RATE CONTROLLING MECHANISMS IN THE EXTRACTION OF ZINC AND COPPER WITH A SUPPORTED LIQUID MEMBRANE

A dissertation submitted to the University of London in partial fulfilment of the requirements of the degree of Doctor of Philosophy and the Diploma of the Imperial College.

by

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UNIV.

To my Parents, Sotiri & Aspasia

and

To my beloved wife, Litsa

for inspiring, encouraging and sustaining

"... Ὡς ἐμεγαλύνθη τά ἔργα σου,

Κύριε, πάντα ἐν σοφίᾳ ἐποίησας..."

(Ψαλμός ΡΓ'. Δαυΐδ)

PREFACE

This dissertation is a description of the work carried out in the Department of Chemical Engineering and Chemical Technology, Imperial College of Science, Technology and Medicine, London, under the supervision of Dr. E. S. Ortiz.

The material presented is the original work of the author, and no part of it has been submitted for a degree at this or any other University.

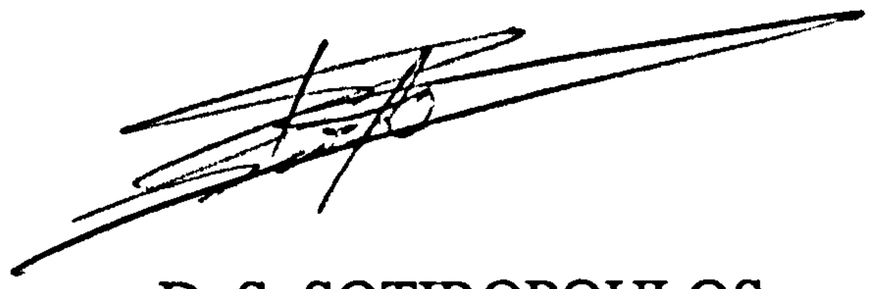
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D. S. SOTIROPOULOS

ABSTRACT

The extraction of zinc and copper from single and mixed sulphate solutions through a supported liquid membrane containing di(2-ethylhexyl) phosphoric acid, (DEHPA) in n-dodecane was investigated. The objectives of this work were to establish the rate controlling mechanisms of extraction and the interactions between the two metals.

Two hydrophobic polypropylene hollow fibres, (MICRODYN, S6/2, and Q3/2), of diameters 1.8mm and 0.6mm, and thickness 0.4mm and 0.2mm respectively, were used in order to study the effect of the Reynolds number and the role of the membrane thickness on the extraction flux. The effect of increasing the number of hollow fibres in the module was investigated in two bundles of four fibres, one of each fibre size.

Experiments were carried out at Re numbers in the range between 5 and 128, with metal concentrations varying between 66 ppm and 840 ppm, and DEHPA concentrations of 0.05M, 0.1M, 0.15M and 0.2M. All experiments were conducted at 25°C and with an ionic strength of 1.0 in the aqueous feed. It was observed that the predominant rate controlling step in the mechanism of extraction changes as the concentrations of metal, DEHPA and the hydrodynamic parameters are varied.

Results also show that zinc is extracted preferentially from mixed feeds. The efficiency of separation between the metals is better at pH 3 than at pH 4.

A mathematical model for the zinc extraction system, which includes the extraction and stripping reactions as well as mass transfer coefficients was used to predict the zinc flux. The mass transfer coefficients were calculated using equations reported in the literature.

The agreement between the experimental results and the results predicted by the model was in general good, except for those at Re=15 and Re=128, for DEHPA 0.2M in which the fit is poor at zinc concentrations above 200 ppm.

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NOMENCLATURE

The following symbols were used except when otherwise defined in the text.

α_o	activity of DEHPA dimer (kmol/m^3)
α_{zo}	activity of organic zinc (kmol/m^3)
C	molar concentration (kmol/m^3)
$\mathcal{D}_{AB}$	mutual diffusion coefficient (m^2/s)
Di	inside diameter of the fibre (m)
Do	outside diameter of the fibre (m)
I	ionic strength (kmol/m^3)
K	mass transfer coefficient (m/s)
$k_{I\alpha}$	extraction rate constant (m/s)
$k'_{I\alpha}$	stripping rate constant (m/s)
L	length of the fibre (m)
Q_F	Feed flow rate (m^3/s)
Q_S	Strip flow rate (m^3/s)
R_z	zinc interfacial extraction flux (kmol m^{-2} s^{-1})
r	cylindrical coordinate
r'	radius of the fibre(m)
r_o	cylinder radius(m)
T	absolute temperature (K)
t	time (s)
u	fluid velocity(m/s)

x rectangular coordinate(m)

$\chi_{fd,h}$ hydrodynamic entry length(m)

Greek letters

γ activity coefficient

δ thickness of the fibre (m)

δ' hydrodynamic boundary layer thickness (m)

μ_w viscosity of water (kg/ms)

μ_d viscosity of dodecane (kg/ms)

ν kinematic viscosity (m^2/s)

φ an association parameter for solvent in Wilke and Chang correlation

Subscripts

A,B component A (solute) and component B (solvent)

H Hydrogen ion

i interfacial values

o DEHPA dimer

zα aqueous phase zinc ions

zo organic phase zinc

Dimensionless Groups

Re Reynolds number

Sc	Schmidt number
Sh	Sherwood number

CHAPTER 1

INTRODUCTION

The continuous increase of world's needs for most of the known metals and the decrease in grade of the available ores make it interesting to find effective and efficient methods for processing waste solutions containing metal ions even at very low concentrations. Consequently novel separation techniques suitable for the separation of solutes from dilute feeds, such as the supported liquid membrane, are gaining considerable attention for their possible application in recovering and separating metal species from aqueous solutions.

Supported liquid membranes (SLMs) consist of a solution of a reactant in a solvent which is contained within the pores of a polymeric solid. In this liquid membrane phase, a solute from a feed solution is extracted, usually selectively by combining with the reactant to form a complex. The complex then diffuses through the membrane and is stripped at the other side of the membrane. This carrier-mediated transport of solute is affected by the diffusional resistances and the reaction kinetics of the extraction and stripping steps; many studies have been conducted on the permeation of metal ions through SLMs.

A suitable membrane geometry is that of a hollow fibre, as shown in Figure 1.1. A schematic representation of the cross and axial sections of a Hollow Fibre Supported Liquid Membrane (HFSLM) is shown in Figure 1.2.

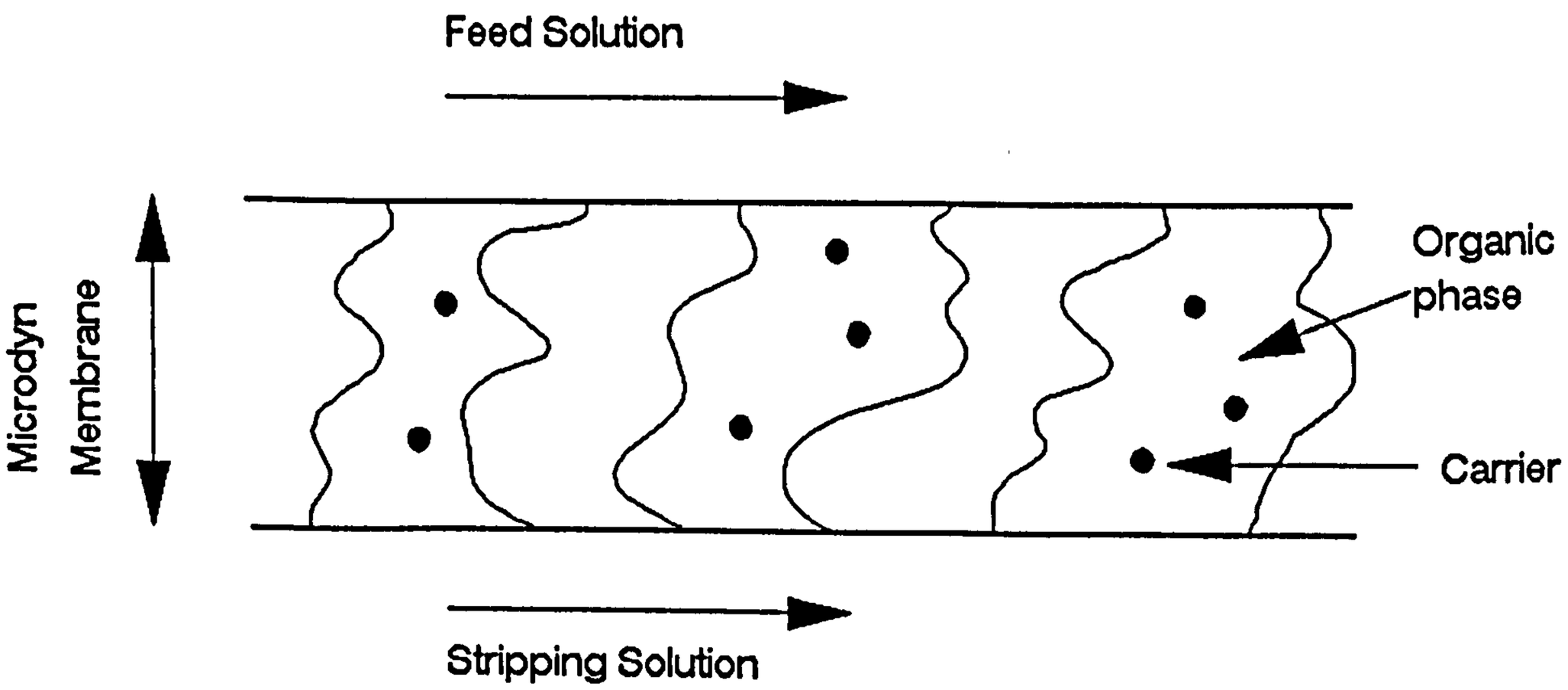


Figure 1.1 Schematic representation of SLM.

Although SLMs should be as thin as possible to minimize diffusion resistance, the membrane must be strong enough to withstand an appreciable pressure difference between feed and stripping streams and it must hold sufficient solvent with an appreciable area for phase contact. Since the membrane solvent is held in the pore structure solely by capillary forces, it is inevitable that during the separation process the solvent and/or carrier is to some extent washed or forced out of the membrane; in addition, dissolution may result in losses to the process stream. This will give rise to the imbibition of the solvent-water interface into the pores, and to pinhole leaks in the membrane, which will cause a decrease in the separation performance of the SLM. Therefore, a compromise must be reached between the membrane diffusional resistance and its stability, and in order to consider this balance, the role of diffusional resistance of the membrane in the kinetics of extraction must be investigated.

Di(2-ethylhexyl) phosphoric acid has been widely used to extract and separate a number of metals Zn(II), Cu(II), Co(II), Ni(II), Fe(III), In(II), in a wide range of operating conditions due to its chemical stability, high selectivity for metal species and extremely low aqueous solubility, (Brisk and McManamey, 1969a; Komasawa et al., 1981; Cianetti and Danesi, 1983a; Komasawa and Otake, 1983b; Ihm et al., 1988; Dreisinger and Cooper, 1989; Miyake et al., 1990; Juang and Su, 1992; Juang, 1993b; Juang and Jiang, 1994).

Ajawin et al., (1980,83) and Murthy, (1987) investigated the equilibrium and kinetics of extraction and stripping of zinc as well as the location of the

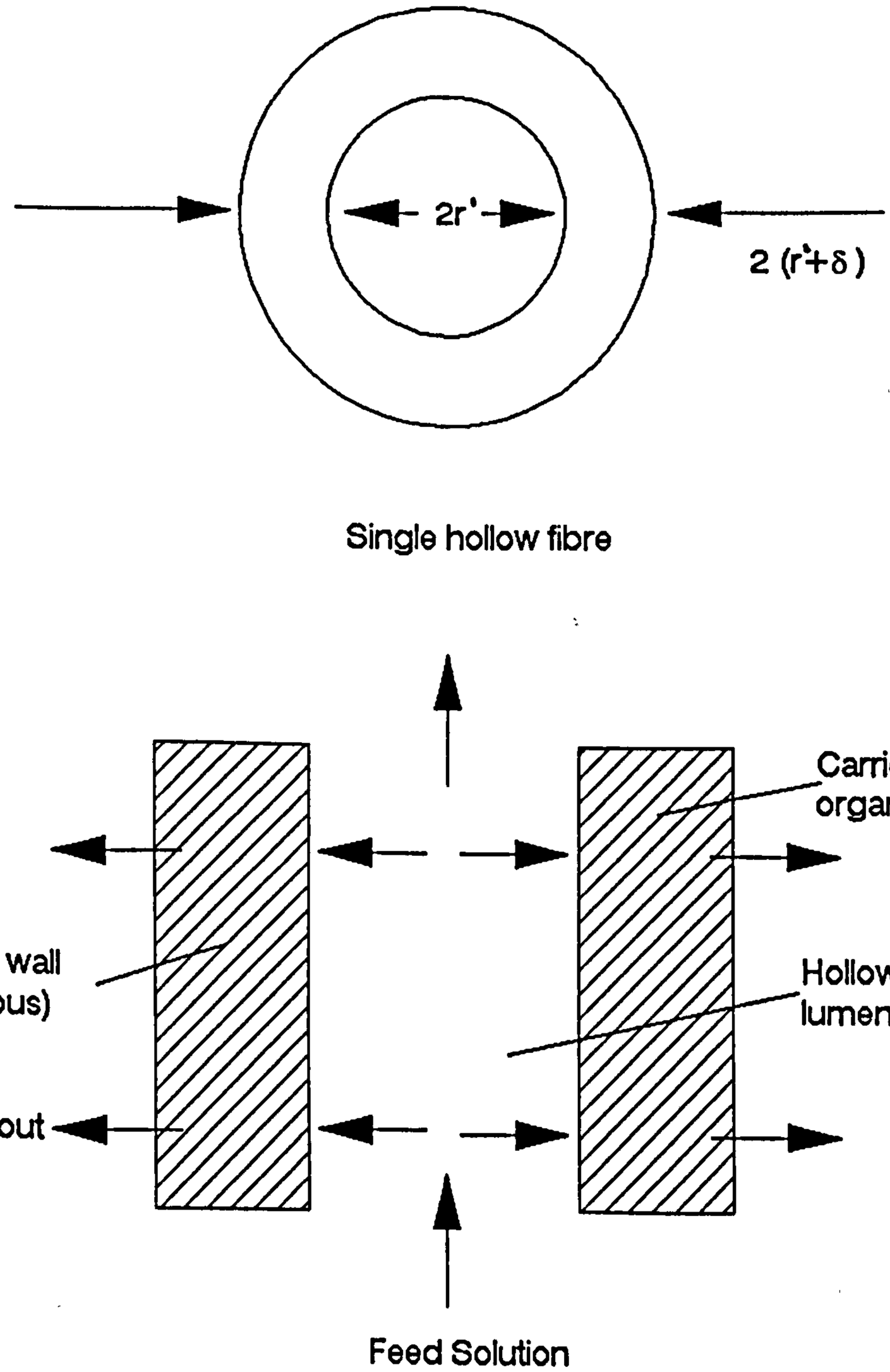


Figure 1.2 Schematic representation of a hollow fibre supported liquid membrane, (HFSLM), r' is the radius and δ is the wall thickness of the fibre.

rate controlling reactions. They concluded that in both processes the rate controlling reaction is interfacial and proposed rate equations that included the resistances in the diffusional films of two phase conventional solvent extraction. Saeed&Ortiz,(1990) used these equations to model the extraction process in a two phase spray column. These equations can provide the basis for a model of the rate of extraction with the SLM together with a suitable mathematical description of the hydrodynamic conditions of the system.

The objectives of this work were:

(i) to study the performance of a supported liquid membrane containing di(2-ethylhexyl) phosphoric acid in the extraction of zinc and copper over a wide range of conditions and establish the rate controlling mechanism of extraction at different set of conditions. For this two sizes of fibre were used of different diameter and thickness, in order to enlarge the range of hydrodynamic conditions and the thickness of the diffusional film resistance in the liquid membrane.

(ii) to investigate the interaction between the two metals when extracted from mixed feeds.

(iii) to develop a model for the rate of zinc extraction with the supported liquid membrane based on the kinetics of chemical reaction and the rate of diffusional transfer.

This thesis consists of seven chapters. The next chapter reviews the literature relevant to all areas of this work. A mathematical model for estimating the Zn flux, applicable to the present work, is developed in chapter 3. The experimental procedure, results and discussion of results are

presented in Chapter 4. Chapter 5 deals with the comparison of experimental and predicted results using the equation developed in chapter 3. The main conclusions are presented in chapter 6. Finally, the suggestions for future work are given in chapter 7.

CHAPTER 2

LITERATURE SURVEY

2.1 Liquid -liquid extraction using DEHPA

Di(2-ethylhexyl) phosphoric acid (abbreviated as DEHPA) has been shown to be an effective extractant in hydrometallurgical processes for the separation and purification of divalent transition metals such as copper,

cobalt, nickel, manganese and zinc (Flett and Spink, 1976; Sekine and Hasegawa, 1977; Sato et al., 1978) for over three decades and therefore the relevant literature is quite abundant. Hence, only the parts of the literature which are relevant to this work will be reviewed.

2.1.1 Extraction mechanism of DEHPA

The extraction mechanism involves the exchange of the hydrogen ions associated with DEHPA in the organic phase for the metallic ions present in the aqueous phase. The complex formed is soluble in the organic phase and the reaction can be expressed as:

$$2(RO)_2\overset{\overset{O}{\|}}{P}-OH \;+\; M^{2+} \;\Leftrightarrow\; M\left[OP\cdot(OH)_2\right]_2 \;+\; 2H^{+} \qquad (2.1)$$

organic phase | aqueous phase | organic phase | aqueous phase

where $(RO)_2\overset{\overset{O}{\|}}{P}-OH$ = DEHPA

and M^{2+} =Divalent metal cation

Thus for a reversible reaction

$$K = \frac{\left[M\left(O\overset{O}{\overset{\|}{P}}-(OR)2\right)2\right]\left[H^{+}\right]^{2}}{\left[M^{2+}\right]\left[(RO)_{2}\cdot\overset{O}{\overset{\|}{P}}-OH\right]^{2}} \qquad (2.2)$$

From equation (2.2) it follows that for the case of divalent metals, the amount of metal extracted is directly proportional to the square of the extractant and inversely proportional to the square of the hydrogen ion concentration. So extraction can be increased by raising the concentration of the extractant and decreased by lowering the pH.

There are generally three principal groups of extractants, (Tavlarides 1987), acidic, basic, and solvating. Applications in supported liquid membrane extraction of metals is generally restricted to the former two groups.

Di(2-ethylhexyl) phosphoric acid (DEHPA, HR), has been used for a long time for the extraction and separation of a number of metals such as Cu(II), Co(II), Ni(II) and Zn(II), as well as Fe(III), In(III), Y(III), Zr(IV) and U(VI) in a wide range of operating conditions due to its chemical stability, high selectivity for metal species and extremely low aqueous solubility, (Komasawa et al., 1981; Cianetti and Danesi, 1983a; Komasawa and Otake,

1983b; Ihm et al., 1988; Johnston, 1988; Dreisinger and Cooper, 1989; Miyake et al., 1990 and Juang and Su 1992). This extractant has excellent properties for the extraction of zinc and has been used to extract it from different media, nitrate (Grimm and Kolarik 1974a; Rice and Smith, 1975; Sato and Ueda, 1974; Sato et al., 1978a), perchlorate, (Smelov et al., 1972; Grimm and Kolarik, 1974b; Sastre and Muhammed, 1984), sulphate, Forrest and Hughes, 1978; Ajawin et al., 1980, 1983; Sastre and Muhammed, 1984; Huang and Juang, 1986b; Bart et al., 1992). Besides DEHPA has been used in many industrial processes for several metals and some of these processes have been applied to the zinc recovery or purification, (Nogueira and Regife, 1977; Nogueira et al., 1980; Thorsen, 1983; Valle and Juan Garcia, 1984; Heng et al., 1986).

