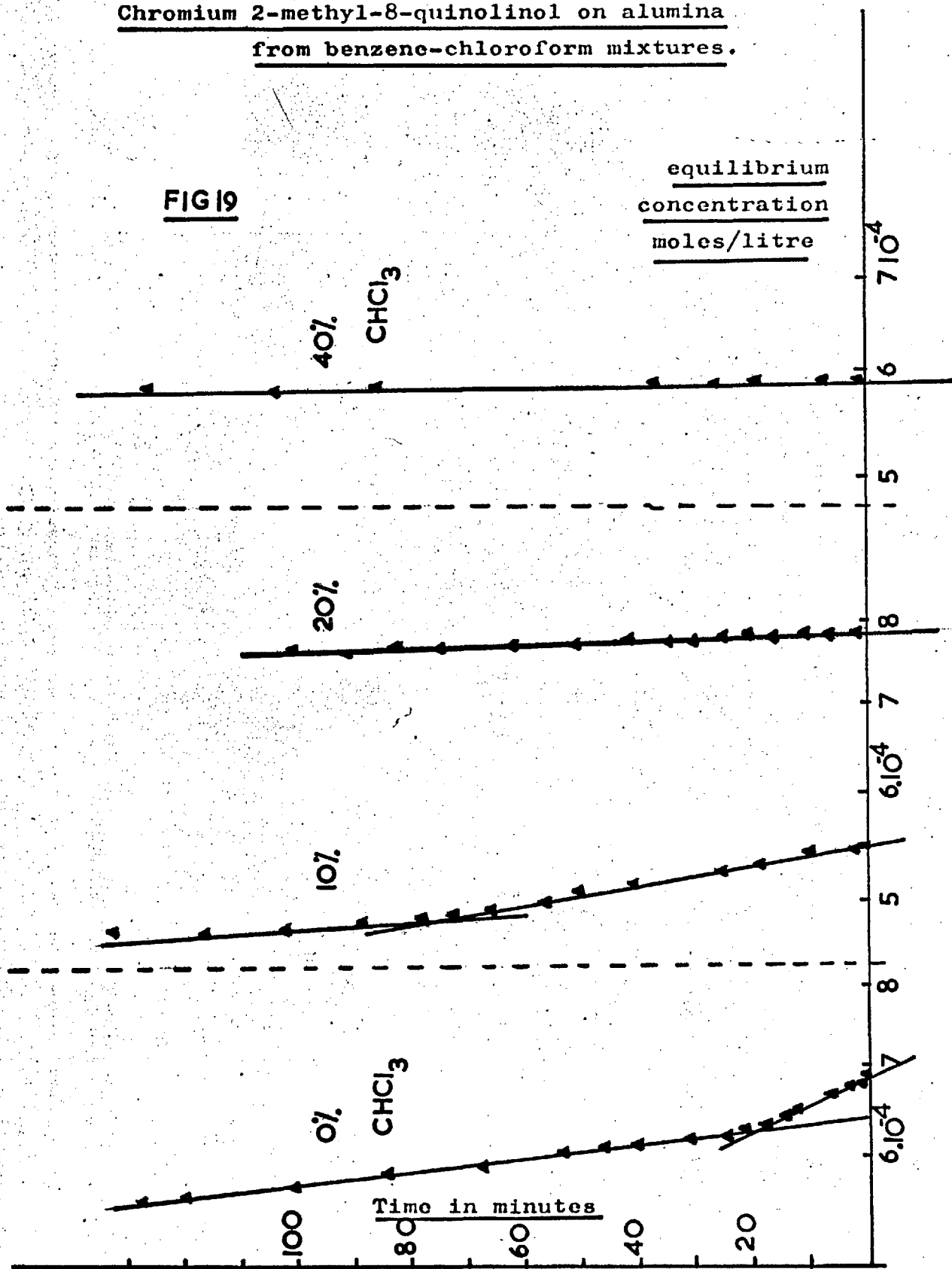
FIG 18



Chromium 2-methyl-8-quinolinol on alumina
from benzene-chloroform mixtures.

FIG 19

equilibrium
concentration
moles/litre



Chromium 2-methyl-8-quinolinol

Variation of rate constant with
solvent composition

- a) Stage I on alumina.
- b) Stage I on silica gel.
- c) Stage II on silica gel.