Also, alkylphosphoric acid has received much attention due to its potential in the reprocessing of nuclear fuel and in selective hydrometallurgical recovery of metals, (Inoue and Nakashio, 1982), as well as the extraction of rare earth elements, (Minagawa, 1990; Hung, 1992; Thakur et al., 1992). It is known that extraction of rare earth elements with DEHPA is a rapid process.

Many studies of metal extraction with alkyl phosphoric acid, (DEHPA) have been carried out from the view point of equilibrium and kinetics, (Kimura, 1960/61; Roddy et al., 1971; Vandergrift and Horwitz, 1977; Islam and Bismas, 1978; Danesi and Cianetti, 1982; Ajawin et al., 1983; Komasawa and Otake, 1983a; Huang and Juang, 1986a).

Harada et al., (1989), concluded that in order to increase the rate of extraction, it is desirable to select diluents in which the distribution of the chelating agent in the aqueous phase is as large as possible, neglecting loss of the agent in the aqueous phase, and also to modify the chelating agent so that the distribution of the agent is the aqueous phase becomes large. As a result of this action, the 1:1 metal complex formation comes to play a significant role in the rate of extraction.

Miyake et al., (1986) reported that reagents in current use for the extraction of copper are all of the o-hydroxyoxime type, such as LIX series and SME 529. To clarify the mechanism of solvent extraction of metal ion by these commercial chelating agents, it is most important to decide where chelate complex formation occurs. There are two different views on the locus of chelate formation. (Carter and Freiser, 1980; Akiba and Freiser, 1982), claimed that the metal complex is produced in the aqueous phase. On the other hand (Flett et al., 1973; Komasawa et al., 1980b,c and Miyake et al., 1983) claimed that the reaction of metal complex formation occurs at the organic-aqueous interface because commercial chelating agent has very low solubility in the aqueous phase.

It has been reported that DEHPA and its metal complexes are interfacially active, (Vandergrift and Horwitz, 1977, 1980; Miyake et al., 1990; Ihm et al., 1988). As has been stated in these independent papers, the formation of metal complexes with DEHPA proceeds mainly at the interfaces, since the aqueous solubility of DEHPA is expected to be extremely low. As a result, the rate of metal extraction depends on the interfacial concentration of

DEHPA molecules equivalent to the surface exchange, or on its reciprocal, i.e., the molecular area occupied by a statistical DEHPA molecule at the interface.

The enrichment or separation of Zn(II) and Cu(II) from sulphate solutions by solvent extraction is of major interest in the hydrometallurgical process, (Hughes 1975; Forrest and Hughes, 1978; Beneitez and Calderon, 1990). Although an oxime type reagent, for example, LIX or SME 529, could be used to remove small amounts of Cu(II) from an aqueous feed containing large amounts of Zn(II), a sharp separation of Zn(II) from Cu(II) can be achieved, according to the solution of pH, by use of di(2-ethylhexyl) phosphoric acid (Hughes 1975; Forrest and Hughes, 1978; Cox and Flett, 1987).

Also, the enrichment or separation of Co^{2+} and Ni^{2+} ions by solvent extraction is of major interest in hydrometallurgical processes, (Ritcey and Ashbrook, 1979; Komasawa et al., 1983c; Danesi et al., 1985c; Cox and Flett, 1987). The extractant di(2-ethylhexyl) phosphoric acid (DEHPA) has been widely used to perform this operation from sulphuric acid solutions, due to its high stability and selectivity for metals as well as extremely low aqueous solubility (Ritcey and Ashbrook, 1979; Komasawa et al., 1983c; Danesi et al., 1985c; Cox and Flett, 1987).

The solubility of DEHPA in acidic aqueous solutions is considered to be negligibly small (Ritcey and Ashbrook, 1979; Komasawa et al., 1981; Huang and Juang, 1986b; Cox and Flett, 1987; Miyake et al., 1990), so the total amount of DEHPA in the membrane phase is kept constant.

Several studies with solid supported liquid membranes (SSLM) where DEHPA was used as the carrier have been reported. DEHPA was used to remove Eu(III) from chloride media by (Danesi et al. 1982). In their work, diffusion through the membrane and aqueous film diffusion on the feed side of the membrane were considered the only rate determining steps. Flett et al., (1982), used mixtures of DEHPA and tri-n-octylphosphine oxide (TOPO) to recover uranium from wet process phosphoric acid, but the effects of aqueous diffusion processes and chemical reaction rates were disregarded.

Komasawa et al, (1983a), used DEHPA to increase the permeation rate of Cu^{2+} with 2-hydroxy-5-nonyl-benzophenone oxime carrier in order to avoid the strong dependence on the chemical kinetic rate observed for this system.

Harada and Shiomi, (1984) showed that efficient separation of zinc and iron can be performed with the help of these two carriers (TOA, DEHPA).
The separation of zinc from diluted feed streams containing other metal ions is known to be effective using organophosphorus liquid ion-exchangers as carriers, (Draxler and Marr, 1986).
Teramoto et al., (1989), demonstrated that zinc is effectively removed from its dilute solutions by using di(2-ethylhexyl)phosphoric acid as the carrier.

Mohapatra et al., (1992a) showed that the rate of permeation of Co(II) through a supported liquid membrane (SLM) containing di(2-ethylhexyl) phosphoric acid in kerosene is primarily controlled by diffusion through the aqueous boundary layer at a lower metal ion concentration and pH.

The transport of Co(II) ions through SLMs containing DEHPA has been freequently examined. (Huang and Juang, 1988; Chaudry et al., 1990; Huang and Tsai, 1991a; Mohapatra et al., 1992a).

However, less work has been on elucidating the nature of complex formation at the feed-membrane interface, (Mohapatra et al., 1992a). Furthermore, most authors have assumed that contributions due to interfacial chemical reaction or aqueous film diffusion are negligible, (Chaudry, 1990; Yi and Tavlarides, 1992).

Scott and Ibhadon, (1993), have demonstrated that the selective separation of metal cations of cerium using DEHPA immobilized in a liquid membrane has been demonstrated. This behaviour is similar to that experienced in the separation of Cu(II) from Zn(II) by (Loiacono, 1986).

2.1.2 Reaction stoichiometry

Dialkyl phosphoric acids exist as the dimeric form in most diluents of low polarity, which do not form strong hydrogen bonds with these acids (Dyrssen, 1957; Peppard et al., 1958; Baes et al., 1958; Ulyanov and Sviridova, 1963; Yagodin and Tarasov, 1969). The state of the DEHPA in both organic and aqueous phases, is characterized by the dimerization, distribution and acid dissociation constants, the values of which are determined by using the phase distribution data for DEHPA. As a rule, the distribution data are obtained by analysis of DEHPA content in the aqueous phase, which can be measured spectrophotometrically, (Komasawa et al., 1981), colorimetrically, (Ulyanov and Sviridova, 1963), or radiometrically

with ^{32} P-labeled DEHPA, (Kolarik, 1967; Smelov and Lanin, 1969; Ulyanov and Sviridova, 1970; Liem, 1972).

Huang and Juang, (1986a), proposed the spectrophotometrical method since it possessed high sensitivity, (Bhattacharyya and Murty, 1974).

Extensive studies using cryoscopic and isopiestic techniques, (Baes et al., 1958; Diamond and Tuck, 1960; Ferraro et al., 1961; Ferraro and Peppard, 1963; Peppard et al., 1957a,b, 1958, 1960, 1965; Rao et al., 1966), have been performed to determine the degree of association of DEHPA and other organophosphorus acids in organic solvents. These studies conclude that this organic acid exists as a dimer in non-polar solvents, i.e. n-heptane, n-octane. It has also been reported, (Diamond and Tuck, 1960), that the acid is predominantly monomeric in alcohols whereas in chloroform and acetone both the monomer and dimer forms coexist.

The possibility of higher aggregates for DEHPA has been suggested, (Ferraro et al., 1961; Ferraro and Peppard, 1963). The work of Baes and Baker, (1960), showed deviation of up to a 35% from the ideal behaviour of DEHPA dimer for iron extraction and therefore suggested possible partial trimerization of the acid.

Kertes, (1971) pointed out that such deviations could be explained in terms of non-specific and non-ideal behaviour of the dimer rather than further association. Baes and Baker, (1960), have reported the non-ideal behaviour of dimeric DEHPA in n-octane in terms of activity coefficients when extracting rare earth metals from sulphate and nitrate solutions .

Alstad et al., (1974) found that DEHPA forms non-ideal solutions in an aliphatic isoparaffinic diluent such as shell Sol T. They suggested that the deviations from ideal behaviour are due to the increase in solute-solvent interaction with increase in DEHPA concentrations and expressed the non-ideal behaviour in terms of activities.

Danesi and Vandergrift, (1981a) evaluated the activity coefficients of DEHPA in n-dodecane from liquid-liquid distribution studies of Eu^{3+}, Tm^{3+} and Ca^{2+}. They found that all the three systems gave identical values of activities.

They attributed the deviations from ideality to weak H_2R_2-H_2R_2 dipole-dipole interactions only and not to the formation of trimeric or higher polymeric species. (Baes and Baker, 1960; Ferraro et al., 1961; Peppard et al., 1965) while (Alstad et al., 1974), attributed the non-ideality to solute-solvent interactions. Danesi and Vandergrift also compared the activity coefficients in different diluents reported in literature. (Alstad et al., 1974; Baes, 1962; Danesi and Vandergrift, 1981a) found that they were in good agreement thus showing that the solute-solute interactions are appreciably affected by the different nature and degree of purity of the aliphatic diluent.

Other investigators, (Smelov et al., 1972; Komasawa et al., 1981; Huang and Juang, 1986b), reported the dimerization of DEHPA in non-polar solvents. They found that DEHPA was a strong acid and that the majority of the molecules were dimerized in non-polar solvents, i.e. n-heptane, n-octane and kerosene. Their studies on the distribution of DEHPA between low-polarity diluents and aqueous solutions indicate that the solubility of

DEHPA in aqueous solutions is extremely low, which is suitable for commercial operation.

Mc Dowell and Coleman, (1963), proposed a generalized reaction stoichiometry for the liquid-liquid extraction of metals with DEHPA. Their equation is of the form

$$M^{z+} + \frac{m}{2}H_2R_2 \Leftrightarrow MA_z(m-z)HR + zH^+ \qquad (2.3)$$

where m is a constant. They argued that satisfying the coordination number of the metal is more important than the chelation by hydrogen bond pairs. Since for many polyvalent cations the accepted coordination number is twice the valence, this equation could explain the observed experimental results.
Kertes, (1971) reported that in most chelating extractive systems whenever the coordination number of the metal equals twice its ionic charge, the chelate formed satisfied the coordination requirements of the metal and the metal was readily extractable into both polar and non-polar solvents.
The reversible nature of the above reaction with respect to hydrogen ion can be used to recover the metal from the organic phase by stripping with an aqueous acidic solution.

The reaction stoichiometry of divalent metals extraction with DEHPA has been extensively studied, (Komasawa et al., 1981; Cianetti and Danesi, 1983a; Komasawa and Otake, 1983b; Ihm et al., 1988; Dreisinger and Cooper, 1989; Miyake et al., 1990; Juang and Su, 1992). Based on the fact

that the kinetic data of solvent extraction cannot be explained by an interfacial reaction mechanism but are successfully modeled by an interfacial diffusion with an aqueous reaction mechanism, Dreisinger and Cooper, 1989), proposed that complex formation between Co(II) ions and DEHPA probably occurs in the aqueous layer adjacent to the organic-aqueous interface. From the nature of DEHPA, such as its interfacial activity and extremely low aqueous solubility, however, most researchers have indicated that the formation of metal-DEHPA complexes is very likely to be interfacial, (Brisk and McManamey, 1969a; Cianetti and Danesi, 1983a; Komasawa and Otake, 1983b; Ihm et al., 1988; Miyake et al., 1990).

It has been shown that the reaction between copper ion and DEHPA occurs at the membrane interfaces according to the following reaction equation, (Komasawa and Otake, 1983b; Melzner et al., 1984; Huang and Juang, 1988).

$$Cu^{2+} + 2(RH)_2 \Leftrightarrow CuR_2 \cdot 2RH + 2H^+ \qquad (2.4)$$

When an aqueous feed solution containing copper ions flows through the lumen of an HFSLM, the copper ions are continuously extracted by the carrier present in the membrane phase, causing the copper ion concentration of the feed solution to gradually decrease along the hollow fibre.

The reaction stoichiometry of Co^{2+} and Ni^{2+} ion extraction with DEHPA has been extensively studied, (Grimm and Kolarik, 1974a; Komasawa et al., 1981; Preston, 1982; Huang and Tsai, 1989; Miyake et al., 1990; Huang and Tsai, 1991a; Juang and Su, 1992).

2.1.3 Equilibrium studies

Many papers dealing with the equilibrium constants of DEHPA have been published, considerable discrepancies remain among the values given by the various authors. These discrepancies may have been caused by using $DEH^{32}PA$ containing some radioactive impurity (Liem, 1972) by phase separations, particularly with similar densities of the phases and the tendency of the system to form stable emulsion, by the impurity of DEHPA (Yagodin and Tarasov, 1969). However, Liem, (1972), re-examined his original data using purified $DEH^{32}PA$ and found that the disagreement between the values reported was still present and could hardly be explained.

The equilibrium constants of DEHPA were determined in the nitrate, (Komasawa et al., 1981) and perchlorate media, (Kolarik, 1967; Ulyanov and Sviridova 1963, 1970; Liem, 1972). It was found that the effect of the type of salts were not negligible.

Smelov et al., (1972), investigated the equilibrium extraction of zinc from nitric acid and perchloric acid solutions into DEHPA dissolved in various diluents. Their results agree with the equation mentioned earlier on but the value of m was dependent on the nature of the diluent used. It was found to be 3 for saturated aliphatic hydrocarbons in which case the extracted complex was $ZnR_2H_2R_2$. This last conclusion agrees with the findings of (Kimura, 1960/61) and (Sato and Ueda, 1974). The degree of extraction was found to decrease in the order saturated aliphatic hydrocarbons > Carbon tetrachloride > o-xylene > benzene > chloroform. This was explained in terms of dimer solvation; with the extraction decreasing as the diluent ability

to solvate polar molecules increases. The same effect of diluent has also been suggested by (Niitsu and Sekine, 1975).

Also, the author studied the extraction of zinc at varying concentrations from nitrate solutions using DEHPA dissolved in different diluents. The composition of the extracted zinc species was shown to depend on the type of diluent used. For aliphatic diluents, e.g. hexane and octane, the species ZnR_2HR was suggested, while $ZnR_2H_2R_2$ was formed in other diluents such as benzene, o-xylene, CCl_4, and chloroform. Ajawin et al., (1980) suggested that only ZnR_2HR is formed when extracting zinc from aqueous sulphate solution using DEHPA dissolved in n-heptane.

Grimm and Kolarik, (1974a) studied the extraction of zinc at tracer level from nitrate and chloride solutions using DEHPA dissolved in n-dodecane. They found that the species ZnR_2HR and ZnR_2H_2 were formed. At macro concentrations of zinc they found that the extracted species had the composition $(ZnR_2)_n$ where the values of n varied between 2 and 3.5, depending on the diluent used, (Grimm and Kolarik, 1974b).

The authors also, studied the extraction of bivalent transition metals: Cu, Co, Ni, Zn and Cd into solutions of DEHPA in n-dodecane. Their results for zinc show that both the complexes ZnR_2HR and $ZnR_2H_2R_2$ are formed in the organic phase, while Cianetti and Danesi, (1983a), reported that only one complex, $ZnR_2H_2R_2$, is formed when using DEHPA activity instead of concentrations.

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Cognet et al., (1976/77), have shown that the ionic strength has little influence on the extraction of copper by a cationic extractant and that the effect of increasing concentration of chloride is a decrease in extraction at constant concentration of H^+ ions.

The extraction is of the same order of magnitude from sulphate and chloride solution at the same true concentration of H^+; but the apparent concentration in H^+ ignoring the formation of hydrogenosulphate ions is more important from the practical point of view the extraction is much higher in sulphate solution than in chloride solution at the same apparent concentration of H^+. In order to operate in chloride solution, it is therefore important to consume the H^+ ions resulting from the extractions for instance with the oxidation of cuprous ions by air as in the process proposed by, (Demarthe et al., 1976).

Baker et al., (1977), observed a limiting flux value in the permeation of Cu^{2+} through a SSLM consisting of pure LIX 64N when the metal concentration was increased. This was attributed to the limited solubility of the extracted copper complex. In fact, they isolated a green precipitate, which is characteristic of this copper complex, from the membrane phase. Imato et al., (1981), while studying the transport of Cu^{2+} with LIX 64N at high copper concentration, did not observe the precipitate. A possible explanation is that they employed LIX 65N diluted with phosphorous esters.

Largman and Sifniades, (1978) proposed that the rates of chemical reaction are the only active resistance in the transport of copper at macro-concentrations using SSLM consisting of a variety of hydroxyoxime carriers. Organic diffusion is quoted in this work as the main resistance only for fresh

membranes. Aqueous diffusion contribution is disregarded. Choy et al., (1974), reported the existence of an induction time prior to the attainment of steady state in their study of the transport of sodium macroconcentrations using monensine and cholanic acid as carriers. This induction time was explained in the form of an added diffusion resistance in the membrane. No theoretical basis equations were given.

Kolarik, (1982), reviewed the liquid-liquid equilibrium involving acidic organophosphorus extractants up to 1978, Coleman and Roddy, (1971) and Danesi and Chiarizia, (1980), reviewed the kinetics of liquid-liquid extraction up to 1969 and 1979 respectively.

Nakashio et al., (1982) studied the separation of both metals Cu(II) and Zn(II) with PC-88A, and found that zinc and copper are extracted completely into organic phase at pH=4 and pH=6 in the case of n-heptane diluent. This extractability is the same as the result of (Grimm and Kolarik, 1974a) obtained from DEHPA in n-dodecane diluent system. The extractability in toluene diluent was found to be lower than that in n-heptane. The extracted species were found to be $CuR_2.2HR$ for copper and $ZnR_2.HR$ for zinc. In addition, they proved that PC-88A is superior to DEHPA at least with respect to the separation of copper and zinc.

Komasawa et al., (1983b) found that the extract compositions obtained for copper, Nakashio et al., (1982), zinc, Nakashio et al., (1982) and lanthanides Enxin et al., (1980) with EHPNA have also been found to be the same as those when DEHPA is used. (Kojima et al., 1969; McDowell and

Coleman, 1965; Smelov et al., 1972). The pH functionality of EHPNA is generally lower than that for DEHPA.

Komasawa et al., (1983c) used DEHPA for the separation of cobalt and nickel from aqueous solution, and reported interaction throughout the experiments.

Sastre and Muhammed, (1984) showed that the species extracted into the organic phase have the composition ZnR_2HR and $ZnR_2H_2R_2$ for both perchlorate and sulphate systems. (Grimm et al., 1974a) are in agreement with their finding that the composition of the aqueous phase does not affect the species formed in the organic phase.

Miralles et al., (1986), reported the metal distribution studies of zinc between aqueous nitrate solutions and organophosphorus reagents dissolved in toluene. They found that the complexes ZnR_2HR and $ZnR_2H_2R_2$ were formed when DEHPA was used as an extractant.

Yoshizuka et al., (1986a), found that when the pH of the aqueous solution is above 5.0, the rate of copper extraction with the extractant is determined by either the diffusion rate of copper in the aqueous solution or of the extractant in the organic solution. However, for lower pH, the role of the interfacial reaction becomes significant in the extraction process.

Sato et al., (1989a) found that it is anticipated that the extraction mechanism in the high pH range was different from that in the low pH range, namely that the extraction rate was controlled by interfacial reaction in the low pH range and by diffusion of chemical species in the high pH range.