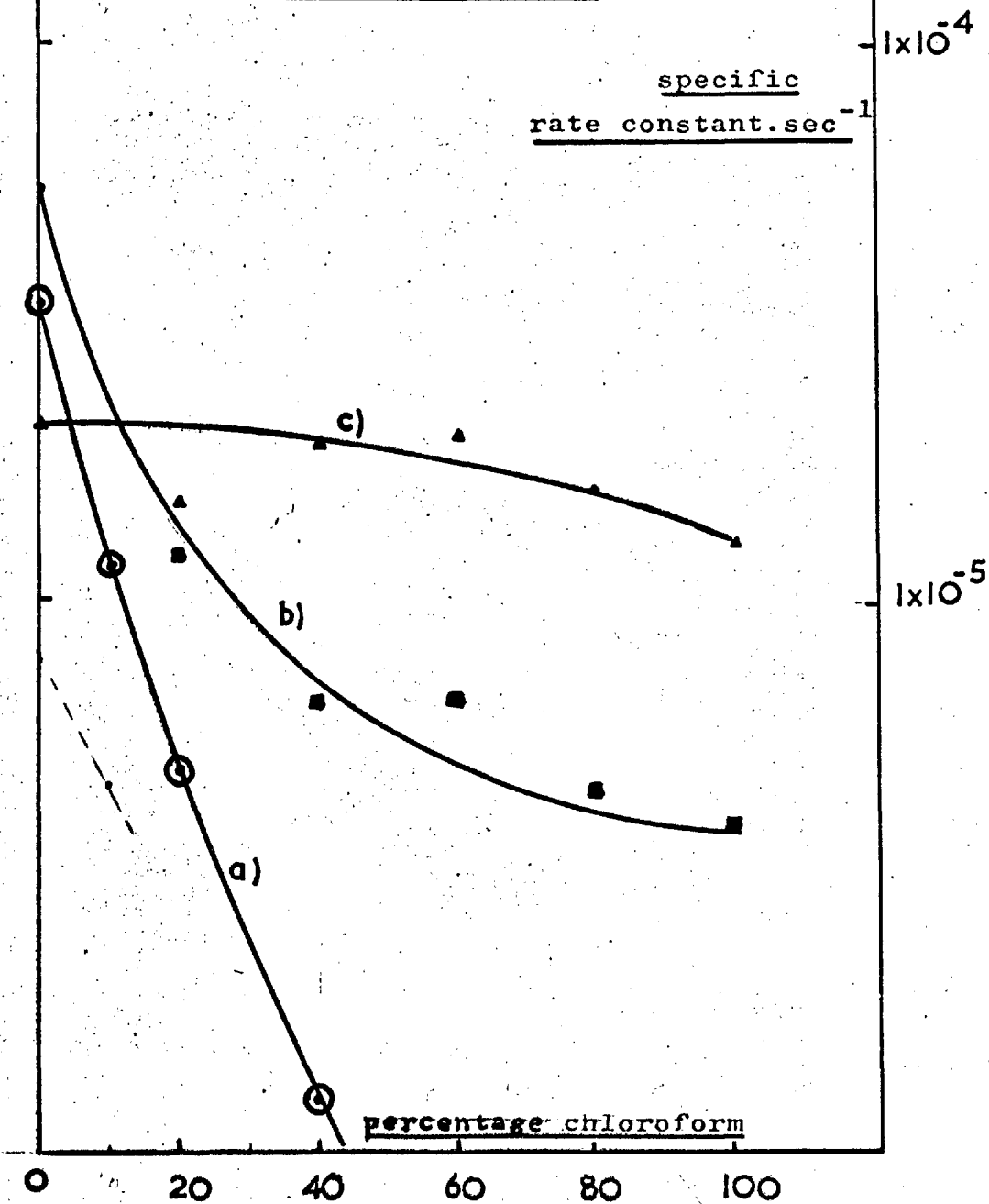


FIG 21. Effect of stirring on the rate of adsorption.

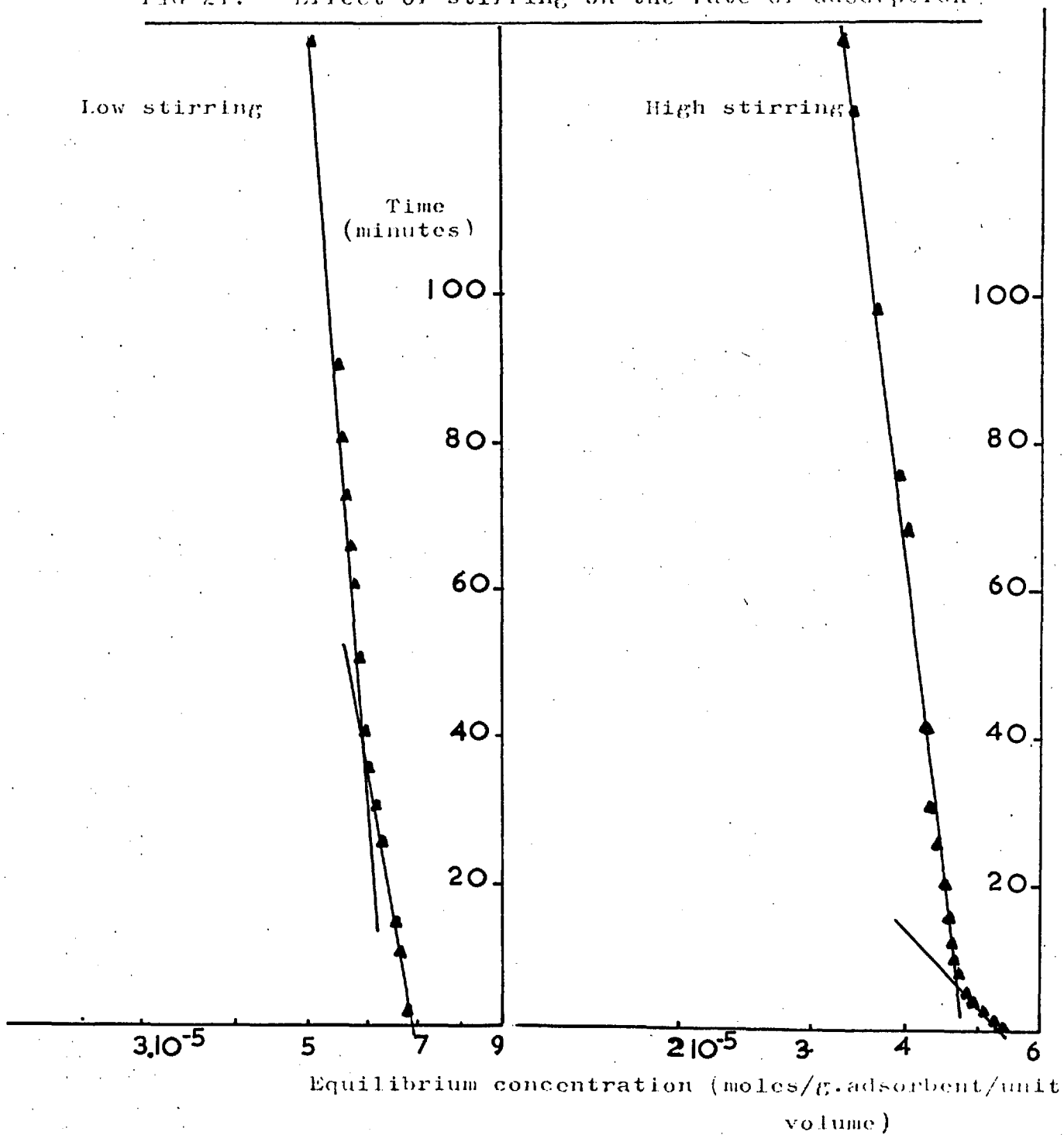
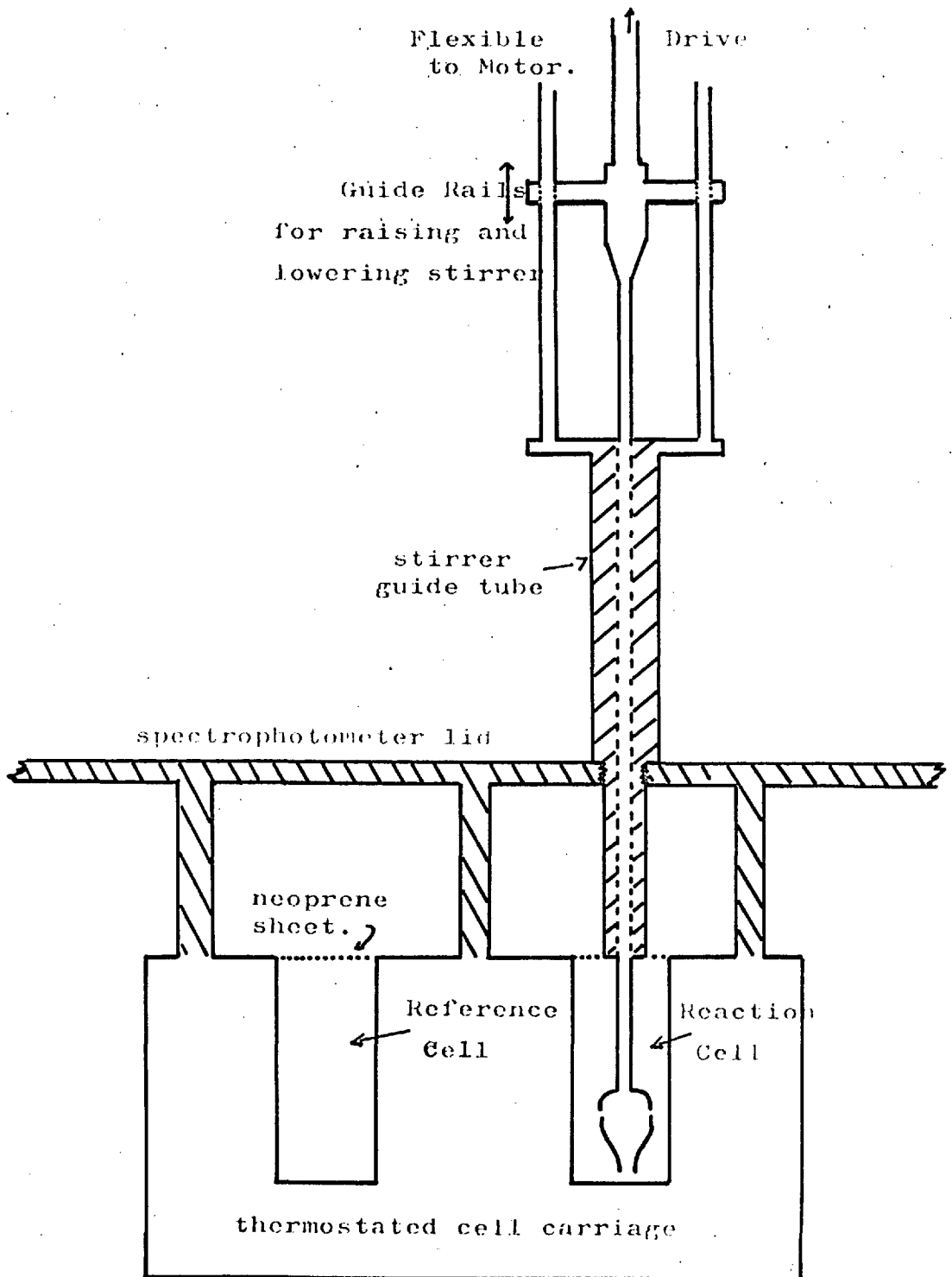