Several papers, (Ajawin et al., 1983; Cianetti and Danesi, 1983a; Forrest and Hughes, 1978; Grimm and Kolarik, 1974a; Huang and Juang, 1986b; Kimura, 1960; Koncar et al., 1988; Li et al., 1986; Martin, 1973; Miralles et al., 1986; Murthy, 1987; Reinhardt et al., 1975; Sastre and Muhammed, 1984; Shibata and Nishimura, 1977; Smelov et al., 1972), have been published on the equilibrium studies of zinc metal with DEHPA.

The transport of chemical species through the SLM, (Cussler, 1976; Danesi et al., 1981; Marr and Kopp, 1982; Babcock et al., 1980b), occurs when a chemical potential gradient is established between the feed and the strip solutions. The chemical gradient is generated from the concentration difference of the chemical species which influences the chemical equilibrium of extraction and stripping at the feed side and strip side of the membrane interfaces, respectively.

The mechanism of Cu(II) extraction with DEHPA deduced here, especially for the forward extraction process, (Juang and Chang, 1993), is somewhat different from those found from nitrate or perchlorate solutions as stated above, (Komasawa and Otake, 1983b; Miyake et al., 1990).
Juang and Chang, (1993), found that the species extracted into the organic phase is found to be $CuR_2(HR)_2$, and also the extraction rate can be successfully described by the combined processes of the interfacial reaction and the complex diffusion in the organic stagnant film, and the stripping rate, mainly by the diffusion process of the complex.

Furthermore, it is well recognised that all transport and reaction processes may play important roles for the SLM transport process, (Danesi and Reichley-Yinger, 1986a; Yi and Tavlarides, 1992), including the transport of VO^{2+} through DEHPA-SLMs. For example, the deviations originating in the non-negligible value of the distribution ratio at the membrane strip interface have been reported in the transport of Eu^{3+} across DEHPA-SLMs, (Danesi and Reichley-Yinger 1986a).

The transport of divalent metals such as, Cu^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} through SLMs containing DEHPA has been extensively examined, (Chaudry et al., 1990; Fernandez et al., 1986a; Huang and Juang, 1987; Huang and Tsai, 1991a; Juang, 1993b; Marchese et al., 1993 and Mohapatra et al., 1992a).

2.1.4 Kinetic studies

E. S. Ortiz and co-workers were amongst the first to investigate the kinetics of extraction of Zn^{2+} by DEHPA.

Several studies dealing with the kinetic scheme of metal extraction by di(2-ethylhexyl) phosphoric acid have been published, (Karpacheva and Ilozheva, 1967; Coleman and Roddy, 1971; Roddy et al., 1971; Sato et al., 1978b; Islam and Biswas, 1979; Ajawin et al., 1983; Komasawa and Otake, 1983a). These metals mainly consist of the first-row transition elements, (Karpacheva and Ilozheva, 1967; Roddy et al., 1971; Islam and Biswas, 1979; Ajawin et al., 1983; Komasawa and Otake, 1983a), actinides (Coleman and Roddy, 1971) and aluminium, (Sato et al., 1978b).

Of these papers, studies concerning copper, nickel, cobalt and iron are specially emphasized (Karpacheva and Ilozheva, 1967; Komasawa and Otake, 1983a; Roddy et al., 1971). In the case of zinc, only (Ajawin et al., 1983) have measured the extraction rate using a constant interfacial area cell, (Ajawin et al., 1983), though solvent extraction techniques have been successfully applied on a commercial scale to recover zinc from secondary materials and wastes (Flett, 1979).

Also, the kinetics of the extraction of several divalent metals with DEHPA have extensively been investigated using a constant interfacial area cell, especially from aqueous nitrate or perchlorate solutions. However, there are some discrepancies among these results. For example, Cianetti and Danesi, (1983a) and Vandergrift and Horwitz, (1977), separately indicated that the rate is mainly controlled by the diffusion of the metal ion through a structured layer of an interfacial water layer adjacent to the interface in the extraction of Zn(II), Co(II), Ni(II) and Ca(II), from nitrate solutions, respectively.

Danesi and Vandergrift, (1981b) studied the extraction kinetics of Fe(III) perchlorate solutions. They found that the liquid-liquid mass transfer was controlled by a set of parallel interfacial reactions between the aqueous iron species and interfacially absorbed DEHPA. Similar conclusions also have been reached (Vandergrift and Horwitz, 1977), where the extraction kinetics of Ca^{2+} from dilute HNO_3 solutions were investigated. In this case, because of the faster reaction rate inherent to Ca^{2+} and the lower degree of stirring

of the two phases (60rpm), residual diffusional resistances also contributed to the rate of mass transfer.

A kinetics study showed that the extraction process of cobalt by di(2-ethylhexyl) phosphoric acid is slow (Brisk and McManamey, 1969b). This was also shown by the published kinetics data of cobalt extraction by a liquid surfactant membrane, (Strzelbicki and Charewicz, 1978).

Ajawin et al., (1980) reported the kinetics of extraction of zinc by DEHPA in n-heptane. They found that the extraction reaction is interfacial and the flux was directly proportional to aqueous zinc and organic DEHPA concentrations and inversely proportional to hydrogen ion concentration. They also proposed a mechanism for the interfacial transfer of zinc from the aqueous to the organic phase. Results were interpreted in terms of DEHPA concentrations.

Danesi et al., (1981), indicated that the reason for the diffusion in the membrane as a possible resistance to the permeation process is most likely due to the lack of available information on the kinetic behaviour of chemical reaction occuring at the organic-aqueous interface. Actually, the permeation rate, being controlled mainly by interfacial chemical reaction, (Komasawa et al., 1983a) or by aqueous film and membrane diffusion, (Danesi et al., 1982) has been found.

Cianetti and Danesi, (1983a), also studied the mass transfer rate of zinc between aqueous nitrate solutions and n-dodecane solutions of DEHPA

using a constant interfacial area cell. They interpreted the results in terms of consequtive two step chemical reactions taking place at the interface. The activity coefficients of DEHPA dimer were calculated from previous reportings, (Danesi and Vandergrift, 1981a).

Komasawa et al., (1983b), found that the overall extract composition for cobalt, nickel and sodium with EHPNA are identical to those obtained for DEHPA. In addition the extract composition obtained for copper and zinc, (Nakashio et al., 1982) with EHPNA have also been found to be the same as those when DEHPA is used. The pH functionality of EHPNA is generally lower than that EHPNA is better for the separation of nickel and cobalt.

Ujita et al., (1984), showed the extraction of Cu^{2+} and Zn^{2+} with the liquid membrane comprising LIX64N as extractant. In this case, pH of the feed solution was kept constant at pH 4, and ionic strength at 0.7. The favourable separation and concentration of Cu^{2+} from the solution containing Cu^{2+} and Zn^{2+} can take place effectively.
Also, showed the separation of Fe^{3+} from the solution containing Fe^{3+} and Cu^{2+}. Where DEHPA was used for the preparation of the liquid membrane. Again, in this case the pH of the solution was maintained at pH 4 and at ionic strength of 0.7.

Harada et al., (1984c) studied the separation of zinc and found that the interference effect of these metals on the permeation rates is rather small, due to no mixed complex consisting of both metals is formed. An efficient

separation of zinc and iron was performed with the help of DEHPA and TOA (Tri-n-octylamine) carriers respectively.

The kinetics of copper extraction with commercial chelating extractants have attracted the interest of many investigators, (Danesi and Chiarizia, 1980; Inoue and Nakashio, 1980), particularly for hydroxyoximes (LIX 65N), (Atwood et al., 1975; Fleming et al., 1978; Flett et al., 1973; Freeman and Tavlarides, 1982; Hummelstedt et al., 1980; Kojima and Miyauchi, 1981), Komasawa et al., 1980b,c; Komasawa and Otake, 1983a; Preston and Luklinska, 1980; Van der Zeeuw and Kok, 1979b) and SME 529, (Miyake et al., 1983; Preston and Luklinska, 1980), because of the practical importance for copper recovery by solvent extraction or by using a liquid membrane which contains a chelating extractant as a carrier. In spite of the many works performed, considerable disagreement still exists in the rate expressions. There are two main reasons for this disagreement. The first is the heterogeneous reaction, and the second is the fact that in most of these papers commercial chelating extractants, which are a mixture of more than one compound, have been used.

Yoshizuka et al., (1985b), proved that the rate of copper extraction with HR is determined by the interfacial reaction between the adsorbed extractant (HR) and the adsorbed complex (CuR^{+}) and by the mass transfer steps of each species.

The important role of interfacial reaction on the extraction mechanism, (Danesi and Chiarizia, 1980; Flett et al., 1973; Komasawa et al., 1980b;

Miyake et al., 1983; Teramoto and Tanimoto, 1983; Yoshizuka et al., 1985b), has been emphasized in a number of papers concerning the kinetics, of metal extraction with commercial extractants.

However, in most papers concerning the coupled transport of metal through the supported liquid membrane of a hollow fibre, it has been shown that the effect of interfacial reaction on the permeation rate was negligibly small, (Danesi, 1984b; Noble, 1983b; Noble, 1984).

Loiacono et al., (1986), reported a good separation of copper from zinc at pH values between 2 and 3, the organic solution comprising LIX64N in kerosene. In addition the copper-zinc separation at high concentration, similar to actual hydrometallurgical conditions again with organic solution of LIX64N in kerosene was achieved. A good agreement of the experimental results with the theoretical values was observed.

Bart et al., (1986), showed that kinetical controlled regimes offer better mass transfer results in comparison to diffusional controlled ones in the case of copper.

Huang and Juang, (1986a) studied the kinetics of the extraction of zinc from aqueous sulphate solution by DEHPA in kerosene using a constant interfacial area cell. On the basis of the extractant they used and the reaction mechanism, they proposed that the rate controlling step is interfacial. Effects of the total sulphate concentration in the aqueous phase on the extraction and stripping rates were also investigated. They also interpreted the results in terms of DEHPA concentration.

Murthy, (1987) investigated the rate of stripping of zinc from DEHPA in n-heptane into aqueous sulphuric acid solution in a stirred cell with a well defined interfacial area and reported that the rate controlling reaction occured at the interface. The equilibrium and kinetic data were interpreted in terms of DEHPA activity taking into account the non-ideal behaviour of DEHPA.

A previously obtained model, (Ajawin et al., 1980) for initial rates of extraction was also modified considering the non-ideal behaviour of DEHPA.

Huang and Juang, (1988), found that the measured rates of zinc agreed with the predicted ones assuming membrane diffusion control. However, the permeation rates of zinc were controlled by aqueous film and membrane diffusion when the membrane phase dimer at DEHPA, $(HR)_2$, was higher and $[H^+]$ was lower. Such an observation is similar to that found by (Danesi et al., 1982) and (Nishiki and Bautista, 1983) for Eu^{3+} transport with DEHPA as a mobile carrier.

Hence, the permeation processes of metal are mainly controlled by membrane diffusion but controlled by aqueous film and membrane diffusion when lower metal concentration in the feed solution higher $(HR)_2$ and lower (H^+) are simultaneously employed.

Dreisinger and Cooper, (1989), have studied the kinetics of Zn (II), Co(II) and Ni(II) extraction from perchlorate solutions using the rotating diffusion cell. They found that, however, the kinetic data of Co(II) can be analyzed in

terms of a mass transfer (across both films adjacent to the interface) with an aqueous chemical reaction mechanism. But for Zn(II), the extraction rate is so fast that mass transfer alone is rate-controlling. For Ni(II), it can be analyzed in terms of a slow reaction in the aqueous film and the aqueous bulk phase.

On the other hand, fewer works were carried in such an extraction from sulphate solutions, especially for Cu(II). Brisk and McManamey, (1969a), studied the extraction kinetics of Cu(II) and Co(II) by an equilibrium extraction technique. They found the interfacial reaction resistance being between 30% and 75% of the total mass-transfer resistance. For the kinetic studies of Co(II) and Ni(II) extraction using a steady - state stirred cell, Golding and Pushparajah, (1985), suggested that the overall mass transfer rate can be considered diffusion controlled, since there is no overall increase in the extraction rate when the DEHPA concentration is increased from 10 to 20 vol %. It should be noted that the interfacial properties of DEHPA were not considered in the above two papers.

It is believed that a stronger aqueous complexation of divalent metals or even DEHPA molecules in sulphate solutions does exist, (Svendsen et al., 1990), which can affect the extraction mechanism and kinetics or the interfacial characteristics.

Campderros and Marchese, (1990), found that there is no extraction of cobalt ion below pH=3. Above this value the extraction of cobalt increases with increasing pH, reaching a maximum at values higher than 5. The organic phase consisted of a solution of DEHPA in kerosene. The

investigators noted that when pure carrier was used as organic phase, the amount of transported cobalt decreases due to the increase of viscosity which decreases the diffusion facility. Also, they performed an experiment without DEHPA concentration in the organic phase, up to a maximum value after which the cobalt diffusivity starts to decrease with the increase in the organic phase viscosity.

The extractability of PC-88A was found to be similar to that of DEHPA, but some discrepancies were observed. For example, compared with the results of (Grimm and Kolarik, 1974a) for n-heptane diluent is somewhat superior to DEHPA with respect to separation of copper and zinc. Also, the extractabilities of these extractants are affected by organic solvents. Hence, the capability of an extractant may be improved further by appropriate selection of organic solvent.

Tsuneyuki and Hashizume, (1993) contacted an experiment and considered that the reaction zone would be near the inner wall of the fibre because the fibre was hydrophobic. Feed and organic solution were supplied cocurrently.

Juang and Chang, (1993), found that the extraction rate is proportional to the Cu(II) concentration. The extraction rate also is proportional to the dimeric DEHPA concentration. The extraction rate decreases with an increase in the hydrogen ion concentration. Moreover, the stripping rate is proportional to the Cu(II) - DEHPA complex concentration.

From the nature of DEHPA such as interfacial activity and extremely low aqueous solubility, it is inferred that the formation reaction of metal

complexes is very likely to be interfacial, (Aparicio and Muhammed, 1989; Cianetti and Danesi, 1983a; Huang and Juang, 1986a; Ihm et al., 1988; Komasawa and Otake, 1983b; Miyake et al.,1990; Svendsen et al., 1990).

In general, the transport of metallic species through SLMs is considered as a combination of extraction and stripping processes. The extraction chemistry is essentially the same as that found in solvent extraction, but the overall transport process is governed by kinetic rather than equilibrium parameters, namely occuring under non-equilibrium conditions, (Danesi, 1984/85).

Consequently, it is possible to evaluate the kinetic parameters of solvent extraction reaction from the measured transport rates across SLMs, as long as the accurate transport properties (mass transfer coefficients) of relevant geometry are available, (Plucinski and Nitsch, 1988; Yi and Tavlarides, 1992).

Alonso et al., (1993) used a bundle of three fibres. They showed that the kinetic control of the extraction process can be located

(i) in the diffusion of the solute in the aqueous phase

(ii) in the mass transport through the fibre membrane

(iii) in an intermediate region where the kinetic control is shared between both phases.

2.2 Liquid membranes

Liquid membranes have an attractive role in separation science, (Schulz, 1988). Their high specificity and potential for industrial-scale processes with economic advantages make them the optimal solution of some important problems, such as processing dilute metal solution in separation and recovery of metals of metallurgical importance, (Marchese et al., 1993).

In general there are two main types of liquid membrane systems that have been considered for practical applications, the liquid surfactant membranes, which consists of a water-in-oil-water emulsion, (Li, 1968, 1971b,c; Strzelbicki and Charewicz, 1978; Shiau, 1992) and the supported liquid membrane, (Cussler, 1971; Schultz, 1977; Baker et al., 1977; Largman and Sifniades, 1978; Lee et al., 1978; Babcock et al., 1980b; Nair and Hwang, 1991), which consists of an organic phase held by capillary forces within the pores of a microporous membrane. The emulsion - type membranes share some of the problems common to solvent extraction, e.g. poor phase separation and solvent entrainment. In addition, they exhibit poor stability. SLMs avoid problems associated with emulsion - making, de - emulsifications and emulsion stability, (Way et al., 1982). In addition, separation by this technique offers several advantages over classical solvent extraction processes, in spite of it reducing the relative amount of organic phase necessary for extraction.

Hence, highly selective and expensive extractants can also be used, which could not be economic in solvent extraction.

2.2.1 Supported liquid membranes.

The requirement for a world with minimum pollution has brought about the need for clean technologies in industrial production. A way to accomplish this could be the recovery and recycling of substances not used in industrial cycles.

As an alternative to conventional unit operations, processes using supported liquid membranes (SLMs) could become very competitive when the species used for separation and concentration are ions in aqueous solutions, (Bloch, 1970; Cussler and Evans, 1974a; Baker et al., 1977; Drioli et al., 1981; Lonsdale, 1982; Way et al., 1982; Danesi, 1984-85; Loiacono et al., 1986).

As mentioned above , the liquid membrane process is a novel technique for the selective separation and concentration of the solute of interest from dilute solutions, since it combines the processes of extraction, stripping and regeneration into a single stage. (Danesi, 1984-85; Matsuyama et al., 1987; Huang and Juang, 1988; Plucinski and Nitsch, 1988; Noble et al., 1989; de Haan et al., 1989; Chaudry et al., 1990; Huang and Tsai, 1991a; Mohapatra et al., 1992a). The supported liquid membranes (SLMs), which use a porous polymer membrane impregnated with complexing carriers to separate the feed and strip phases, represent one of the feasible types of liquid membranes. They have been applied mostly to study the transport of individual species, (Danesi, 1984-85; Huang and Juang, 1988; Plucinski and Nitsch, 1988; de Haan et al., 1989; Noble et al., 1989; Chaudry et al., 1990; Mohapatra et al., 1992a), as well as the separation of species from

multicomponent mixtures (Danesi, 1984-85; Matsuyama et al., 1987; Noble et al., 1989; Huang and Tsai, 1991a).

Ward and Robb, (1967) impregnated a porous cellulose acetate film with the carrier containing liquid. This method has been the most prevalent for supporting liquid membranes. To increase the surface area available, porous hollow fibres have been used as supports. (Hughes et al., 1981), and (Babcock, 1979a). This method of supporting liquid membranes has great promise for industrial application.

Keller and Stein, (1967) and Malone and Anderson, (1977), have shown that for microporous membranes with porosity, greater than 8% , the membrane behaves essentially as a homogeneous film offering only diffusional effect. This behaviour arises from the fact that the membrane has nonporous meterial through which no mass transfer occurs.

Cussler and Evans, (1974b) and Baker et al., (1977), also proposed coupled transport through liquid membranes as a new technology for the selective separation and concentration of metals from dilute aqueous solutions. Theoretical treatments of coupled transport phenomena have been generally restricted to the limiting case where the chemical reactions between the membrane carrier and the permeating solute are fast, (Ward, 1970; Cussler, 1971, 1976; Reusch and Cussler, 1973).

In this instance the membrane permeability can be treated only in terms of diffusional processes inside the membrane layer. The assumptions made, (Danesi et al., 1981), were:

(a) steady state

(b) linear concentration gradient throughout the membrane.

The liquid membrane is held in the pores of a porous membrane due to capillary forces, and the carrier species is constrained to remain in the liquid membrane due to a large solubility difference compared to the solution contacting the membrane, (Noble and Way, 1987). Reactive supported liquid membrane systems, with mobile and reactive carriers, have been extensively studied. (Stroeve and Varanasi, 1982; Way et al., 1982; Danesi, 1984b; Izatt and Co-workers, 1986a; Ward, 1986; King, 1987; Stroeve and Kim, 1987; Kim and Stroeve, 1988a, 1988b). Facilitated ion transport in membrane systems has also been studied, (Le Blanc et al., 1980; Goddard, 1974; Ruckenstein and Sasidhar, 1982; Leiber et al., 1985; Way and Co - workers, 1987). For facilitated ion - pair transport, (Reusch and Cussler, 1973), showed selective transport of potassium over monovalent ions by the cyclic polyether dibenzo-18-crown-6 dissolved in water - saturated chloroform. They proposed a mechanism of facilitated ion-pair transport, and showed that the primary factor in determining selectivity is the ratio of the unsolved cation radius to polyether central ring radius.