FIG 22 Kinetics of Adsorption Apparatus.



CHAPTER 8

HEATS OF PREFERENTIAL ADSORPTION.

One of the best methods of studying adsorption processes is by means of calorimetric investigations of the enthalpy changes on adsorption. With a suitably chosen system close approximations to the behaviour on a chromatographic column may be made.

Three methods have been used for these studies, in one, (83) the heat of adsorption is calculated from heats of immersion, in another the heat of adsorption is estimated by measuring the heats of wetting of the adsorbent by the pure solvent and by the solute (84).

The best method as far as relating the enthalpy effects to chromatographic procedures is concerned, is to measure the heat of preferential adsorption, or more strictly, the heat of replacement. Experimentally two systems have been used, in one (84) the adsorbent previously moistened with solvent is added to a large volume of solution, in the other procedure a known quantity of solute is injected into a stream of solvent flowing through a column of adsorbent held in a calorimeter (85). A modification of the latter experimental procedure was used for the present work since it is a system closely analogous to a chromatographic column.

Experimental Details:

The calorimeter used for these studies was constructed according to Groszcek's specification (86), and the whole apparatus, stock solutions, solvents etc., kept in a room at a set temperature of $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The solvent system was controlled via a constant delivery but infinitely variable peristaltic pump, and was so designed that the solvent flow passed through an annular jacket around the sample. This allowed the sample to be in thermal equilibrium with the flowing solvent. The heats of preferential adsorption were determined by injecting samples into the solvent flow and measuring the heat evolved on adsorption, so it was important to ensure that injection of samples into the solvent flow did not cause spurious heat effects. These unwanted heat effects could be due to physical factors, e.g. the sample and solvent not being in thermal equilibrium, or sudden variation in the sample flow, or change of a chemical nature, in particular dilution of the sample.

Tests carried out by injecting samples of benzene into a benzene flow showed that with this system the heat changes caused by injecting a solvent sample into the solvent flow within the calorimeter were less than 2% of the heat effects observed during

preferential adsorption of the metal chelates. By using fused alumina, which has a negligible adsorption capacity for the metal chelates, it was determined that the heat changes caused by injecting chelate samples was of the same order as those caused by injecting pure solvent into the solvent stream. This was to be expected as the chelate samples used were only 10^{-2} to 10^{-3} M.

The change in resistance of the thermistors, in the calorimeter was measured by means of a Wheatstone bridge circuit (Fig. 23), where the change in potential across the resistance R was amplified such that 100 μ v was equated to 2mv, which was the full scale deflection of the pen potentiometric recorder (Leeds and Northrup model W with A.Z.A.R. attachment), used for presentation of the resistance changes. The expedients used to equilibrate solutions and solvents also served to provide an excellently steady base line to the recorder. As the base line was adjusted by means of A.Z.A.R. to approximately centre scale, it was impossible to use the commercial Leeds and Northrup analogue integrator, which integrates from the mechanical position of the pen. This meant that heats of preferential adsorption were calculated from peak heights above the base line, but, as the peaks were narrow-based isosceles triangles, and estimations of the heats of preferential

adsorption calculated from manually integrated areas agreed, this method appeared to cause but slight loss of accuracy.

The calorimetric values of the observed heats of preferential adsorption were determined by reproducing the observed peaks with a 1 cm x 0.1 cm 2 ohm heater which was coiled into a flat spiral and inserted in the adsorbent bed. The heating coil was manganin wire spot welded to thick leads. The welded joints were tightly bound with thin copper wire and then dipped in solder to ensure good electrical contact. Details of the heater construction are shown in (Fig. 23).

Known voltages could be supplied to the heater by means of a Solatron constant D C voltage source *type* SO AS 1412.

It is known that the heats of preferential adsorption decrease with increasing surface coverage, (87) and so care was taken to ensure that each sample of chelate was adsorbed on a fresh surface. This required the adsorbent bed to be changed for each determination. Weighed quantities of adsorbent were used in order to make the system as reproducible as possible. The heater assembly was so designed that the heating spiral was in a fixed position relative to the thermistors and the top of the adsorbent bed. This again was intended to optimise

the reproducibility of the determination. Tests showed that these precautions made the electrical calibrations very reproducible.

Relationship between the measured heat changes
and the free energy of adsorption

In an adsorption process there should be a heat change owing to the solute changing its environment from the solvent to the adsorbent (87, 88), provided that any displaced species does not provide an equal and opposite heat effect.