Baker and co - workers, (1977), separated copper from iron by using coupled transport, from a mixture of copper and iron ions. A pH difference of one to two units is sufficient to drive the copper, through the membrane at a high rate and separate it from iron.

Matson, Kimura and co - workers, (1977,79), have done preliminary studies on facilitated transport under industrial conditions. Economic calculations

based on these studies indicated cost savings of 30-50% were possible over conventional separation processes for removing H_2S and CO_2 from gasified coal and Kitagawa et al., (1977), discussed applications of the liquid membrane technique to the removal of NH_4^+, Cr^{6+}, Cu^{2+}, $Hg^{2+}$and Cd^{2+} from industrial waste water.

Babcock, Baker and co - workers, (1979a,b, 1980a,-d), have studied facilitated transport of metal ions using supported liquid membranes. Porous polypropylene flat sheet membranes or porous polymer hollow fibre membranes were impregnated with a hydrocarbon solvent containing an appropriate carrier. The applications considered were the control of heavy metal pollutants, and the recovery of copper, uranium and cobalt.

Le Blanc et al., (1980), studied the mass transfer characteristics of a new facilitated transport membrane which overcomes several experimental problems. The carrier is bound by strong electrostatic charges and cannot be washed or forced out of the membrane. This configuration would be ideal for practical gas separation where high pressure differences are commonly encountered.

Also, Halwachs and Schugerl, (1980), presented a general discussion of liquid membranes and describe some possible industrial applications. Hughes et al., (1981), presented the results of a bench and pilot scale study of ethylene and propylene transport using a silver ion carrier immobilized in anisotropic, porous hollow fibre membranes. This work was the first to report facilitated transport liquid membranes used on a commercial scale.

Lozowski et al., (1982) gave a theoretical derivation of the diffusion flux expression for facilitated ion-pair transport within reactive membranes. Douglas et al., (1982), observed two kinds of interfacial effects during experiments. Concentration polarization at the aqueous phase-membrane interface and that the rate of the complexation reaction at the interface limited the transport rate.

The transport properties of (SLM) with respect to metal species present in aqueous solutions have been described by (Cussler and Evans, 1974b; Cussler, 1976; Lonsdale, 1982; Marr and Kopp, 1982 and Way et al., 1982). SLMs represent an attractive alternative to liquid-liquid extraction for the selective removal and concentration of metal ions from solutions, and some interesting papers have been published describing their possible application to the recovery of metals such as Cu, U, Cr, Co, and Ni, (Baker et al., 1977; Babcock et al., 1980b, d; Pearson, 1983).

Teramoto and Tanimoto, (1983) have reported that the reproduction of hollow fibre SLM is achieved by flowing the membrane solution through the fibre inside, and suggested that the decrease in permeation rate would be prevented by adding a small amount of organic solution to the strip solution. Metal ions can be highly concentrated from dilute aqueous solutions by use of a SLM with the forced flow of extractant solution through the strip channel.

The use of liquid membranes containing carriers has been extended to the transport of ions from aqueous solutions, (Baker et al., 1977; Largman and Sifniades, 1978; Lee et al., 1978). Referring to these processes as coupled transport.

There are some problems to be solved for the practical applications of SLMs: the specific surface area of the SLM is comparatively small, diffusion resistance across the SLM is large and so on. Considerable efforts to obtain a large specific surface area have been made by use of hollow fibre tubes, (Babcock et al., 1983; Hardwick, 1983; Noble, 1983a; Taga et al., 1981; Teramoto and Tanimoto, 1983; Valenzuela et al., 1982). It is anticipated, however, that fibre tubes tend to come in contact with each other and then a liquid meniscus around the contact point between the tubes is formed by membrane solution. Uniform flows on both sides of the SLM are desirable to avoid the pressure distribution or the maldistribution flow which causes a decrease in SLM stability or permeation efficiency. To obtain an effective permeation, therefore, a large SLM length, a small channel depth (i.e., a large specific surface area) or a small u is required, (u=velocity of feed solution), (Takahashi and Takeuchi, 1985).

The major uncertainty in the use of SLMs for industrial separation processes resides on the very little information presently available on SLM stability. Results have been obtained on the life-time of SLMs ranging from a few days to several months. As pointed out in (Pearson, 1983) probable causes of membrane instability can be:

(a) loss of extractant by solubility in adjacent aqueous solutions,

(b) progressive wettability of the support pores induced by the lowering of the organic-active nature of many carrier molecules and

(c) the differential pressures existing between the inside and the outside of the SLM caused by the pumping of the solutions when hollow fibre SLMs are used.

According to the studies of (Danesi 1984-85) on the stability of SLMs the lifetime of SLMs containing acidic carriers, such as DEHPA, is lowered when one of the aqueous solutions has high pHs. Since the water solubility of these carriers increases at high pHs, this observation is in agreement with:

(a) No detailed or quantitative measurements have been performed on cause

(b) Finally, as far as cause is concerned,

Danesi et al., (1984-85) observed that SLM life-times at least as long as 2 months can be obtained with Accurel polypropylene hollow-fibre SLMs containing tridodecyl amine in n-dodecane as carrier, when the outside and inside hydraulic pressure are balanced.

Past development work with SLM separation has focused on membrane preparations, on mechanisms of separation, and on quantitative characterization of separations. Several studies on membrane separations have investigated facilitated transport, (Noble, 1984; Chiarizia et al., 1983) and have screened applicability of SLMs to various separations, (Danesi et al., 1983a,b; Danesi et al., 1984).

Danesi et al., (1984), showed that hollow fibre SLMs are the most practical membrane shape to be used for SLM separations, because of the high ratio of membrane area to feed volume attainable. The experiments performed with hollow fibre SLM modules operated in series in a once-through mode have also indicated that in this case high cobalt recoveries are obtained with fibres of moderate lengths only when dilute metal feed solutions and low linear flow velocities (7.2×10^{-2} cm/s) are used.

Compared to other studied acidic or chelating reagent for Co-Ni separations, H(DTMPP) seems by far the best in terms of selectivity.

Danesi and Cianetti, (1984a) demonstrated that the single stage character of supported liquid membrane (SLM) separations of metal ions in solution can be in principle obviated by using complete SLM systems. Where a liquid acidic membrane and a liquid neutral membrane, separated by suitable aqueous electrolytic solutions, are permeated in series by the metal ions. They have also shown that in a composite SLM, where the intermediate aqueous compartment is reduced to a thin slab sandwiched between the two acidic and neutral SLMs, the overall permeability is only controlled by the permeability through the first SLM. Furthermore, there is essentially no accumulation of metal ions inside the composite SLM. This situation, which holds when the metal cations are present at concentration levels so low that the composition of the aqueous compartments can be assumed as constant with, is quantitatively predicted by the equations which describe the rate of permeation through two SLMs in series.

Attractive applications of hollow fibre modules have been attempted in hydrometallurgical processes, i.e., the recovery of uranium with supported liquid membranes, (Babcock et al., 1980c; Babcock et al., 1983), and the recovery of copper by the membrane extraction process (Kim, 1984).

As mentioned earlier on, membrane liquids in SLMs are held in the pore structure of support solids solely by capillary force. Hence, in a situation of SLM separations, it is inevitable that the solvent and/or carrier as the

constituent of membrane liquid would be more or less washed or forced out of the support solid in addition to the dissolving loss to the process stream. Two methods for continuous regeneration of SLMs have been developed with single hollow fibre, (Danesi and Rickert, 1986; Tanigaki et al., 1986) and a laminated nonwoven film, (Fujinawa and Hozawa, 1986), the stabilities of these SLMs have been demonstrated in continuous operation for one to several weeks.

Danesi and Rickert, (1986), used a vertical, single HFSLM module with a reservoir for membrane solvents at the top of the module, from which the solvent continuously soaked into the porous support by capillary action. They showed that no apparent correlation was observed between the HFSLM stability and the fibre pore-size and dimensions. The performance of the HFSLM decling as a result of loss of the liquid membrane phase from the fibre pores. The initial permeability of the HFSLM can be fully restored by a simple re-impregnation procedure. They also showed that the life-time of HFSLMs can be increased to more than 38 days of continuous operation by incorporating into the module design a small reservoir containing the liquid membrane.

(Tanigaki et al., 1986; Fujinawa and Hozawa, 1986), on the other hand, utilized a pressure flow of membrane solvents throughout the SLM of single fibre and laminated film in horizontal configuration, respectively, where the pressure flow comes from sucking under reduced pressures at the one end of the SLM and soaking into it at the other end.

Gutknecht et al., (1986), indicated that the use of liquid membrane technique is suitable for a nearly complete and very selective metal recovery, especially from solutions which contain very low metal concentrations, (Cu, Co, Ni, Zn).

Loiacono et al., (1986), performed experiments using supported liquid membranes for the separation of Cu(II)-Zn(II). An assumption of absence of radial concentration gradients (because of the very small fibre diameter) and absence of backmixing (because of the very high length /diameter ratio of the fibre has been made). The driving force in this process is the pH gradient existing between the two sides of the membrane. A good separation of copper from zinc can be performed at pH values between 1 and 3.

In addition coupled transport in SLMs is a promising technology for the recovery and separation of metal ions from aqueous solutions, even at high concentrations. The good stability of a SLM encourages possible industrial applications of the system described.

Gu and Wasan, (1986), developed a method to enhance the liquid membrane extraction of heavy metals such as cobalt, copper and nickel. The method consists of introducing anion ligands, such as acetate to the aqueous solution containing metal ions. By selecting a suitable ligand for accelerating extraction in specific systems offers an important opportunity in the improvement of liquid membrane separation.

Generally, application screening studies have been with flat sheet membranes or single hollow fibre modules and have resulted in determination of

permeability with respect to feed rate or stirring rate at isothermal conditions. No studies with large-scale hollow fibre modules have been documented, and several areas of uncertainty currently exist in the SLM extraction processes, (Dworzak and Naser, 1987). These areas include operating characteristics, long-term durability and reliability scale-up effects and verification of diffusion models upon which future design correlation may be based.

Hollow fibre supported liquid membrane (HFSLM) is expected to be a simple and energy saving operation for the recovery and enrichment of metals from dilute aqueous solutions, (Danesi, 1984b, 1984-85; Danesi et al., 1985b; Danesi and Rickert, 1986; Izatt et al., 1986b; Babcock et al., 1986; Loiacono et al., 1986; Tanigaki et al., 1987). However, it has not yet been successfully demonstrated as an industrially feasible operation.

One of the biggest problem which makes supported liquid membrane operation difficult as an industrially feasible operation is the instability of the liquid membrane, (Babcock et al., 1980c, 1983; Teramoto and Tanimoto, 1983; Pearson, 1983; Flett and Pearson, 1985; Danesi et al., 1985b; Danesi and Rickert, 1986; Danesi, 1984-85; and Loiacono et al., 1986). The organic phase is sustained in the micropores of the support membrane. Therefore, the small pressure difference across the membrane and the large interfacial tension increase membrane stability, (Pearson, 1983; Danesi, 1984-85). The size of the micropores should be small, but a too small diameter hinders diffusion, which in turn makes the permeation flux low, (Babcock et al., 1980b). Support membranes with micropores between 0.1

to 1μm are usually considered to be appropriate. Increased viscosity (Gotoh et al., 1984) and the use of a relatively thick support membrane wall, (Pearson, 1983; Flett and Pearson, 1985; Danesi et al., 1985b), increases the lifetime of a liquid membrane. The dissolution loss of the organic solvent or carrier to the aqueous phase is known to decrease the lifetime of a liquid membrane, (Pearson, 1983; Danesi, 1984-85; Gotoh, 1984; Fujinawa and Hozawa, 1986).

The use of hydrophobic membranes whose pores are filled with the organic membrane solution seems to be favourable for obtaining high stability and permeability and even if the organic membrane solution in the micropores of the support membrane dissolves in the aqueous feed and strip solutions, the pores are rapidly refilled with the organic solution.

Several experimental investigations, (Danesi and Rickert, 1986; Tanigaki et al., 1987; Izatt et al., 1989), have been made for the extraction of various metal ions through hollow fibre supported liquid membranes (HFSLM). Although many models have been reported for flat-plate-type supported liquid membranes, (Danesi et al., 1981; Way et al., 1982; Chiarizia and Castagnola, 1983; Danesi et al., 1983; Cianetti and Danesi, 1983b; Komasawa and Otake, 1983b; Huang and Juang, 1988), models of the HFSLM system are considerably fewer. Teramoto and Tanimoto, (1983) proposed a permeation mechanism to describe the extraction process of copper ion through an HFSLM.

A large number of papers have been published dealing with SLM systems, (Lonsdale, 1982; Danesi, 1984-85; Schulz, 1988; Noble and Koval, 1989; Way et al., 1985; Michaels, 1990; Pearson, 1983), as applied to the extraction of lanthanides and actinides, using extractants like di(2-ethylhexyl) phosphoric acid.

The transport flux increases with an increase in the carrier concentration to a maximum and then falls due to the increased viscosity of the carrier, (Gill and Marwah, 1994).

Prasad and Sirkar, (1987b, 1988), and Dahuron and Cussler, (1988) have reported the correlations of two liquid-phase mass transfer coefficients, k_t and k_s on the tube (lumen) and shell sides in multiple MHF modules. It is difficult to make a multiple HF module having a calming section at the entrance and exit on the shell side, while a single MHF contactor can be designed to eliminate any end effects. Although having no commercial use because of a small surface area per volume ratio, such single HF devices might be suitable for investigating interphase mass transfer.

Supported liquid membranes (SLMs), which employ a porous membrane support impregnated with complexing carriers to separate the feed and strip phases, have been applied to study not only the transport of the individual species, (Chaudry et al., 1990; de Haan et al., 1989; Fernandez et al., 1986a; Huang and Juang, 1987; Marchese et al., 1993; Mohapatra et al., 1992a; Mohapatra and Kanungo, 1992b; Plucinski and Nitsch, 1988; Yi and Tavlarides, 1992), but also the separation of multicomponent mixtures, (Huang and Tsai, 1991a; Juang, 1993b; Matsuyama et al., 1987).

Many workers reported the advantages of working with non-dispersive extraction systems using microporous membranes, (Kiani et al., 1984; Prasad et al., 1986; Prasad and Sirkar, 1987a, b) and more specifically with the use of hollow fibre modules, (D'elia et al., 1986; Matsumoto et al., 1987; Alexander and Callahan, 1987; Prasad and Sirkar, 1988; Sato et al., 1990).

Hollow fibre modules have been used in selective removal and recovery of metals from aqueous solutions, i.e., the recovery of uranium with supported liquid membranes, (Babcock et. al., 1980b,d; Hofman et al., 1992), the recovery of copper, (Kim, 1984; Yoshizuka et al., 1986a; Matsumoto et al., 1990b; Sato et al., 1990) of zinc, (Sato et al., 1989c), as well as in the recovery of diluted compounds from wastewater effluents, such as phenol, (Sengupta et al., 1988a; Urtiaga et al., 1990, 1992a, b).

Working with solid supported liquid membranes, Verhaege, (1985) studied the application of different extractants to the recovery of chromium from electroplating rinse waters. Loiacono et al., (1986) and Molinari et al., (1989), reported several experimental findings on the recovery of Cr(vi) with flat supported liquid membranes, stating that in the researched conditions the supported liquid membrane (SLM) kept constant the extraction capacity over periods of 30 days.

Danesi and Rickert, (1986), have suggested that probable causes of SLM instability are loss of the carrier extractant by its solubility, progressive wettability of the support pores induced by a lowering of the interfacial tension and the differential pressures existing between both sides of the membrane caused by pumping of the solutions.

2.2.2 Extraction of metal ions with SLM and location of the reaction taking place.

There are two types of facilitation methods used to increase the mass transfer rate across the membrane. In one case a reactant is added into the internal phase so that the solute concentration at the membrane internal phase interface is effectively zero, thus maximising the concentration gradients through the membrane. Chan and Lee, (1984) present a review of the various models which are commonly used to describe this type of facilitated mass transfer phenomena.

In the other type of facilitated transport, a reactant is added to the membrane which reacts with the solute at the external phase membrane interface, for the transfer of zinc ion. In both types of facilitated transport, the reaction taking place at the internal side of the membrane can be very fast, so they are not expected to be rate controlling. Then the possible rate controlling steps are diffusion in the continuous and membrane phases and chemical reaction at the external interface for the carrier-mediated type of transport.

Most theoretical treatments of membrane kinetic behaviour developed during the last decade, however, have assumed extreme conditions in which negligible contributions due to chemical reaction and aqueous phase diffusional process are assumed, as Komasawa et al., (1983b) and Danesi et al., (1981) point out in their respective works. Thus, only the diffusional process in the membrane has been considered as a possible resistance to the permeation process. The reason for this is most likely due to the lack of

available information on the kinetic behaviour of the chemical reaction occuring at the aqueous - organic interface, (Komasawa et al., 1983b).

Ortiz et al., (1977) stressed that an accurate study of the kinetics of an extraction system can only be obtained if the system is under chemical control and the experimental conditions chosen such that chemical reaction rates would exist over the whole range of variables to be studied.

Danesi et al., (1981) and Komasawa et al., (1983b) pointed out the relative importance of the chemical reaction control and diffusion through the continuous phase control in the extraction rate of a carrier facilitated liquid membrane permeation process, specially in those cases where the interfacial chemical reaction is not very fast.

Danesi et al., (1981) also showed the importance of the aqueous phase film diffusional resistance in the extraction of copper with a supported liquid membrane impregnated with LIX 64. By means of their simulated curves, they managed to fit the results of (Baker et al., 1977), who on the other hand had proposed a membrane controlled model for the same system.

Working with the extraction of copper with a membrane impregnated with LIX 65N in dioctyl phthalate, (Imato et al., 1981) analyzed their results assuming that membrane diffusion control conditions applied. They observed that as the hydrogen ion concentration was increased and copper concentration decreased, discrimination between chemical and membrane diffusion control became difficult. This situation may have arisen from their use of asymptotic approximations of the model in the interpretation of results.

The effect of concentrations on the rate controlling mechanisms has not been thoroughlly investigated. Also, the hydrodynamic conditions of the investigations reported in the literature are also narrow. Continuous phase control is found to occur when supported liquid membrane used (Danesi et al., 1981), i.e., for laminar flow in the continuous phase, while for surfactant liquid membranes in stirred tanks the assumed rate controlling step is diffusion in the membrane, (Martin and Davies, 1976-77). At intermediate conditions of turbulence for both continuous and disperse phases, (Komasawa et al., 1983b), interfacial chemical control is observed. These findings are coherent with the effect of turbulence on transfer rate, but when a chemical reaction is present, a high transfer rate may still be low as compared to the possible rate of reaction.

Imato et al., (1981), showed that the copper flux was constant in the range of pH >3 in the feed solution, but decreased with decreasing pH in the range of pH< 3. (1.5 -3.0). Copper concentration in the feed solution hardly influenced the copper flux in the range of 10^{-3} - 10^{-1} mol/dm^3. The copper flux was proportional to oxime concentration in the supported liquid membrane when the pH of the feed solution was 4.47. Copper concentration in the stripping solution had little effect on copper flux. The experimental results were well explained, assuming that the rate determining step was the diffusion of the copper oxime complex in the membrane.

Danesi et al., (1982) and Nishiki and Bautista, (1983), indicated that membrane diffusion and aqueous film diffusion are the only rate controlling factors in Europium (III) transport from chloride medium.

Harada et al., (1984c) summarized the functions of the liquid membrane as followed:

(a) enrichment of metal by uphill transport and

(b) selective separation of metal species.

They proved that the extraction rate of zinc is determined by the diffusional processes. The permeation rate of zinc through the membrane is controlled by the diffusional resistance in the raffinate aqueous phase at high acid concentration in this phase. The interference effect of zinc and iron on the permeation rates is rather small, because no mixed complex consisting of both metals is formed. Selective separation of zinc and iron can be performed with the help of the difference in fluxes of the two metals. Simultaneous enrichment of zinc and iron can be performed at high concentrations of the amine and the acid in aqueous raffinate phase. This arises from the agreement of permeation resistances between iron and zinc, which is realized at the condition of diffusion control in the aqueous raffinate phase. Iron transport through the membrane in zinc-iron separation becomes more rapid than expected, after a long elapsed time.