Consider the adsorption of a chelate from benzene solution on to an adsorbent saturated with benzene. The changes in free energy caused by the adsorption of the chelate may be divided into three sections.

a) A change in free energy owing to the replacement of benzene by chelate, designated as ΔS_e

b) A change in free energy owing to the decrease in concentration of chelate in solution.

c) A change in free energy owing to the increase in concentration of benzene in solution.

Defining x as the number of molecules of chelate adsorbed, C_0 , and B_0 , as the original concentrations of chelate, and benzene, expressed as mole fractions, C_1 , and B_1 , the final concentrations,

and A_c , and A_b , as the areas occupied by one mole of chelate and benzene respectively. Then the adsorption of x moles of chelate causes the desorption of $\frac{A_c}{A_b} x$ moles of benzene. Thus the change in free energy is given by:-

$$\Delta G = \Delta S_e + x RT \ln \frac{C_l}{C_o} + \frac{A_c}{A_b} x RT \ln \frac{B_l}{B_o}$$

But there will be entropy changes associated with the replacement. The desorbed benzene molecules will become more disordered, increase their degrees of freedom and hence gain entropy; on the other hand the more complex chelate molecule may be expected to lose entropy. The net effect ΔS will contribute to the enthalpy changes.

Therefore the heat evolved by the system, $-\Delta H$ may be related to the free energy change of the surface.

$$-\Delta H = - \left[\Delta S_e + x RT \ln \frac{C_l}{C_o} + \frac{A_b}{A_c} x RT \ln \frac{B_l}{B_o} \right] - T\Delta S$$

For the small volumes of very dilute solutions dealt with, the changes in free energy owing to concentration changes will be very small compared with the changes in free energy of the surface and the entropy changes; thus the relationship may be simplified to:-

$$-\Delta H = -\Delta S_e - T\Delta S$$

Provided that the entropy changes are small, or for a series of compounds are of the same order, which is more likely (87), then the heat changes will be directly indicative of the change in free energy of the surface.

Results and Discussions:

The experimental results are tabulated below:-

Cation	+ ΔH k cal mole ⁻¹			8-quinolinethiol chelates on alumina
	2-methyl-8-quinolinol on alumina	chelates on silica gel coated alumina	chelates on alumina	
Fe ^{III}	-21.8	-31.7	-7.5	- 1 (+ 2.4)
Ni ^{II}	-18.7	-31.2	-5	- 1 (+ 3.8)
Cu ^{II}	-12.2	-14.6	-2.5	- 2.6
Cr ^{III}	-10.4	-8.6	-3.0	- 5.6

Standard Deviation + 0.5 K cal Mole⁻¹

With the 2-methyl-8-quinolinol chelates, desorption was negligible and the adsorption process was accompanied purely by an evolution of heat. If desorption followed adsorption it is to be expected that an endothermic process would occur representing the energy required to replace the adsorbed chelate molecule by benzene molecules. This was only noticeable with the iron and nickel 8-quinolinethiol chelates. This would suggest that these chelates are readily desorbed. Chromatographic investigations, reported earlier, showed that all of the 8-quinolinethiol chelates could be eluted from alumina columns, the iron and nickel chelates with R_f values of 0.7 and 0.6. These values varied slightly with the alumina sample; on alumina samples which had been exposed to air slightly higher R_f values were observed.

Chromatographically it had been determined that

the 2-methyl-8-quinolinol chelates were completely retained in alumina and silica gel columns. The 8-quinolinethiol chelates are similar to the 2-methyl-8-quinolinol chelates, and so the entropy changes on adsorption may be expected to be similar. Thus, the difference in the heats of preferential adsorption must be due mainly to a lower free energy change at the surface. This indicates that the 8-quinolinethiol chelates are much less strongly adsorbed. Chromatographic investigations showed that the chelates could in fact be readily eluted from alumina columns.

By comparison of the heats of preferential adsorption it seems probable that for these chelates complete retention is marked by a heat of preferential adsorption of the order of 6 kcal mole⁻¹. Owing to the unknown contribution from entropy changes this particular value is applicable to this system only and it is not possible to define exactly the free energy change corresponding to complete retention by alumina from benzene.

During the kinetics investigations, it had been determined that the adsorption was a two stage process with a change in rate characteristics at the monolayer. Chromatographically it was possible to remove some of the chelates and it was suspected that this was the 'multilayer' quantities. Accordingly adsorbent samples

containing a 'monolayer' of chelate were prepared. This was accomplished by treating the alumina with chelate solution of concentration such that the equilibrium concentration after six hours corresponded to the equilibrium concentration at the point of inflexion on the adsorption isotherm.

The heats of preferential adsorption were determined and, as may be seen from Table 1, were very much less than the heats of adsorption on the clean surfaces, and are comparable to with the heats of preferential adsorption of the 8-quinolinethiol chelates. This gives further confirmation that the heat of preferential adsorption is related to the strength of adsorption and hence the order of elution of the chelates.

The heats of adsorption of the metal chelates cannot be calculated from the heats of preferential adsorption as the heat of adsorption of benzene on an evacuated surface is not known. However, from knowledge of the behaviour of benzene it is highly probable that benzene will be physically adsorbed. Its heat of adsorption may be expected to be low and so the heats of preferential adsorption may be used as an estimation of the heats of adsorption. Certain conclusions may be drawn from the values; the high heats of preferential adsorption for the first stage

of the adsorption of the 2-methyl-8-quinolinol chelates suggest that a low energy chemical bond, such as a hydrogen bond is formed. If the chelate decomposed on the surface, much larger heat effects, indicative of bond dissociations, would be expected. The adsorption of the multilayer quantities of chelate is accompanied by a much smaller heat of preferential adsorption which suggests purely physical adsorption, as does its partially reversible character. Similarly the 8-quinolinethiol chelates are probably physically adsorbed.

The selective elution of the copper 2-methyl-8-quinolinol was considered to be worth investigating calorimetrically. The heats of preferential adsorption show that the copper chelate is more firmly adsorbed than is that of chromium, and so, if the reagent merely replaced the adsorbed chelate, giving rise to a displacement elution, it would be expected that the chromium chelate would also elute,

The heat of preferential adsorption of the copper chelate from dilute reagent solutions on to alumina was determined and an interesting variation with increasing concentrations of reagent was observed.