Takahashi and Takeuchi, (1985) found that the permeation rate depends on both the diffusion resistance and the reaction rate. Fernandez et al., (1986a), have studied the rate of zinc transport from aqueous perchlorate media. They investigated the rate as a function of the chemical composition of the system and the hydrodynamic conditions. However, for other metals such as the first row transition elements, little work was done to clarify the permeation mechanism, although many papers concerning the equilibrium and kinetic behaviour of metals extraction have been published.

D'elia et al., (1986), in order to determine the rate controlling step for mass transfer in hollow fibre extractions made the common hypothesis that the extraction involves three sequential steps: mass transfer from the bulk aqueous feed to the inside surface of the hollow fibre membrane, diffusion across the membrane itself, and mass transfer into the organic solution surrounding the fibre, (Geankoplis, 1972; Cussler, 1984).

Huang and Juang, (1987), found that the permeation rate of zinc was found to be mainly controlled by membrane difusion in the majority of runs, but controlled by aqueous film diffusion and membrane diffusion in a few cases. As has been stated in several studies of solvent extraction, (Cianetti and Danesi, 1983a; Golding and Barclay, 1988; Miyake et al., 1990), the rate of extraction of Co^{2+} and Ni^{2+} ions by DEHPA is not exactly controlled by the complex formation reaction at the aqueous organic interface, but is mainly controlled by the diffusion of the metal complex in the organic mass transfer boundary layer or the diffusion of metal ions in the aqueous mass transfer boundary layer.

As has been indicated previously, (Huang and Juang, 1988; Chaudry et al., 1990; Mohapatra et al., 1992a), the permeation of divalent metals, including Co(II) ions through SLMs containing DEHPA was predominantly controlled by the diffusion process, possibly through the aqueous stagnant layer as well as through the liquid membrane. This means that it is difficult to perform the permeation runs under the extreme conditions in which the interfacial chemical reaction is the unique rate controlling step, although a relatively thin membrane support was employed.

Juang and Jiang, (1994) found that in the calculation $\overline{\kappa_{CoR_2(HR)_2}}$ is to be the most sensitive parameter, which implicity implies that the nature of the membrane support, such as porosity and thickness, plays an important role on the rate and mechanism of SLMs permeation process. Moreover, the role of aqueous layer diffusion becomes more significant under the conditions of low $[Co^{2+}]_f$, high pH_f and high $\overline{[(HR)_2]_o}$ On the other hand, membrane diffusion becomes rate controlling at low pH_f and $[(HR)_2]_o$, as seen from two data sets.

2.2.3 Models of extraction with supported liquid membrane.

In most cases the extraction rate of metal ions is a function of both the kinetics of chemical reactions taking place in the system and the rates of diffusion of the species between the two phases. The simultaneous presence of both chemical reactions and diffusion processes in liquid-liquid mass transfer has been reviewed and several mathematical diffusion models with heterogeneous chemical reactions have been elaborated (Hanson et al., 1974; Yagodin et al., 1974). However, several cases seem to exist where the extraction rate is mainly controlled by interfacial processes, (Ajawin et al., 1983; Komasawa and Otake, 1983a,b; Roddy et al., 1971; Sato et al., 1978b) or by aqueous reactions adjacent to the interface, (Harada et al., 1983c; Karpacheva and Ilozheva, 1967).

Danesi and Vandergrift developed two models which interprete the kinetic data which characterize the interfacial mass transfer of Eu^{3+} and Am^{3+} in the system bis(2-ethylhexyl) phosphate-n-dodecane-NaCl-HCl-water. The first one assumes that the rate is entirely controlled by slow interfacial chemical reactions (kinetic regime) while the second one couples diffusion of the chemical species, through aqueous and organic stagnant layers, with a fast interfacial chemical reaction (diffusional regime). Although both models are adequate to interpret qualitatively the experimental rate data, the best fit of all of the data points is obtained when the liquid-liquid, mass transfer kinetics are assumed to be entirely chemically controlled.

The reaction mechanism which is then derived by the experimental rate data consists of a series of interfacial reactions where the metal cation first forms a complex at the interface, reacting with the interfacially absorbed ligand molecules and then is transferred into the bulk organic ligand molecules. The stoichiometry and the equilibrium constants of the heterogeneous complex formation reaction between Am^{3+}, Eu^{3+} and DEHPA also have been determined. The rate laws of the forward and reverse complex formation reaction and the rate constants are in agreement with the equilibrium thermodynamic data.

Schultz et al., (1974a,b), reviewed theoretical progress in describing facilitated transport systems. They also evaluated various numerical methods for solving the transport models. Smith et al., (1977), summarized experimental and theoretical work since 1974 on facilitated transport and

Kimura et al., (1979), discussed potential industrial applications of facilitated transport under reaction equilibrium conditions.

Kojima et al., (1969) and Kondo et al., (1978) interpreted their data on the help of mass transfer theory accompanied by chemical reaction. Flett et al., (1973) and Komasawa et al., (1980b), asserted that the rate determining step is interfacial in nature in the extraction of less water soluble chelating agents.

Babcock et al. (1980b,d), found experimentally that in coupled transport of uranium with Alamine 336, the flux increases with carrier concentration, reaching a maximum value at about 30 vol % carrier concentration, above which the flux decreases with increasing carrier concentration. This interesting phenomenon was believed to be caused by two competing factors: the concentration gradient of the uranium complex and the viscosity of the organic phase in the liquid membrane. Babcock et al., (1980b,d) failed to explain the phenomenon quantitatively but pointed out the dominant effects that cause this phenomenon to be:

(1) Carrier concentration effects

(2) Pore size effects

(3) Interfacial effects

Baker et al., (1977) observed a similar phenomenon of limiting flux with respect to the metal concentration in the feed solution. This phenomenon was termed " saturation Phenomena " where the limiting effect was due to saturation of the organic phase with the metal carrier complex. They concluded that the saturation phenomenon was caused mainly by the

solubility and not the stoichiometry of the system. This conclusion was supported indirectly by the observation of a green, water insoluble, organic soluble precipitate formed at the feed membrane interface. A similar observation was observed by (Elhassadi and Do, 1986). When the carrier is diluted with more diluent, the limiting factor becomes the stoichiometry where the supply of available carrier rather than the solubility is important.

Danesi et al., (1981), derived a permeability coefficient equation for the coupled transport of metal ions through solid supported liquid membrane considering:

(a) diffusion through the aqueous side stagnant layers

(b) interfacial chemical reactions

(c) membrane diffusion

could be simultaneously operative as rate controlling effects.

Danesi et al., (1982) proved that the coupled transport of Eu^{3+} and H^{+} ions through (SSLM) controlled by both membrane diffusion and by diffusion through membrane aqueous solution stagnant layers.

The results obtained are in agreement with the predictions expected from a permeability coefficient equation derived on the basis of a model which takes into account aqueous diffusion, interfacial chemical reactions, and membrane diffusion as possible simultaneous rate controlling effects.

Douglas et al., (1982) found that the extraction rate of copper could not be explained by a pseudo first order dependency with respect to copper concentration. It was postulated that the overall extraction rates were

controlled by the complex formation reaction rate and diffusion in the concentration boundary layer.

The transport of Co^{2+} or Ni^{2+} ions through SLMs containing DEHPA has been freequently studied separately, (Huang and Juang, 1988; Chaudry et al., 1990; Mohapatra et al., 1992a) however, fewer works have been carried out on the competitive permeation of Co^{2+} and Ni^{2+} ions. Huang and Tsai, (1991a) studied the effect of different conditions on the separation factor from sulphate solution, but the permeation process was not modelled. On the other hand, Matsuyama et. al., (1987) modelled the permeation rates of Co^{2+} and Ni^{2+} containing 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester as a carrier by neglecting the resistances of some steps such as interfacial reactions, diffusion of hydrogen ions in both liquid phases and of the metal ions in the stripping phase. It seems inapplicable for this system to ignore the diffusional resistance of the metal ions in the stripping phase, in contrast with the reaction mechanism obtained in solvent extraction and as also indicated by (Danesi and Reichley-Yinger, 1986a). The distribution ratios for Co^{2+} and Ni^{2+} ions are not high enough under the stripping conditions used, (Huang and Tsai, 1991a), to neglect the resistance at the stripping side.

Danesi, (1984a,b) proposed a simple model for the once through mode and recycling mode operations of HFSLM. In this model, a parameter, the so called permeation coefficient, is adopted, in the calculation of the permeation rate of copper ion through the membrane. This permeation coefficient is considered to be constant throughout the entire process.

For a hollow fibre supported liquid membrane, the system consists of the following permeation resistances: aqueous film diffusion resistances, chemical reaction resistances and membrane diffusion resistance. Membrane diffusion and aqueous film diffusion are rate controlling steps, with membrane diffusion being more important (Shiau and Chen, 1993).

Juang, (1993b) used a model in which two steps are taken into account, i.e. (1) diffusion of metal ions (Zn(II) and Cu(II)) across the aqueous stagnant layers of feed and strip phases and (2) diffusion of DEHPA (monomer and dimer) and the complexes in the membrane phase. In the description of the permeation model, the following assumptions were made: (1) the resistance of interfacial reactions between DEHPA and metals were ignored, (2) the resistance of diffusion of hydrogen ions in both stagnant layers was also neglected and (3) the diffusion processes could be described by Fick's diffusion equations. It should be noted that the first assumption has been justified for the permeation of Zn(II) through SLM containing DEHPA, (Fernandez et al., 1986a, 1987).

Tanigaki et al., (1987), found that the film resistance in the inside of a hollow fibre can be calculated using the analogy of heat and mass transfer. While, Huang and Juang, (1988), showed that the resistance due to interfacial chemical reaction is negligible. The metal permeation processes are mainly controlled by membrane diffusion in most cases but by aqueous film diffusion and membrane diffusion, or by aqueous film diffusion solely in some cases when lower $[M^{2+}]_f$, higher $[(RH)_2]_t$ and lower $[H^+]o$ are simultaneously employed under the conditions observed.

In addition, two important factors affecting the transport mechanism through supported liquid membrane were observed. One concerns the membrane constant, the smaller the porosity of the membrane, the greater the resistance of membrane diffusion. The other concerns metal concentration in the feed solution $[M^{2+}]_f$, the lower the $[M^{2+}]_f$, the higher the resistance of aqueous film diffusion. The assumption that membrane diffusion control governs the majority of the runs was proved valid.

However, the permeation rates of zinc were controlled by aqueous film and membrane diffusion when $[(RH)_2]_t$, was higher and $[H^+]_o$ was lower. Such an observation is similar to that found by (Danesi et al., 1982; Nishiki and Bautista, 1983), for Eu^{3+} transport with DEHPA as a mobile carrier.

Moreover, the two successive systems that Huang and Juang, (1988), studied proved that the differences in the permeation rate would be decreased when $[(RH)_2]_t$ is higher and $[H^+]_o$ is lower, which corresponds to the conditions that the effect of aqueous film diffusion becomes significant.

Also, Juang, (1993a) found that the permeation model took into account the aqueous film diffusion of the metal ions toward and out of the membrane and the membrane diffusion of the carrier and its metal complexes. The calculated rates are in good agreement with the measured ones under the conditions studied. The application of such a model first requires a good knowledge of the transport parameters for the relevant geometry. Consequently, with known equilibrium data the modelling of the permeation would be possible in the case of relatively fast interfacial reactions.

A higher selectivity in the separation of Co^{2+} from Ni^{2+} ions is obtained when the diffusional resistance in the liquid membrane is dominant.

Sato et al., (1990), assumed that mass transfer of the extractants and complexes in the organic solution is controlled by molecular diffusion of these species in the micropores of the membrane, because the membrane is hydrophobic.
It can be assumed that mass transfer coefficients of metals in both aqueous solutions are equal to each other and that mass transfer of chemical species in the organic solution is mainly controlled by molecular diffusion of chemical species in the micropores of the membrane.

Takeuchi et al., (1990b), tried to do systematic measurements in order to obtain more accurate correlations of k_t and k_s in single hydrophobic MHF contactors using an extraction system of water / iodine / n-heptane.
The membrane mass transfer coefficient, k_m, was also studied.

Miyake et al., (1990), showed that the rate determining step of the extraction of Cu(II) and Co(II) from perchlorate solutions is the diffusion of the metal complex in the organic film. In addition, Ihm et al., (1988) indicated that the resistance of the interfacial reaction is less than 50% of the total resistance for the extraction of Cu(II) from nitrate solution.The remainder of the resistance is ascribed to diffusion near the diffusion. However, Komasawa and Otake, (1983b), found that the rate is controlled by the interfacial chemical reaction in the extraction of Cu(II), Co(II) and Ni(II) from nitrate solutions.

As has been demonstrated in several previous studies of solvent extraction, (Cianetti and Danesi, 1983a; Dreisinger and Cooper, 1989; Miyake et al., 1990), the rate of extraction of Zn(II) or Cu(II) by DEHPA is not exactly controlled by the complex formation reaction at the aqueous organic interface, but is controlled mainly by diffusion of metal ions in the aqueous stagnant layer or by diffusion of the complex in the organic layer.
Using an SLM impregnated with DEHPA the transport of single Zn(II) or Cu(II) ions has been freequently investigated (Fernandez et al., 1986a, 1987; Huang and Juang, 1987, 88), however, fewer works have been carried out in the separation of Zn(II) and Cu(II).

The phenomenon of facilitated transport involves diffusional transport coupled with chemical reactions, so that the kinetic analysis requires the solution of a system of second order non-linear differential equations which does not have an exact analytical solution. The solutions to these problems are usually obtained by numerical techniques. Numerical methods with the channel discretized in both axial and transverse directions have been used by (Kim and Stroeve, 1988a, 89a,b, 1990), to study the problem of non-linear boundary conditions for reactive hollow fibres solving the cases of facilitated ion-pair transport and co-transport.

Ramachandran, (1971), solved competitive transport equations analytically using penetration theory. These results are valid for the case of equal diffusivities of all species. On the same lines Cussler, (1971), derived an analytical solution for the steady state extraction rate for two solute species

competing for the same carrier at membrane interfaces, while substantiating qualitatively he did not provide any quantitative proof of the model.

A number of mathematical models which describe the behaviour of SLM separation processes have been proposed, (Huang and Juang, 1987; Chan and Lee, 1984). Some of them usually assumed that contributions due to interfacial chemical reaction and aqueous film diffusion are negligible. Only diffusion in the membrane is regarded as a possible resistance to the permeation process. Relatively little attention has been paid to elucidating the real effect of the overall resistance operating in the metal transport through the SLM.

The transport mechanism is diffusion controlled (passive transport), if the diffusing species is charged, there must be a co-transport in the same direction (if the co-diffusing species has opposite charge), or in the opposite direction if the charge of the diffusing and co-diffusing species have the same sign. This co-transport is the driving force of the enrichment process.

CHAPTER 3

MATHEMATICAL MODELLING

A model of the extraction of zinc with the supported liquid membrane was developed using the equations for kinetics of extraction and stripping of zinc with DEHPA and those for the diffusional processes in the feed and liquid membrane.

Steady state was assumed throughout.

3.1 Mechanism of Extraction of Liquid Membrane

The transport of metal through a liquid membrane containing DEHPA as a mobile carrier is illustrated in Figure 3.1. Zinc ions in the feed solution diffuse towards the interface (x=0), where the complexation of the zinc ion with dimeric DEHPA occurs, (Ajawin et al., 1980) forming mainly the extractable complex species $ZnR_2.HR$. This complex then diffuses through the membrane towards the interface (x=l), where zinc ions are stripped to an acidic solution. This step regenerates the DEHPA carrier which then diffuses back to the interface (x=0), after which the entire process is repeated. Such a process is called the 'shuttle mechanism', and given the different equilibrium conditions at the two interfaces, it is able to transport zinc ion from a low concentration solution to one with higher concentration.

Figure 3.2 shows the concentration profiles for the supported liquid membrane. As the system is assumed to be at steady state, linear concentration gradients exist throughout the system. As the extraction and stripping reactions have been reported as taking place at the interface (Ajawin et al., 1983) and (Murthy, 1987), the mechanism of transfer consists of the following steps in series:

(i) diffusion in the diffusional film in all the feed phase

(ii) extraction with chemical reaction

(iii) diffusion across the liquid membrane

(iv) stripping reaction

(v) diffusion in the diffusional film in the stripping phase.

Any of these steps or a combination of more than one, may be rate controlling in the membrane process depending on the rate of reaction and the hydrodynamic conditions of the feed and stripping phases. The kinetics of the interfacial reaction will be reviewed first.

3.2 Chemical Kinetic Model

Ajawin et al., (1983) and Murthy (1987), studied the extraction equilibrium for the zinc - DEHPA system over a wide range of pH and reported that two complexes of zinc-DEHPA are formed according to the stoichiometry of the reactions

$$Zn^{2+} + 1.5\overline{H_2R_2} \Leftrightarrow \overline{ZnR_2.HR} + 2H^+ \qquad (3.1)$$

$$Zn^{2+} + 2.0\overline{H_2R_2} \Leftrightarrow \overline{ZnR_2.H_2R_2} + 2H^+ \qquad (3.2)$$

Where bars indicate the species in the organic phase and H_2R_2 is DEHPA in dimer form.

Murthy (1987) pointed out that equation (3.1) is the predominant reaction. Using a non-dispersive cell of constant interfacial area, Ajawin et al., (1983)

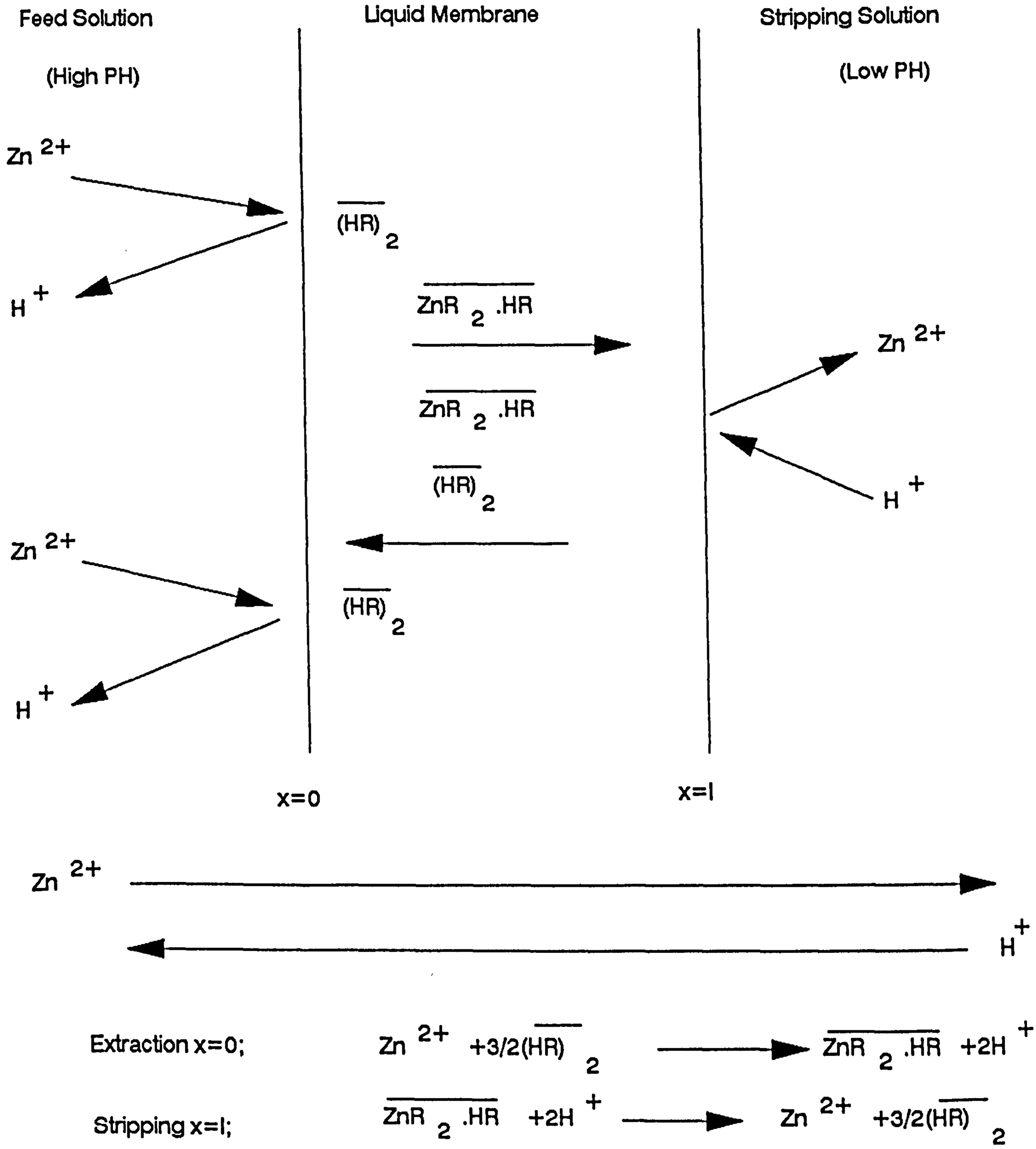


Figure 3.1 Permeation model for the supported liquid membrane.

investigated the kinetics of extraction of zinc by DEHPA and (Murthy 1987) the same reaction in the stripping range of pH.