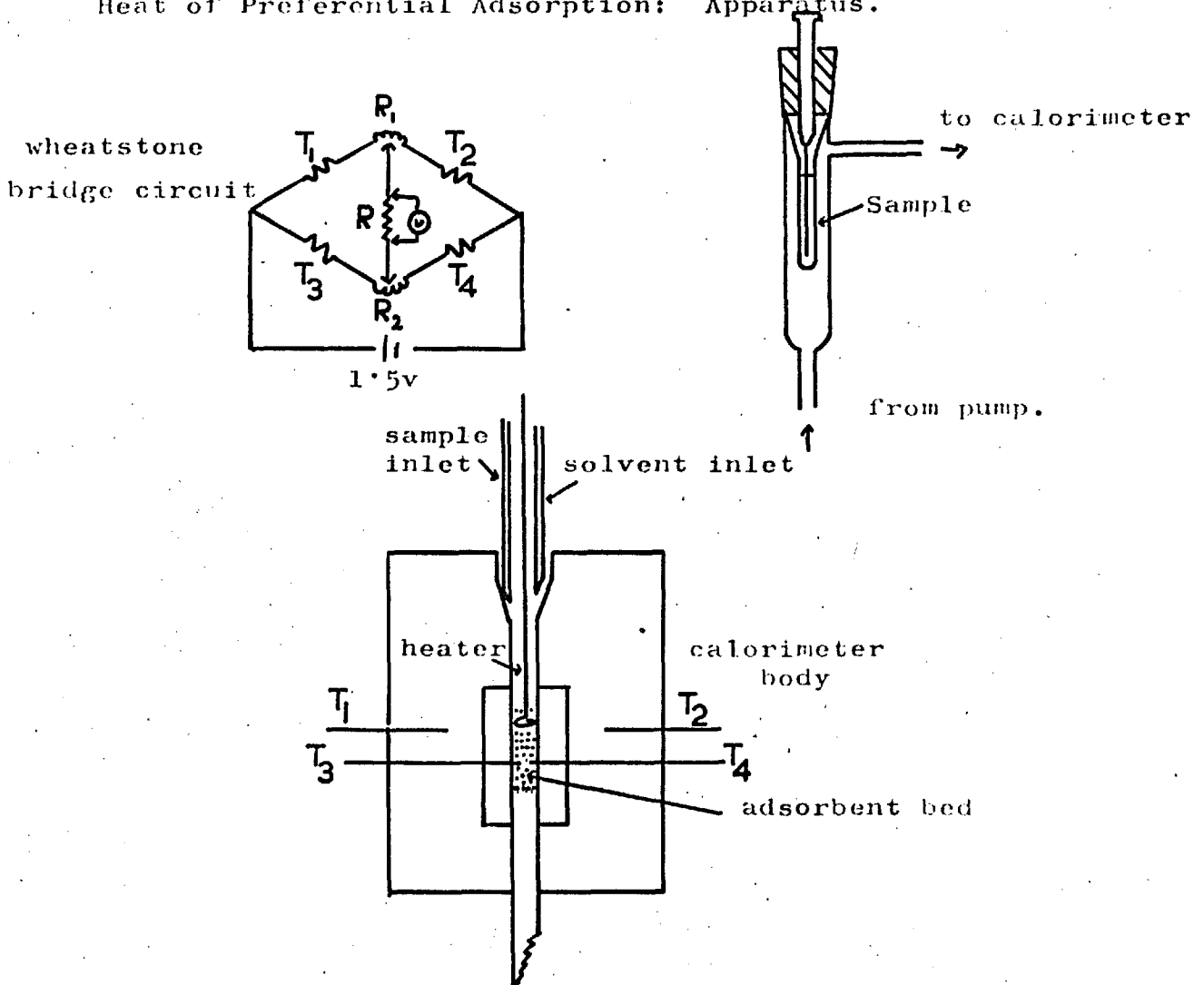
<u>%age 2-methyl-8-quinolinol</u>	<u>Heat envolved Kal mole⁻¹</u>	<u>%age recovery</u>
0%	12.2	0
0.1%	7.0	90% on prolonged elution
0.5%	3.8	100%
1.0%	2.9	100% (Rf - 0.9)

The recovery of the copper chelate is from chromatographic data. The column used was 5 cm x 0.5 cm alumina, and 1 ml of 10^{-3} M copper chelate; i.e. 10^{-5} moles were adsorbed from benzene solution.

The heat of preferential adsorption decreases markedly with reagent concentrations but it is difficult to explain the elution. The concentrations necessary for quantitative elution are too high (3×10^{-2} M) for the reaction to be a simple replacement, and so the reagent effect must be more complicated. Further discussion of this is given in Chapter 9.

FIG. 23

Heat of Preferential Adsorption: Apparatus.



CHAPTER 9.Miscellaneous Investigations.

Although the chromatographic behaviour of the metal chelates had been characterised, and kinetic and calorimetric investigations had helped in explaining this behaviour, there still remained unanswered questions as to the state of the adsorbed species.

It was certain that the chelates were adsorbed in multilayer quantities, but no consistent values for the number of layers could be calculated from adsorption isotherms. The position and orientation of the molecules was unknown, and, as this has an important bearing on the nature of the adsorbed species, it was decided to examine the adsorbed chelate by X-Ray techniques. A recrystallised sample of the nickel chelate was chosen for this study since it was the purest material available.

The silica gel adsorbent was amorphous in character, and in association with the fact that only small quantities of chelate are adsorbed, suggested that powder techniques would be more suitable than single particle methods.

The silica gel used for chromatographic purposes was too coarse for X-Ray use and so pulverised samples of less than 400 mesh were used. The samples

were treated with nickel 2-methyl-8-quinolinol solutions of 75% of the saturation concentration, filtered, rinsed with benzene, and allowed to dry in air.

The silica gel as expected showed no distinct bands on the powder photograph, confirming its amorphous character. The adsorbed nickel chelate and powdered pure chelate gave identical powder pictures although that obtained from the adsorbed species was not quite as sharp.

It is difficult to attribute such a result to an adsorbed species only a few molecules thick. Either the multilayers are much more extensive than suspected, the chelate adsorbing on the adsorbent in a manner akin to crystallisation, or the adsorbed material re-arranges on evaporation of the solvent to give a micro crystalline form of the chelate supported on a silica gel substrate.

Attempts were made to produce a silica gel sample with monolayer coverage of chelate. No X-Ray powder photograph could be obtained with this sample owing to the extremely small quantity of metal chelate present.

Table of 2θ from X-Ray Powder Photographs

Pure Chelate	Adsorbed Chelate		
	Sample 1	Sample 2	Sample 3
32°	32°	32°	32°
45°	45°	45°	46°
56°	56°	55°	55°
66°	66°	66°	66°
75°	75°	76°	75°
85°	86°	85°	85°

Infra red investigations

The best method of studying the bonding and attachment of the metal chelates to the surface is by infra red techniques. The chelates show a very distinctive spectrum in the range 600 cm^{-1} to 1600 cm^{-1} ; the most important bond is at 1100 cm^{-1} and is attributed to the metal to oxygen stretching frequency (89).