They concluded that the rate controlling reaction is interfacial and proposed rate equations for extraction and stripping in the chemical regime, i.e. when the diffusional resistances are negligible.

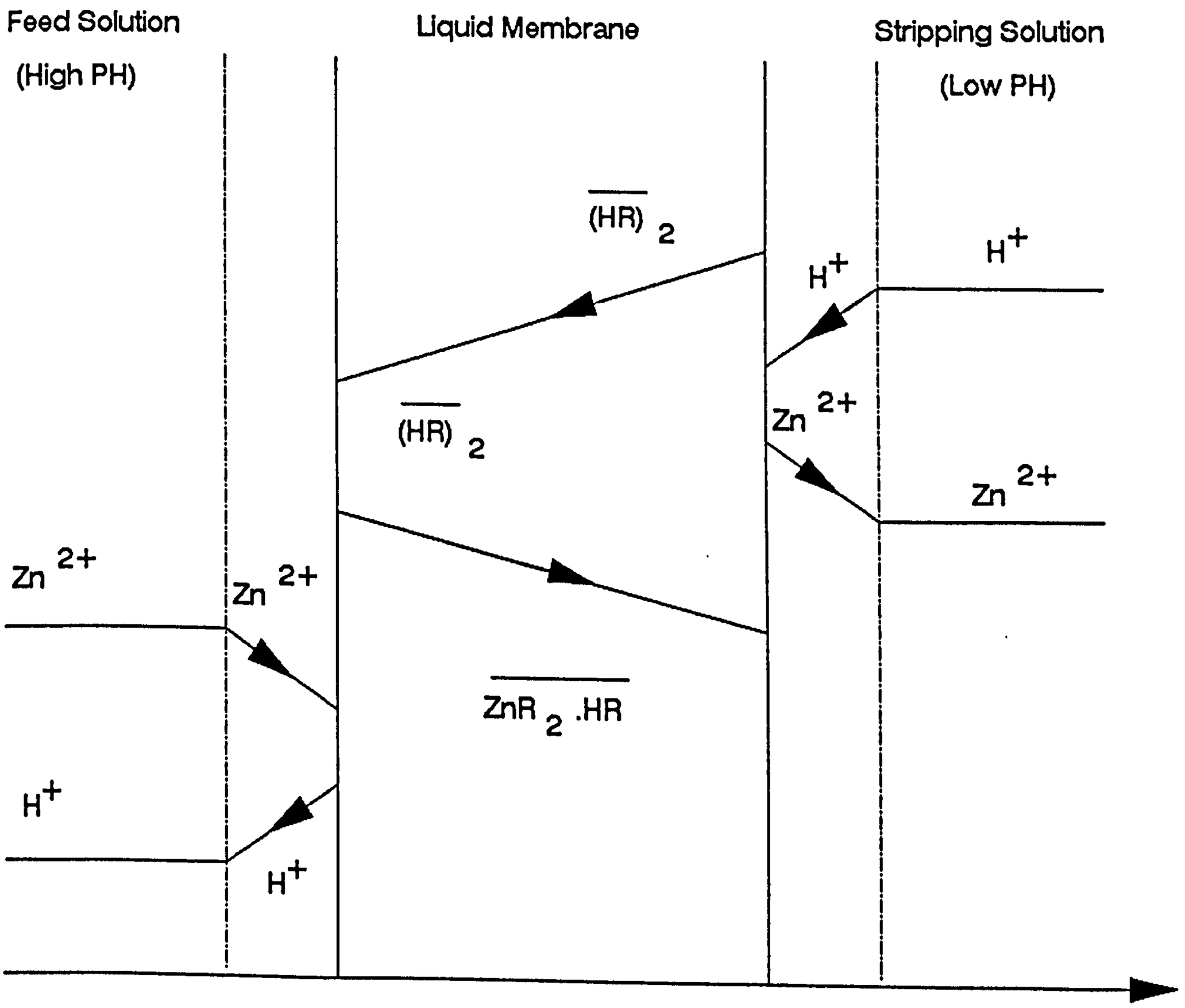


Figure 3.2 Schematic concentration profile for the supported liquid membrane.

The following kinetic model combines the reaction rate for the forward (Ajawin et al., 1983) and reverse reactions (Murthy, 1987) in the chemical control regime.

$$R_z = k_{I\alpha} \frac{C_{z\alpha}\alpha_o}{C_H} - k'_{I\alpha} \frac{C_{zo}C_H}{\alpha_o + x\sqrt{\alpha_o}} \qquad (3.3)$$

Where,

$k_{I\alpha}$ = extraction reaction rate constant, m/s

$k'_{I\alpha}$ = stripping reaction rate constant, m/s

α_o = activity of DEHPA dimer, kmol/m^3

C_H = concentration of hydrogen ions, kmol/m^3

R_z = molar flux of zinc, kmol m^{-2} s^{-1}

and x=0.75 or 0.05 depending upon the use of equations (3.5) and (3.6) for the calculation of activity coeffficient of DEHPA dimer respectively.

The first term on the right hand side of equation (3.3) represents the extraction rate and the second term accounts for the stripping rate.

The activity coefficient of the organic zinc complex (Koncar et.al 1988), can be calculated from the following equation:

$$\frac{1}{\gamma_{zo}} = 1 + 0.616\frac{m}{2}\left(\frac{C_{zo}}{\alpha_o}\right)^{1.387} \qquad (3.4)$$

Where,

γ_{zo} = activity coefficient of organic phase zinc, kmol/m^3

C_{zo} = molar concentration of organic phase zinc, kmol/m^3

α_o = activity of DEHPA dimer, kmol/m^3

Two equations have been proposed for γ_o by

Baes, (1962) who studied the non-ideal behaviour of dimeric DEHPA in n-octane in the range of concentration between 0 and 0.14M. He estimated the practical activity coefficients by two different procedures:

1. The activity coefficient of DEHPA dimer was determined by isopiestic measurements assigning a value of unity to the activity coefficient of the reference solute, triphenyl methane. The activity coefficient was correlated by the expression:

$$\log\gamma_o = -0.586\left(C_o\right)^{1/3} + 0.565\,C_o \qquad (3.5)$$

2. The activity coefficients of dimeric DEHPA were determined using iron extraction results (Baes, 1960) and reported (Baes, 1962) as

$$\log\gamma_o = -0.736\left(C_o\right)^{1/3} \qquad (3.6)$$

and $\alpha_o = \gamma_o \cdot C_o$

Where,

γ_o = activity coefficient of DEHPA dimer, kmol/m^3

C_o = molar concentration of of DEHPA dimer, kmol/m^3

Equations 3.5 and 3.6 indicate that the activity coefficient may vary substantially over a wide range of concentration of DEHPA.

Ajawin et al., (1983) have proposed the following equation for the calculation of the chemical reaction rate constant $k_{I\alpha}$, as a function of ionic strength, I, and temperature, T.

$$\log k_{I\alpha} = 1.6975 - \frac{1.6028 I^{1/2}}{1 + I^{1/2}} - \frac{2165.6}{T} \qquad (3.7)$$

The value of the rate constant of the reverse reaction, $k'_{I\alpha}$, used was that reported by (Saeed, 1989), ($k'_{I\alpha} = 2.96x10^{-5}$ m / s), for T=25°C and I=1.0 kmol/m^3.

3.3 Kinetics of extraction in the mixed control regime

In the mixed control regime, i.e. when there is chemical and mass transfer control, the interfacial flux depends on the mass transfer resistances and the rate of interfacial reaction. In order to simplify the model, the following assumptions have been made:

(a) the system is in steady state.

(b) at the stripping interface the reaction is very fast and the diffusional resistances in the stripping phase are negligible.

(c) neither the flow nor the concentration profiles are fully developed in the lumen of the fibre, given that the Re number is very low; therefore the concentration of metal ion at the centre of the fibre is constant along its length.

(d) the zinc - DEHPA complexes and DEHPA are insoluble in the aqueous phase and zinc and hydrogen ions are insoluble in the organic phase.

From the assumption (d) it follows that the zinc transfer from the aqueous to organic phase can only take place via a chemical reaction. Therefore, the mass transfer rate of zinc from the bulk aqueous phase to the interface must be equal to the rate of chemical reaction. As the interfacial concentrations are not measurable quantities, these can be obtained from the flux equations of the species involved which are related by the reaction stoichiometry

$$R_z = K_{z\alpha}\left(C_{z\alpha} - C_{z\alpha i}\right) \tag{3.8a}$$

$$= \frac{1}{m/2} K_o \left(\alpha_o - \alpha_{oi}\right) \tag{3.8b}$$

$$= -\frac{1}{2} K_H \left(C_H - C_{Hi}\right) \tag{3.8c}$$

$$= -K_{zo}\left(\alpha_{zo} - \alpha_{zoi}\right) \tag{3.8d}$$

Where

subscript i indicates values at the interface

$K_{z\alpha}$ mass transfer coefficient of zinc in the aqueous phase

K_H mass transfer coefficient of hydrogen ions in the aqueous phase

K_{zo} mass transfer coefficient of zinc - DEHPA complex and

K_o mass transfer coefficient of DEHPA.

The value of m/2 is the stoichiometric factor for DEHPA dimer for the overall reaction. Its values (Murthy, 1987), are 1.7 and 1.8 depending upon the use of equations (3.5) and (3.6) for the calculation of DEHPA activity coefficients respectively.

By eliminating the interfacial values from equations (3.3) and (3.8), the final kinetic expression for the overall interfacial reaction becomes

$$R_z = k_{I\alpha} \frac{\left(C_{z\alpha} - \frac{R_z}{K_{z\alpha}}\right)\left(\alpha_o - \frac{m}{2}\frac{R_z}{K_o}\right)}{\left(C_H + 2\frac{R_z}{K_H}\right)}$$

$$-k'_{I\alpha} \frac{\left(\alpha_{zo} + \frac{R_z}{K_{zo}}\right)\left(C_H + 2\frac{R_z}{K_H}\right)}{\left(\alpha_o - \frac{m}{2}\frac{R_z}{K_o}\right) + x\left(\alpha_o - \frac{m}{2}\frac{R_z}{K_o}\right)^{1/2}} \qquad (3.9)$$

This gives R_Z in terms of bulk concentrations of the species involved, individual mass transfer coefficients and specific reaction rate constants for the extraction and stripping reactions.

Although the intrinsic diffusivities of Zn^{2+} and H^+ are different, electric neutrality in the bulk phase must be maintained so that $K_{z\alpha} = K_H$

3.4 Hydrodynamic conditions

As the diffusional resistances in the stripping phase have been neglected and the feed will be pumped into the lumen of the fibre, only the internal flow in the fibre will be considered.

3.4.1 Internal flow in the fibre

Laminar flow in a circular tube of radius r_o is schematically shown in Figure 3.3, where fluid enters the tube with a uniform velocity. It is known that, when a fluid makes contact with the surface, viscous effects become important and a boundary layer develops with increasing x. This development occurs at the expense of a shrinking inviscid flow region at the centre and concludes with boundary layer merger at the centerline. Following this merger, viscous effects extend over the entire cross section and the velocity profile no longer changes with increasing x. The flow is then said to be fully developed, and the distance from the entrance at which this condition is achieved is termed the hydrodynamic entry length, $\chi_{fd,h}$. As shown in Figure 3.3, the fully developed velocity profile is parabolic for laminar flow in a circular tube. For turbulent flow, the profile is flatter due to turbulent mixing in the radial direction.

Equations for the thickness of the boundary layer indicate that the greater the flow rate the thinner δ'. So, by changing the flow rate the consequent

change in the thickness of the boundary layer may have an influence on the mass transfer rate across the liquid membrane.

As the Reynolds number in hollow fibres is very low, the entrance region may be very long and thus dominate the rate of mass transfer inside the fibre. So, in reference order to calculate the entrance region Figure 3.4 was used. This figure gives the solution to the equations for the boundary layer in the entry region for heat transfer. The dashed lines give the results for the thermal entry region for fully developed laminar flow, while the continuous line gives the values of the heat transfer coefficients for heat transfer in the hydrodynamic entry region. Using similitude analysis, the graph can be used for mass transfer by simply substituting the Nusselt number by the Sherwood number,

$$Sh = \frac{K_{z\alpha} \cdot Di}{\mathcal{D}} \qquad (3.10)$$

Where,

Di = diameter of the fibre

$\mathcal{D}$ = diffusivity of Zn in the aqueous phase.

and the Prandtl number by the Schmidt number

$$Sc = \frac{\nu}{\mathcal{D}} \qquad (3.11)$$

Then for the given value of the Sc number in the feed, and the different experimental values of the Re numbers, the mass transfer entry length can be calculated.

It can be seen in Figure 3.4 that the value of the heat transfer coefficient decreases with tube length in the entrance region, while it remains constant at fully developed conditions. The same is therefore true for the mass transfer coefficients in the lumen of the fibre.

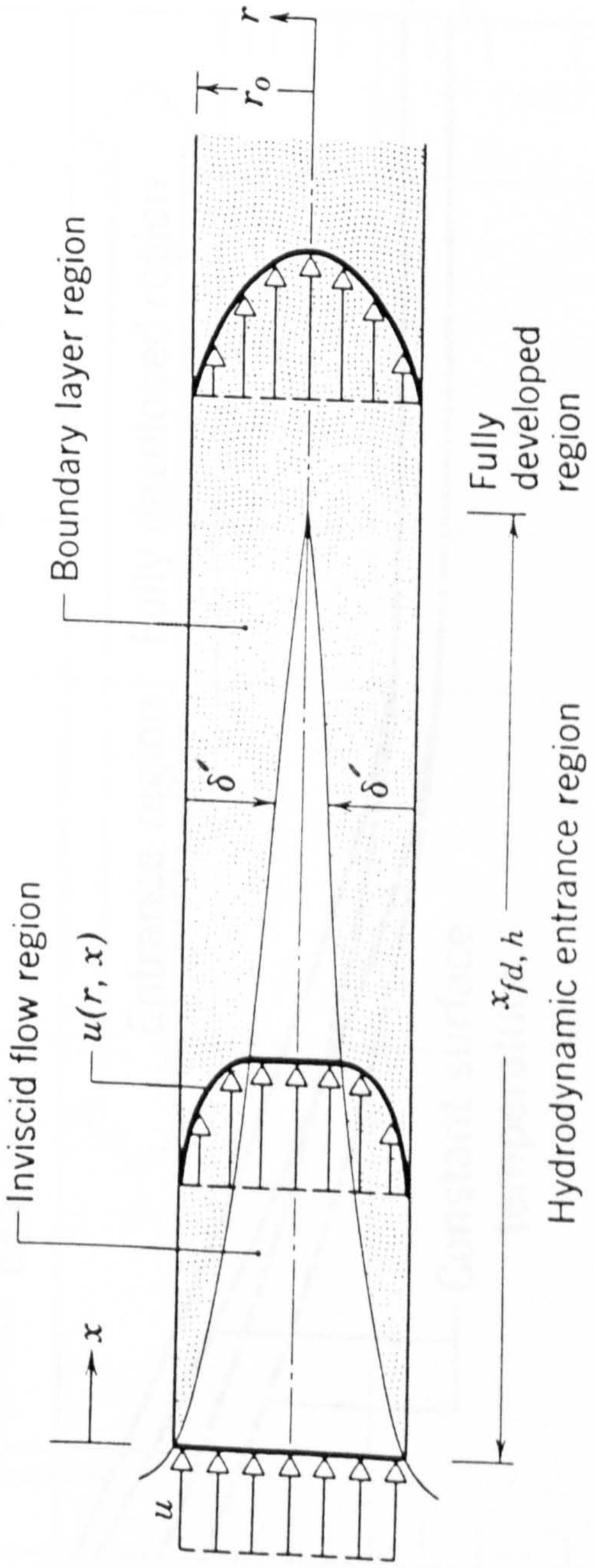


Figure 3.3 Schematic illustration of laminar, hydrodynamic boundary layer development in a circular tube and its influence on the mass transfer of ions across it into the supported liquid membrane (Incropera and De Witt, 1981)

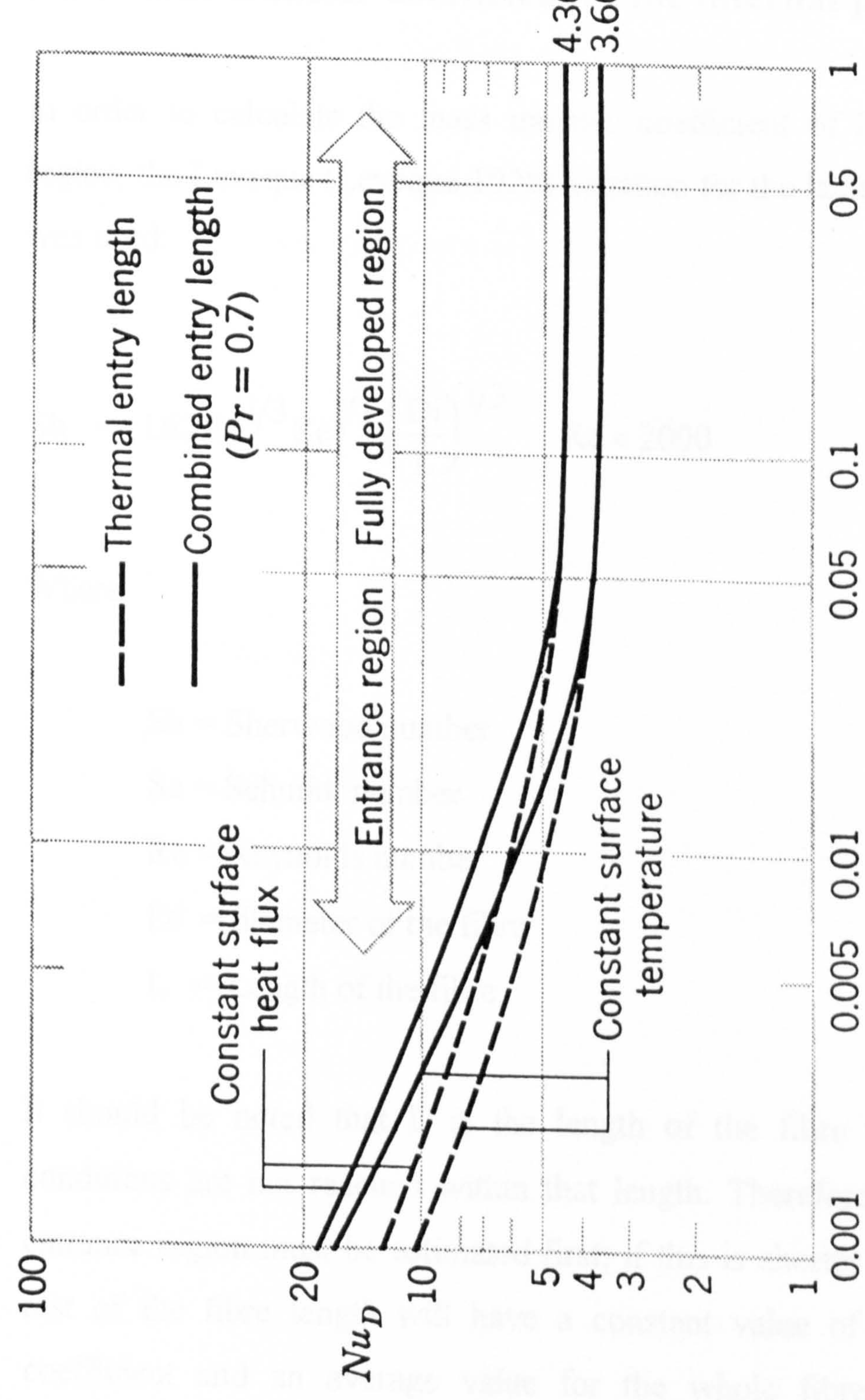


Figure 3.4 Local Nusselt number obtained from entry length solutions for laminar flow in a circular tube (Kays).

3.5 Mass transfer coefficients

3.5.1 Mass transfer coefficient in the internal phase.

In order to calculate the mass transfer coefficient of Zn in the entrance region, the Leveque (Leveque 1928) equation for the laminar boundary layer was used:

$$Sh = 1.62\,Re^{1/3}\,Sc^{1/3}\left(\frac{Di}{L}\right)^{1/3} \qquad Re < 2000 \qquad (3.12)$$

Where

Sh = Sherwood number

Sc = Schmidt number

Re = Reynolds number

Di = diameter of the fibre

L = Length of the fibre

It should be noted that L is the length of the fibre if fully developed conditions are not reached within that length. Therefore the length of the entrance region must be estimated first; if this is shorter than the fibre, the rest of the fibre length will have a constant value of the mass transfer coefficient and an average value for the whole fibre will have to be calculated.

Once the Sh number is obtained the mass transfer coefficient of Zn in the aqueous phase can be obtained using the definition of the Sh number.

3.5.2 Mass transfer coefficient in the liquid membrane

As the liquid membrane is quiescent, the mass transfer coefficients of DEHPA and the zinc complex were calculated using the following equation:

$$K_{zo} = \frac{\mathcal{D}_{complex}}{\delta} \qquad (3.13)$$

Where

δ =thickness of the fibre

In order to calculate the mass transfer coefficients of DEHPA and the Zn - DEHPA complex the values of the diffusion coefficients are needed. The equation used for the calculation of $\mathcal{D}$ is given in section 4.7.3, Chapter 4.

CHAPTER 4

EXPERIMENTAL PROCEDURES AND RESULTS

In this chapter the experimental procedure and the results for the extraction of Zn and Cu, both from single and mixed feeds are presented. All tables are located in Appendix E, and when relevant to the discussion of results, they are also shown in the text.

As described later on in this chapter the experiments were carried out in a once-through mode of operation.

All procedures described for $ZnSO_4.7H_2O$ apply also to $CuSO_4.5H_2O$; therefore the latter will be omitted for the sake of brevity.

4.1 Reagents

The $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, 99.5%, Na_2SO_4 and H_2SO_4 were of Analar grade with purities of 99.5%; and 98% minimum respectively supplied by BDH and were used without further purification.

The n-dodecane, supplied by Aldrich Chemical Co. Ltd., was of 99% purity and was used without further purification. The di(2-ethylhexyl) phosphoric acid (DEHPA) was of technical grade/GPR obtained from BDH Ltd. and contained up to 4% by volume of mono (2-ethylhexyl) phosphoric acid (MEHPA) plus a small amount of metal ions, mainly Fe^{3+}. The detailed purification procedure according to Union Carbide (1972) is given in Appendix A.

4.2 Preparation of Solutions

The aqueous feed solution was prepared by dissolving calculated amounts

of $ZnSO_4.7H_2O$ in deionized water.

Calculated amounts of Na_2SO_4 were also added to the aqueous phase in order to ensure that ionic strength of the solution should remain the same for all the runs. The required pH of the feed solution was obtained by dropwise addition of H_2SO_4. The aqueous phase contained zinc sulphate, sodium sulphate and sulphuric acid.

Zinc sulphate and sulphuric acid are not dissociated completely. These two species dissociate according to the following equations:

$$2ZnSO_4 + 2H^+ \Leftrightarrow Zn^{2+} + (SO_4H)_2Zn$$

$$HSO_4^- \Leftrightarrow H^+ + SO_4^{2-}$$

whereas sodium sulphate is assumed to be completely dissociated. In order to calculate the composition of the aqueous phase, i.e. Zn^{2+} and H^+ concentrations and ionic strength, a set of mass balance and dissociation equilibrium equations were solved. A complete procedure is given in Appendix C.

The organic phase was prepared by dissolving a calculated quantity of purified DEHPA, in n-dodecane. The resulting solution was clear and colourless. In the calculations, the molecular weight of DEHPA was taken to be 322.43.

4.3 Apparatus description

4.3.1 Design of the module

Two types of modules were used, one with a single fibre and the other with a bundle of four fibres. The modules were made of glass and look like small shell-and-tube heat exchangers, fitted with a jacket for constant temperature. A schematic drawing of the experimental set up is shown in Figure 4.1 for the single fibre module. The inner diameter of the shell glass tube was 13 mm and the overall length of the glass module 50cm.
The module was mounted horizontally onto a laboratory support stand.

All microporous hydrophobic polypropylene hollow fibres used in the experiments were glued at both ends with an epoxy resin within the PTFE adaptors and tightened with rubber O-rings. Each adaptor was 8 cm in length. The membrane was soaked with the organic solution and placed inside the glass tube. The effective length of the membrane was 35 cm.
Two different types of hollow fibres (provided by MICRODYN, WUPPERTAL, Germany), were used: S6/2 and Q3/2. Type S6/2 has a thickness δ equal to 0.4mm and internal diameter Di equal to 1.8mm, and Q3/2 has Di=0.6mm and δ equal to 0.2mm. These two fibres provide a large difference in internal diameter and membrane thickness to allow for study of feed phase and liquid membrane diffusional resistances. The specifications of the hollow fibres are shown in Table E1, Appendix E.
Product and strip solution receiver tanks were located to the side of the SLM module. A Watson-Marlow peristaltic pump with acid resistant viton

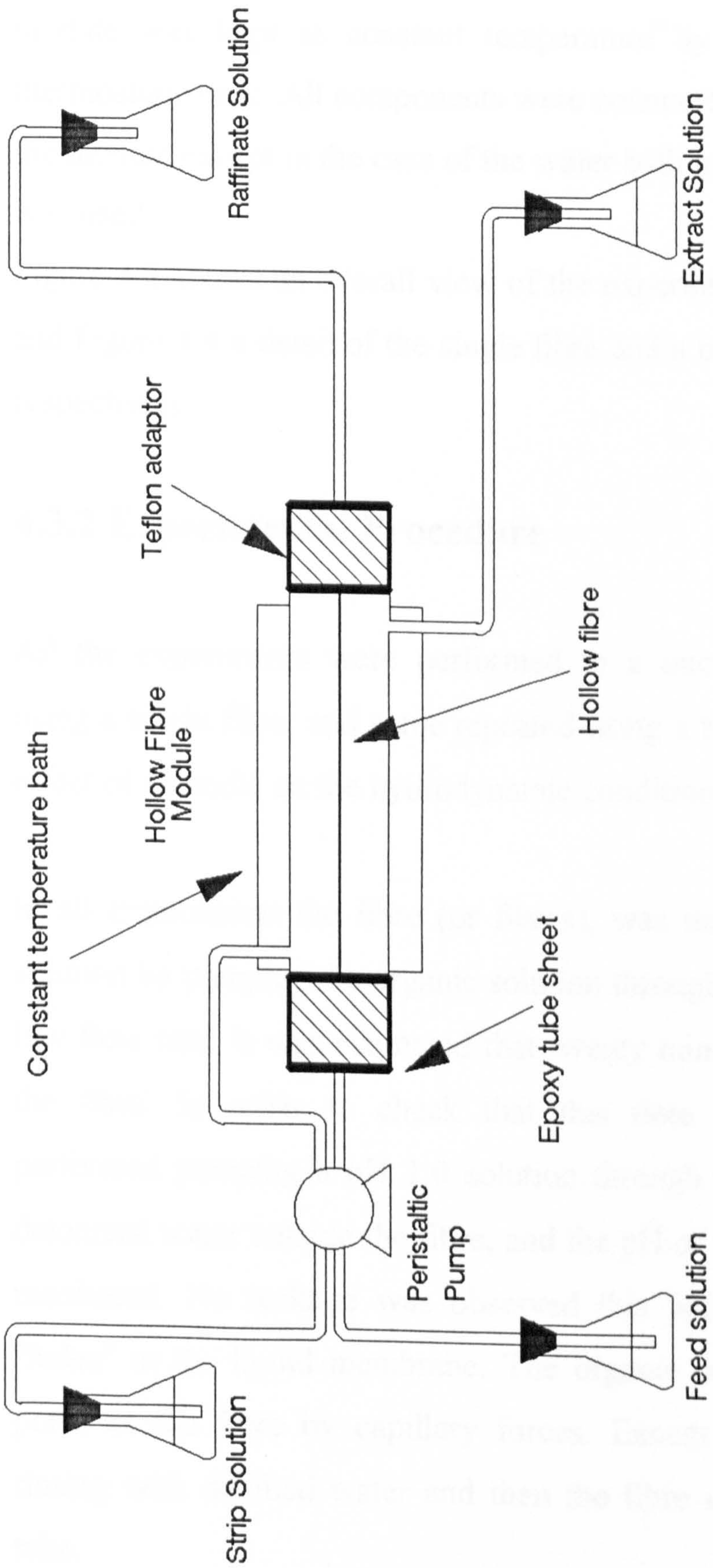


Figure 4.1 Schematic diagram of once-through mode of operation of the microporous hollow fibre module using a single fibre.

tubing was used to pump both the feed and the stripping solutions. The module was kept at constant temperature* by water circulation from a thermostatic tank. All components were connected by 3mm PVC tubing into the module except in the case of the water bath in which 9 mm rubber tubing was used.

Figure 4.2 shows an overall view of the experimental set up and Figure 4.3 and Figure 4.4 a detail of the single fibre and a bundle of four fibres module respectively.

4.3.2 Experimental Procedure

All the experiments were performed in a once-through mode operation, using a single fibre, and some repeated using a bundle of fibres to study the effect of a bundle on the hydrodynamic conditions surrounding the fibre.

In all experiments the fibre (or fibres), was impregnated with an organic solution by pumping the organic solution through the lumen of the fibre at a low flow rate. It was estimated that twenty minutes were adequate to soak the fibre. In order to check that this time was sufficient, runs were performed pumping a pH 1.0 solution through the lumen of the fibre and deionised water outside the fibre, and the pH of the outlet water stream was monitored. No leakage was observed this indicating that there were no "holes" in the liquid membrane. The organic solution was retained in the pores of the fibre by capillary forces. Excess solution was removed by rinsing with distilled water and then the fibre was placed inside the glass tube.

* Temperature: 25^{o}C

Figure 4.2 Overall view of the apparatus used in the experimental work
(a) Peristaltic Pump
(b) Hollow Fibre Module
(c) Thermostatic Bath

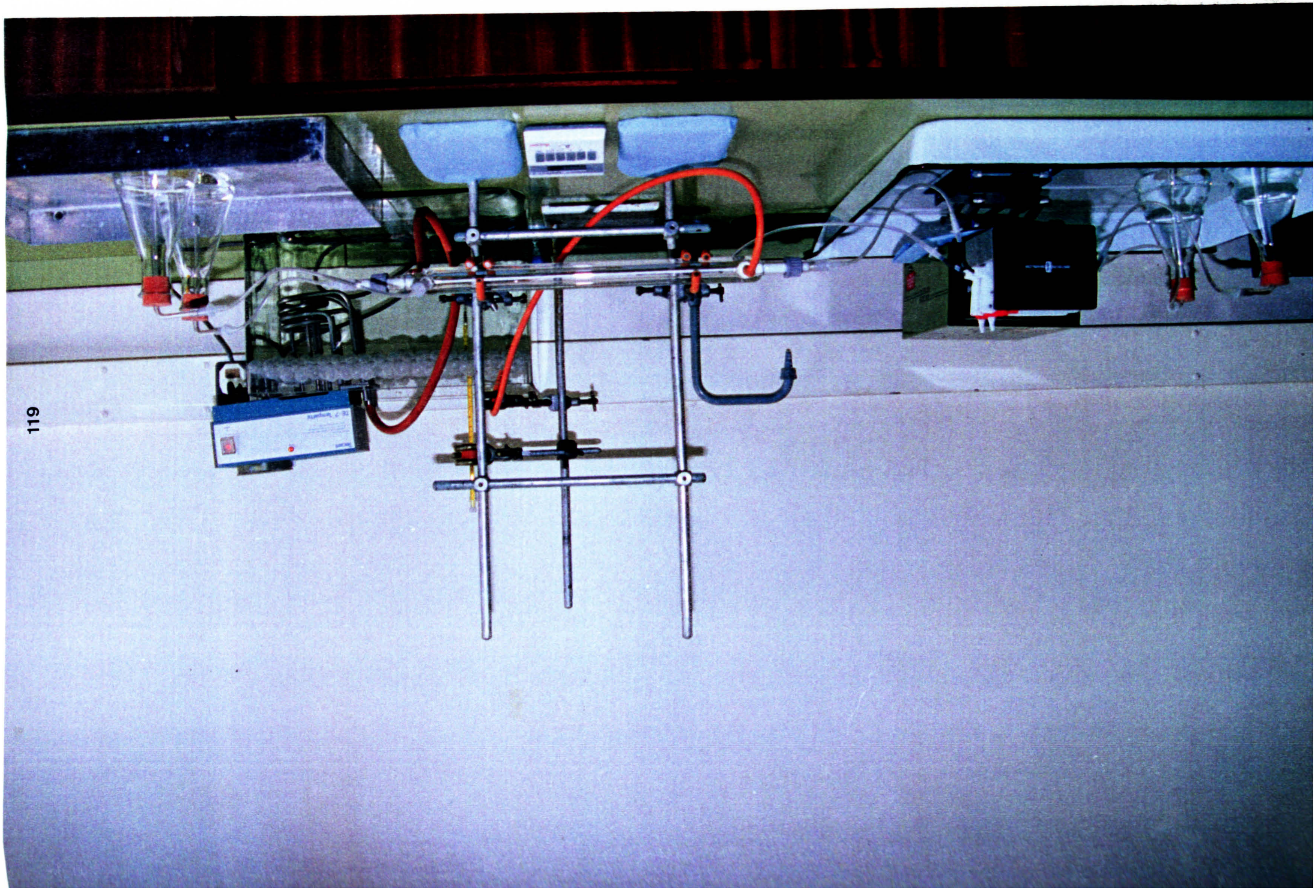


Figure 4.3 Components of the Hollow Fibre Module, with a single hollow fibre of type S6/2, including:

(a) Glass Module
(b) Hollow Fibre (S6/2)
(c) Teflon Adaptors
(d) Screw caps
(e) rubber o-rings

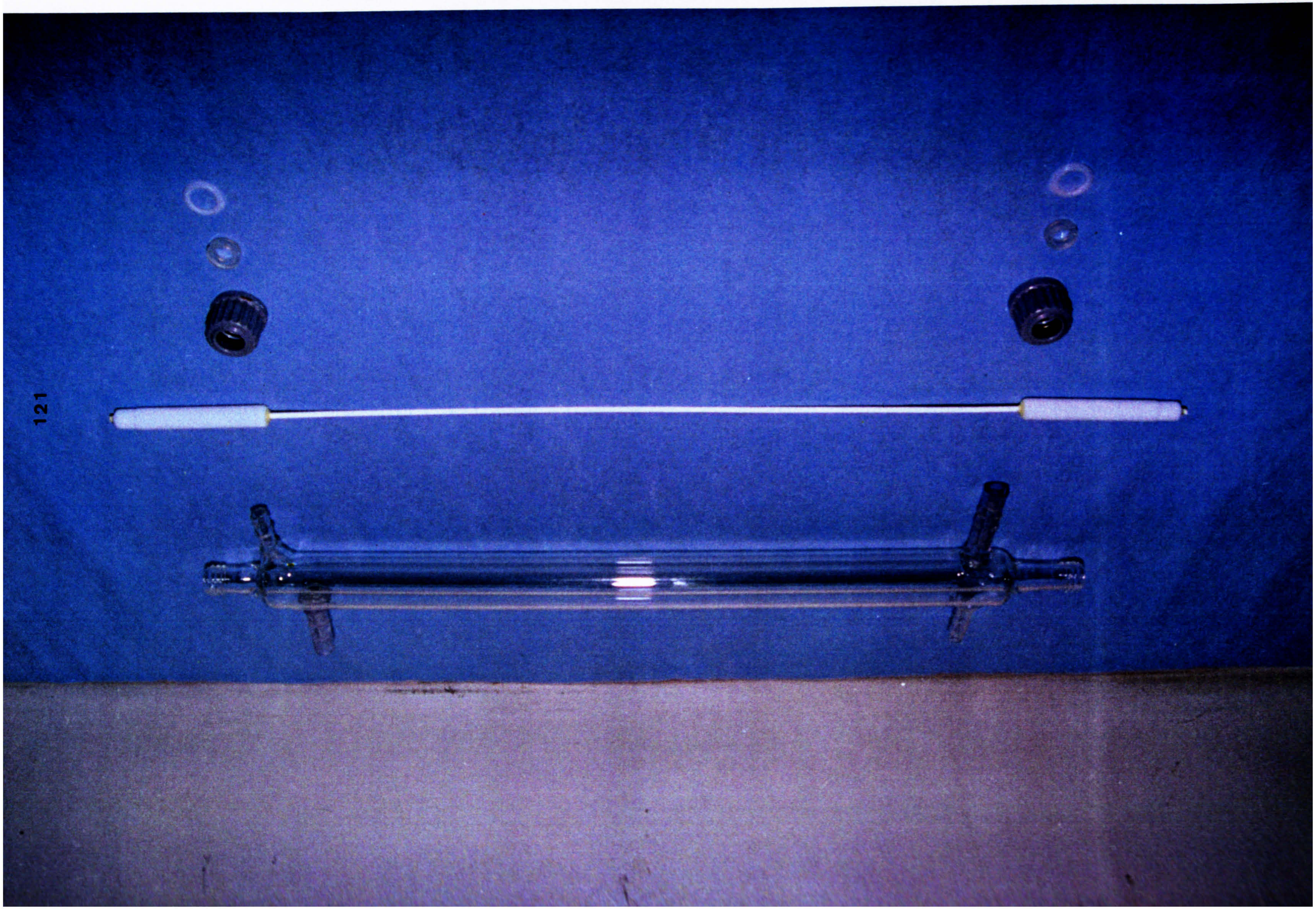
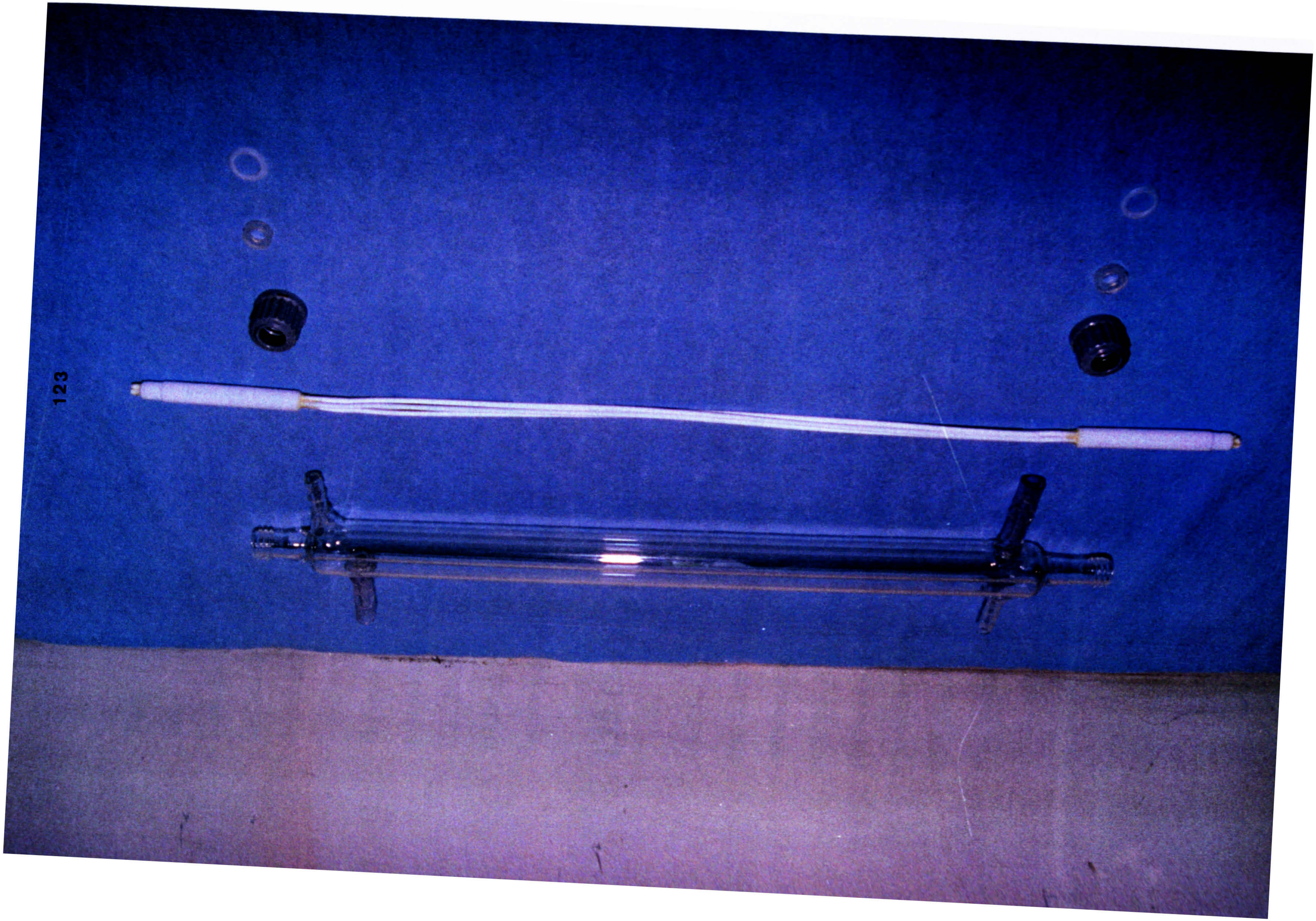