In examining the adsorbed chelates, the intention was to compare the spectrum of the pure and adsorbed chelate. In particular, it was intended to look for decomposition of the chelate, which would be shown by the disappearance of, or a large shift in, the metal-oxygen bond, and to look for evidence of bonding to the adsorbent surface.

Experimental:

The infra red spectra were determined by the pressed disc method. Most samples were pressed in

potassium bromide, although some were used as self supporting discs. This latter procedure enabled greater quantities to be used, but this advantage was reduced by the increased scattering.

Two methods of obtaining spectra of the adsorbed chelate were used. In the first, discs, usually in potassium bromide, were made up with adsorbent previously treated with chelate; in the second, self supporting discs were equilibrated with chelate solutions, soaked in benzene for ten minutes to remove any unadsorbed chelate, and also any free ligand that may have been produced on adsorption, and finally dried at 50°C to remove benzene.

The initial determination of the spectra was carried out using a Grubb and Parsons Spectromaster. The results were variable owing to lack of sensitivity. Much better results were obtained later by use of a Perkin Elmer 621 grating instrument.

The spectra of the pure chelates and of the adsorbent samples could be readily obtained, but great difficulty was encountered in studying the adsorbed chelate. The quantity of adsorbed chelate was very low, less than 50µg in a 0.5 g disc, and both silica gel and alumina show strong broad bands in the 1000 cm⁻¹ region. Experimentally it was found impossible to identify bonds in the 1250 cm⁻¹

to 900 cm^{-1} region on silica gel substrates, or below 1200 cm^{-1} on alumina. The sharp chelate metal to oxygen stretching frequency at 1110 cm^{-1} could not be identified on silica gel and only appeared as a shoulder in the 1120 cm^{-1} region on alumina in about 50% of the samples investigated. This slight shift in position of the metal to oxygen bond may be due to distortion and reflection, or possibly a slight weakening of the bond on adsorption of the chelate. This would be expected if the oxygen atom was active in the adsorption process but cannot be confirmed by the available infra red evidence.

More success was obtained, particularly with silica gel as support, in studying changes in the adsorbent spectrum before and after adsorption. The silica gel samples used showed a broad peak with a maximum at 3550 cm^{-1} and a sharp peak with a maximum at 3740 cm^{-1} . This latter peak is attributable to free surface OH groups (90). On adsorption of the chelate this sharp band disappeared. No new sharp band was formed, the only peak to appear was a shoulder on the broad band at about 3530 cm^{-1} .

With the alumina samples no change in the spectrum was noticeable. The alumina shows a very broad, more rounded, absorption band than does silica gel, without any significant highlights, and this

makes comparison of spectra much more difficult. Attempts were made to compensate for the adsorption of the adsorbent by using the instrument in a double beam mode. The results were not very satisfactory. In theory, the spectrum of the discs containing equivalent amounts of adsorbent should be identical, but in practice the distortion of the bands owing to finite particle sizes is so great that accurate matching is impossible. The best results, both when studying the spectrum of the adsorbed chelate, and changes in the adsorbent spectrum, were obtained by attenuating the reference beam and increasing the sensitivity of the instrument so as to amplify the uncompensated adsorption by a factor of ten.

The results of the infra red investigations are tabulated, showing the chelate bonds which were positively identified in the adsorbed state. From the results it is apparent that the chelates do not decompose extensively on the adsorbent, and that adsorption of the chelates is accompanied by the disappearance of free surface hydroxyl groups on a silica gel surface.

Infra Red Bands Identified

Pure Chelate (Iron)	On Silica Gel	On Alumina
702 cm^{-1}		
747 cm^{-1}	747 cm^{-1}	
831 cm^{-1}	830 cm^{-1}	
865 cm^{-1}	870 cm^{-1}	
1051 cm^{-1}		
1110 cm^{-1}		1120 - 30 cm^{-1}
1275 cm^{-1}	1275 cm^{-1}	1275 cm^{-1}
1305 cm^{-1}		
1320 cm^{-1}	1320 cm^{-1}	1320 cm^{-1}
1335 cm^{-1}	1335 cm^{-1}	1335 cm^{-1}
1378 cm^{-1}	1380 cm^{-1}	138- cm^{-1}
1428 cm^{-1}	1428 cm^{-1}	1425 cm^{-1}
1451 cm^{-1}	1455 cm^{-1}	1455 cm^{-1}
1460 cm^{-1}	1460 cm^{-1}	1465 cm^{-1}
1503 cm^{-1}	1500 cm^{-1}	1505 cm^{-1}
1565 cm^{-1}	1570 cm^{-1}	1572 cm^{-1}

The Elution of Copper 2-methyl-8-quinolinol
with Reagent Solutions

The sensitivity of the copper 2-methyl-8-quinolinol chelate to dilute reagent solutions has already received comment in previous chapters. This sensitivity made the copper chelate unique among the chelates studied, and finding the explanation for this could conceivably increase the possibility of eluting other chelates chromatographically.

Study of the chelates showed that the copper chelate was unique in that the stable chelate on precipitation from aqueous solution was $\text{Cu} (\text{C}_{10}\text{H}_8\text{NO})_2 \cdot 2\text{H}_2\text{O}$; a brown compound, which, on drying at 110°C , yields a green anhydrous compound $\text{Cu} (\text{C}_{10}\text{H}_8\text{NO})_2$.

This suggested that the copper chelate as used for chromatographic purposes was potentially capable of adding on two water molecules, or possible one further bidentate ligand. In order to determine the feasibility of this, an attempt to form a triligand chelate from reagent and the green compound was attempted in benzene. No evidence for its formation could be obtained. However, a Job's Law investigation of cuprous chloride and 2-methyl-8-quinolinol indicated that the stable compound in absolute alcohol was the 1:3 chelate.

These results suggested that the elution of the copper chelate could be due to the formation, possibly only at the surface, of a triligand chelate which disrupts the electron distribution of the chelate ring system sufficiently to break the hydrogen bond attaching the molecule to the surface. Alternatively, and in view of the fact that other triligand chelates are firmly adsorbed, a more likely explanation, the desorption of the copper chelate may be due to a ligand exchange mechanism, again involving a triligand intermediate. In this case the intermediate reverts to the diligand form by the displacement of the ligand partially attached to the surface, leaving the copper chelate free to move a short distance before re-adsorption. Both explanations would give rise to the observed facts, that the chelate elutes with excess reagent, but as no discernable spectral differences exist between benzene solutions of the diligand chelate and benzene solutions of the diligand chelate and free ligand that are not attributable to the free ligand alone, it is proposed that the second mechanism is the more likely.

In order to try and determine whether one of these two possible mechanisms operated, or whether it was simply a displacement mechanism, the elution of the copper chelate with related ligands

was attempted.

The first requirement of the related ligand was that elution of a mixed ligand chelate could be recognised, and so attention was concentrated on those derivatives of 8-quinolinol whose copper chelates would be readily distinguished spectrophotometrically from the copper 2-methyl-8-quinolinol chelate.

The reagents investigated were: I 2-methyl-5; 7-dibromo 8 quinolinol; II 6-nitro-8-quinolinol; III 2-methyl-5-phenylazo-8-quinolinol; IV 2-methyl-5-carboxyphenylazo-8-quinolinol, used as its ethyl ester; and V 2-methyl-5- sulphophenylazo-8-quinolinol. Of these compounds, I, which formed a copper chelate showed a maximum adsorption at 430 m μ , and IV, whose copper chelate had a maximum adsorption at 500 m μ , appeared the most suitable. However, their chromatographic behaviour showed some interesting differences. The azo derivative IV, did not elute its copper chelate from alumina under any of the conditions investigated, in common with compounds III and V. The dibromo derivative eluted approximately 90% of the corresponding copper chelate when used as a 2% solution in (1 + 1) benzene chloroform. The lower solubility of the dibromo chelates made the use of benzene alone difficult.

When the compounds were used in the attempted

elution of the 2-methyl-8-quinolinol copper chelate no elution was obtained with compounds II to V. The dibromo derivative was found, by subsequent elution of the remaining copper chelate with 2-methyl-8-quinolinol, to elute an variable amount of the copper chelate which in no case was greater than 5% of the quantity of the copper chelate sample used. As this derivative was prepared by bromination of 2-methyl-8-quinolinol, this result may easily be due to traces of the original material in the dibromo derivative.

From these results it seems that confirmation of the proposed mechanism of elution, via an intermediate triligand complex is difficult. More sophisticated techniques are required to examine this elution, for instance rate of desorption, and its dependence on free reagent concentration, would help to determine the exact role of the reagent. The possible elution of mixed ligand chelates would depend on the choice of a foreign ligand such that the stabilities of the 'pure' and 'mixed' chelates are similar, and yet the chelates must be readily distinguishable. Labelled 2-methyl-8-quinolinol may be useful in this context if the eluting chelate can be separated rapidly from the free ligand so as to minimise the chances of ligand exchange in the bulk solution.

CONCLUSION

The chromatographic behaviour of the metal chelates may be summarised as follows:-

Chelates containing oxygen in the chelate ring are strongly adsorbed on adsorbents having hydroxyl groups, particularly where there is a possibility of electron mobility in the molecule, as is the case with the quinolinol chelates.

Substitution of electron withdrawing groups, particularly in the 5:7-positions, weakens the adsorption but no significant differences in ease of elution were noticed.

Comparison of the chromatographic behaviour of the free reagent and of the chelates show that, in the case of the 8-quinolinol and β diketones, formation of the metal chelates greatly alters the chromatographic characteristics of the reagent. This is indicative of a different adsorption mechanism, and, since the formation of the chelate ring structure alters the most polar grouping of the ligand (in the case of the 8-quinolinol, the hydroxyl group), the explanation for the strong adsorption of the metal chelates must lie in the properties of the chelate structure as a whole rather than in the properties of the component parts.

Adsorption on adsorbents such as alumina and

silica gel is dependent, to a large extent, on the presence of groups in the molecule that may function as localised electron donating or accepting areas. The normal type of grouping for this purpose is well known, any cation or anion, carbonyl group, amine group, hydroxy group, to name but a few. However, aromatic systems also show strong adsorption on these adsorbents, to which is brought about by the localisation and donation of the π electron system.

It is postulated that with the metal 8-quinolinol chelates, a similar system operates. With the metals studied the d orbitals are involved in chelate bonding and may act as a link by which the aromatic π electrons of each individual ligand can be linked with those of the other ligands. This would mean that the chelate ring system, and in particular the metal atoms, the oxygen and nitrogen atoms directly bonded to it, may act as a focus for the π electron system, thus providing a 'grouping' that will be strongly adsorbed on alumina or silica gel.

The effect of substituents in the five and seven positions may be explained on this model by considering the groups in the context of their

electron withdrawing capacity. From their peripheral positioning these groups can only influence their associated ligand. Thus, while they may tend to inhibit the localisation of electrons in the chelate ring system, the substituents investigated, the halogens, are not sufficiently strong electron withdrawing groups to prevent this localisation in the vicinity of the chelate ring, and therefore to effect significantly the strong adsorption of the metal chelate.

With the 8-quinolinethiol chelates, the adsorption of the metal chelates, while stronger than that of the parent compound, is not so marked compared with the 8-quinolinol chelates. This is a further indication that the adsorption of the chelates studied is influenced almost entirely by the atoms in the chelate ring. The carbon skeleton and the structure of the two series of chelates are identical. The only significant change has been to exchange an atom which readily forms hydrogen bonds, oxygen, for one that is much less likely to do so, sulphur. Obviously this could be an oversimplification of the case; all the other differences between the two series of metal chelates may also effect the adsorption to an unknown extent.

The presence of d electrons in the sulphur containing chelates that are not present in the oxygen containing series may disarrange the electron distribution, but it is probable the replacement in the critical area of the molecule of an atom compatible with the adsorbent surface by an incompatible atom is the major, if not the only, factor in altering the chromatographic behaviour of two series of chelates that are in many respects very similar.

A consideration of the physico-chemical aspects of the 2-methyl-8-quinolinol chelates lead to the conclusion that, mechanistically, two sequential low energy processes are involved, one of which is *apparently* irreversible and the other probably reversible.

All the evidence, the type of site required, the activation energy of the first stage of the adsorption process, points to the formation of a hydrogen bond between the chelate molecule and a hydroxyl group on the adsorbent surface. The heats of preferential adsorption of the chelates are compatible with this view, being higher than would be expected for physical adsorption. The heats are of the order expected for a chemisorption reaction, ranging up to 30 kcal/mole, which is

sufficient for the replacement of benzene and formation of a hydrogen bond, but not high enough to indicate extensive decomposition of the chelates. Any decomposition by loss of a ligand would have been noticed chromatographically by the elution of the free ligand.

The heats of adsorption of the 8-quinolinethiol chelates on an alumina surface are much lower than those observed with the 8-quinolinol chelates, and it is not unreasonable to postulate that the adsorption of the sulphur-containing chelates is purely physical in character.

As far as analytical usage of the metal chelates for adsorbent chromatographic separation of metals are concerned, it appears that chelates of the 8-quinolinol type are of strictly limited use. The essential point is that dynamic equilibrium is necessary for elution of compounds of a mixture from a column once adsorption has taken place. This is only attained with the copper chelate and reagent solutions as the eluant. The chromium chelate is also separable, but that is a case of lack of adsorption rather than reversible adsorption. It is not possible to quantitatively elute the chromium chelate, once adsorbed; quantitative elution is only obtained when the chelate is passed through

the column in (1 + 1) benzene chloroform, under which conditions it elutes with no measurable retention.

The sulphur analogues of 8-quinolinol, chelating agents of the 8-quinolinethiol type, are much more promising. All of the chelates studied show a reversible type of adsorption and readily elute as sharp distinct bands. Moreover, by suitable choice of eluting solvent, e.g. benzene containing petroleum ether, or chloroform, the R_f value of any chelate may be varied between 0.0 and 0.9. This is clearly indicative of a system in which the adsorption of the adsorbate is of a simple character and closely similar to the adsorption of the solvent system.

From these results, it is apparent that the adsorption chromatography of sulphur chelates is a more promising line of approach for the development of analytical separations of metals based on column chromatography techniques. Two major problems to be solved before this can become a reality, are those of solubility in organic solvents: the 8-quinolinethiol chelates are noticeably less soluble in the common organic solvents than the 8-quinolinol chelates, and the greater problem of stability of the reagent to oxidation. During one

year it has been found that the metal 8-quinolinethiol chelates if kept in stoppered tubes are perfectly stable. No evidence of oxidation of the solid chelates were obtained or of oxidation in dry organic solution. This indicates that the metal chelates are probably stable enough for analysis, if ways of preventing the very rapid decomposition of the reagent in aqueous solution could be found.

In an attempt to overcome the problem of solubility the 2-methyl derivative of 8-quinolinethiol was prepared. The reaction scheme used was a modification of the procedure used by Lee to prepare 8-quinolinethiol (53).

0.1 Mole of 2-methyl quinoline was treated with an excess of chlorosulphonic acid at 120°C. The mixture was kept at this temperature under reflux until all of the 2-methyl quinoline had dissolved. After cooling, the reaction mixture was poured, slowly, and with vigorous stirring, on to 2 kg of crushed ice. The mixed sulphonyl chlorides were extracted with 100 ml. ether, which was removed by pumping off under reduced pressure. The mixed sulphonyl chlorides were then reduced in dry ethereal solution with lithium aluminium hydride

used in 70% excess.

Owing to the instability of the resultant thiols, no attempt was made to isolate and purify the 8-substituted compound. Of the derivatives that were expected to form, the 8, 6 and 4 substituted compounds, only the 8 derivative can form metal chelates. Consequently, the formation and precipitation of the metal chelate ensured that the correct compound was formed. Investigation of the chromatographic properties of chelates formed indicated that they were chromatographically homogeneous, stable on alumina columns, and appreciably more soluble than the 8-quinolinethiol chelates. Unfortunately the yields of useful reagent were very low, and only microgram quantities of chelate were obtained. No R_f values were measurable, but visible separation of a mixture of the chromium, copper, nickel, and iron, chelates were obtained using benzene with 10% 60 - 80° petroleum ether as solvent, and alumina as adsorbent. The order of elution was iron, nickel, copper, chromium.

The physico-chemical aspects of the adsorption of the 8-quinolinol type chelates gave some interesting results. The adsorption isotherm studies showed that the adsorption process was slow to reach equilibrium. This, at first, raised

difficulties in determining the adsorption characteristics of the chelates since it was difficult to decide what was true adsorption and what was a modification of the adsorbed chelate. Investigation of the adsorption on a time basis showed that the adsorption of most chelates was essentially complete in eight to ten hours. The major exception was the iron chelate; the equilibrium concentration of this, in benzene solution in the presence of alumina, was still decreasing after eighteen hours. No evidence of decomposition of the chelate was obtained under these conditions.

From the results of the isotherm studies it is evident that the chelates adsorb in a parallel manner on the surface, and attachment by the end-on adsorption of one ligand is highly unlikely.

On increasing the equilibrium concentration a saturation level is not reached, the adsorption of chelate increased in such quantities that multimolecular adsorption, or possibly incipient crystallisation, occurred. A third possibility, the adsorption of chelate in the pores of the adsorbent is unlikely owing to the size and shape of the molecules. The planar copper chelate exhibits far less tendency to adsorb increasingly with increasing equilibrium concentration than

does the bulkier iron chelate.

The parallel orientation of the molecules to the surface, may be readily explained by the fact that the chelate ring is the essential point of attachment of the molecule to the surface. The formation of the multilayers is more difficult to explain. Most of the chelates have fully satisfied valency requirements, and are unlikely to form inter-layer bonds.

From the rate studies, it appears that the adsorption of the multilayers is a low activation energy reaction in which mass transfer plays a dominant part. This reaction with its low energy of activation and accompanying low heat of adsorption, shows an extremely high apparent entropy change. This suggests that either a chemical process involving a large entropy change, such as partial decomposition, occurs at, or near, the surface, or that very stringent requirements for the juxta-position of the adsorption site, and adsorbate molecule, greatly reduce the rate of adsorption.

Attempts to obtain evidence of decomposition of the chelates by examining the eluant for free ligand, which is known to elute readily under all of the conditions used for the adsorption

and elution of the chelates, were unsuccessful. Only when pyridine or acetic acid were used as eluants was any evidence of the presence of free ligand obtained. Subsequent study of solutions of the chelates in these solvents showed that extensive decomposition occurred, and so the elution of the free ligand is more likely to be due to the influence of the solvent than to decomposition induced by the adsorbent.

As confirmation of the stability of the adsorbed chelates, x ray and infra red studies of chelate samples show that the chelate is present on the surface, and no evidence of decomposition products was obtained. The entropy changes observed cannot therefore be attributed to decomposition of the chelates, and from the available evidence can only be explained by postulating that the probability of adsorption of a molecule with the necessary activation energy is so low that the rate of adsorption is controlled by the factors influencing this probability and not by the activation energy requirements.

There are still some unanswered questions as to the adsorption of the 8-quinolinol chelates on hydroxide adsorbents. In particular, the kinetics and entropies of adsorption require further study. For this purpose an apparatus in which more precise

concentration time relationships than those obtained with a modified Unicam is required. The two essentials are, continuous monitoring of the equilibrium concentration, and larger quantities of chelate, solvent, and adsorbent. The most promising system from this aspect is a flow cell with a separate reaction vessel.

Chromatographically, it appears that separation and elution of oxygen-containing chelates, in particular those with aromatic ligands, is an extremely difficult if not impossible task. Investigation of sulphur, or nitrogen, type ligands promises to be much more rewarding, with substituted 8-quinolinethiol derivatives, especially derivatives more stable to air oxidation than the parent reagent, of particular use.

Calorimetric studies of heats of preferential adsorption can be of great use in these studies, since the heats of preferential adsorption may be determined in any solvent system. This will enable conditions of separation and elution to be optimised without the necessity for lengthy testing of solvent systems on large chromatographic columns.

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