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Figure 4.4 Components of the Hollow Fibre Module, with a bundle of hollow fibres of type S6/2, including:
(a) Glass Module
(b) Hollow Fibres (S6/2)
(c) Teflon Adaptors
(d) Screw caps
(e) rubber o-rings


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The feed solution at pH 3 was pumped through the inside of the hollow fibre, while the strip solution at pH 1 circulated through the outside of the fibre. Both flow rates were controlled, using different diameter viton tubing, by means of a peristaltic pump previously calibrated, (Tables E10 and E11, Appendix E).

The exit raffinate solution and the strip solution were sampled every 30 minutes and the pH was measured periodically throughout the process.
The duration of each experiment was 5 hours and the feed and strip solutions were pumped through cocurrently. All experiments were at least duplicated and the results taken at the steady state region, were averaged.

4.3.3 Cleaning of the fibre

After the completion of each experiment the fibre was cleaned by passing strip solution through the lumen of the fibre as well as the module shell. Any remaining organic solution was finally removed from the fibre using acetone. After three successive runs the fibre was replaced by a new one. This was due to the epoxy resin that wore out. Experiments with an old and a new fibre were carried out to check for membrane ageing. No differences were observed between the two. This was taken as an indication that three runs were not sufficient to change the structure of the membrane substantially.
The glass module was washed with tap water first, then rinsed with deionized water and finally washed with acetone and left to dry.

4.3.4 Analysis of samples.

An atomic absorption spectrophotometer PERKIN-ELMER 1100B was used to analyse the zinc concentration at a wavelength of 213.9nm, and copper concentration at a wavelength of 327.4nm.

As the spectrophotometer gives approximately linear reading only upto a concentration of 1mg/l, the samples were diluted with deionised water to give concentrations of 0.1-1mg/l. Standard solutions were prepared with the same concentration of Na_2SO_4 as the diluted samples. The instrument was calibrated with the standard solutions to obtain a calibration curve prior to the measurement of samples for each run.

The pH was measured with a PHILIPS PW 9409 digital pH meter.

4.4 Experimental Results

A total of 290 runs were carried out

Tables E2 - E9, Appendix E, give the ranges of concentrations and flowrates investigated using the different fibre sizes in single fibre and bundle modules.

Figure 4.5 (Table E12, Appendix E) shows a sample of data showing a typical steady state behaviour of zinc and copper. As it can be seen it takes about an hour for the system to reach steady state. This gives an indication of the time taken by the complex to reach the stripping side of the membrane.

In this section the effect of the metal ion concentration in a single metal feed solution on the flux in the two fibre sizes are presented. Results cover concentrations of DEHPA between 0.05 and 0.2M. Results for the mixed metal feed are presented in section 4.5.

Sections 4.6 and 4.7 are focused on the analysis of the diffusional resistances and compare the results for the two membrane thicknesses and for different values of the Reynolds number.

Results on the effect of the number of hollow fibres in the module and of pH on extraction flux are presented in sections 4.8 and 4.9. Finally in section 4.10 there is an overall discussion on the rate controlling mechanisms at the different set of conditions investigated, followed by the conclusions drawn from the experimental work in section 4.11.

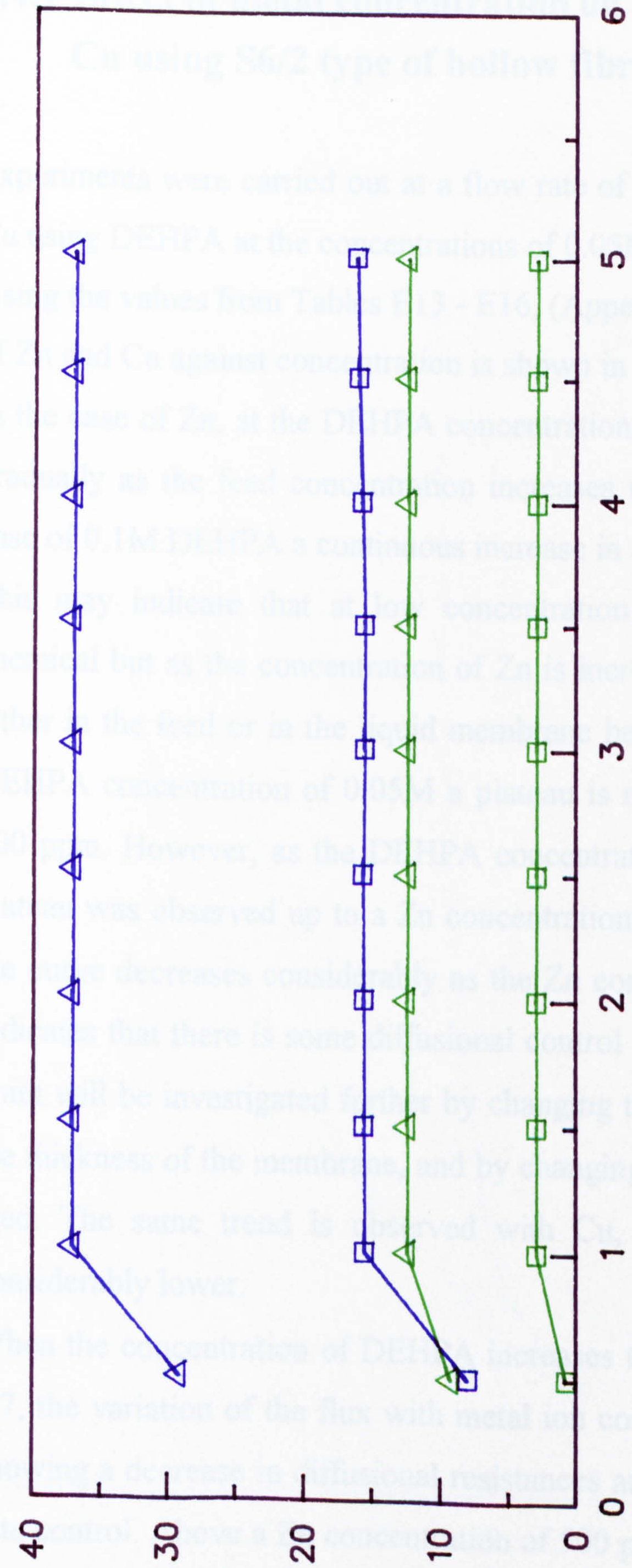


Figure 4.5 Molar flux vs time

4.4.1 Effect of metal concentration on molar flux of Zn and Cu using S6/2 type of hollow fibre.

Experiments were carried out at a flow rate of 1.25 ml/min for both Zn and Cu using DEHPA at the concentrations of 0.05M and 0.lM.

Using the values from Tables E13 - E16, (Appendix E), a plot of molar flux of Zn and Cu against concentration is shown in Figure 4.6.

In the case of Zn, at the DEHPA concentration of 0.05 M the flux increases gradually as the feed concentration increases up to 200 ppm, while in the case of 0.1M DEHPA a continuous increase in flux throughout is observed. This may indicate that at low concentration of Zn the control may be chemical but as the concentration of Zn is increased, diffusional resistances either in the feed or in the liquid membrane begin to affect the flux. At the DEHPA concentration of 0.05M a plateau is reached at a concentration of 200 ppm. However, as the DEHPA concentration is increased to 0.1M no plateau was observed up to a Zn concentration of 800 ppm but the slope of the curve decreases considerably as the Zn concentration is increased. This indicates that there is some diffusional control in the liquid membrane. This point will be investigated further by changing the size of the fibre, and thus the thickness of the membrane, and by changing the Reynolds number of the feed. The same trend is observed with Cu, for which the extraction is considerably lower.

When the concentration of DEHPA increases to 0.15 M and 0.2 M, Figure 4.7, the variation of the flux with metal ion concentration becomes steeper, showing a decrease in diffusional resistances and a switch to more chemical rate control. Above a Zn concentration of 500 ppm a plateau is reached and

Figure 4.6 Effect of metal concentration on the molar flux of Zn and Cu using 0.05M and 0.1M DEHPA.

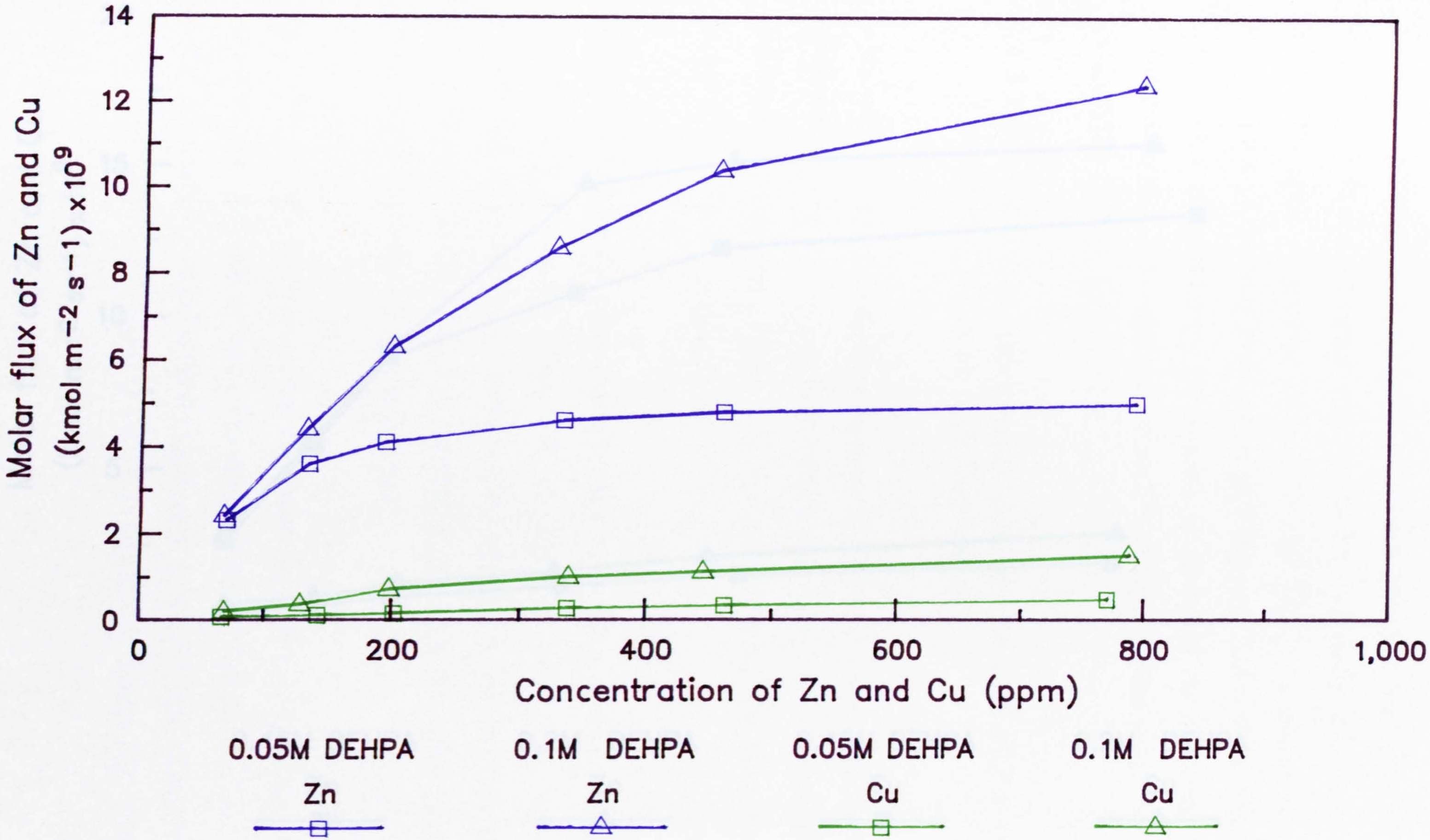
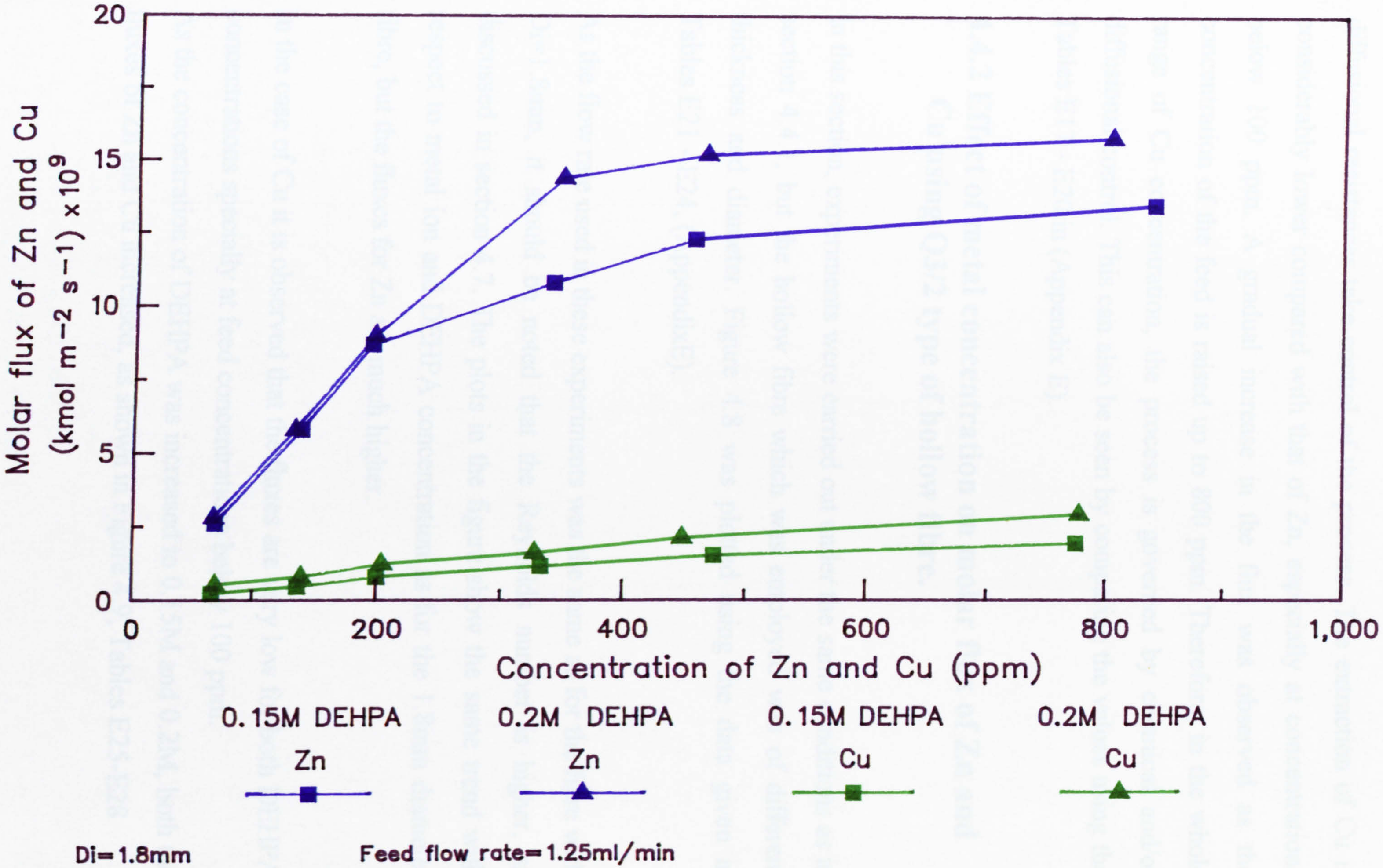


Figure 4.7 Effect of metal concentration on the molar flux of Zn and Cu using 0.15M and 0.2M DEHPA.



diffusional resistances take control of the process. The extraction of Cu is considerably lower compared with that of Zn, especially at concentrations below 100 ppm. A gradual increase in the flux was observed as the concentration of the feed is raised up to 800 ppm. Therefore, in the whole range of Cu concentration, the process is governed by chemical and/or diffusional control. This can also be seen by comparing the values using the Tables E17 - E20 in (Appendix E).

4.4.2 Effect of metal concentration on molar flux of Zn and Cu using Q3/2 type of hollow fibre.

In this section, experiments were carried out under the same conditions as in section 4.4.1, but the hollow fibre which was employed was of different thickness and diameter. Figure 4.8 was plotted using the data given in Tables E21 - E24, (AppendixE).

As the flow rate used in these experiments was the same as for the fibre with Di=1.8mm, it should be noted that the Reynolds number is higher, as discussed in section 4.7. The plots in the figure show the same trend with respect to metal ion and DEHPA concentration as for the 1.8mm diameter fibre, but the fluxes for Zn are much higher.

In the case of Cu it is observed that the fluxes are very low for both DEHPA concentrations specially at feed concentrations below 100 ppm.
As the concentration of DEHPA was increased to 0.15M and 0.2M, both the fluxes of Zn and Cu increased, as shown in Figure 4.9, Tables E25-E28

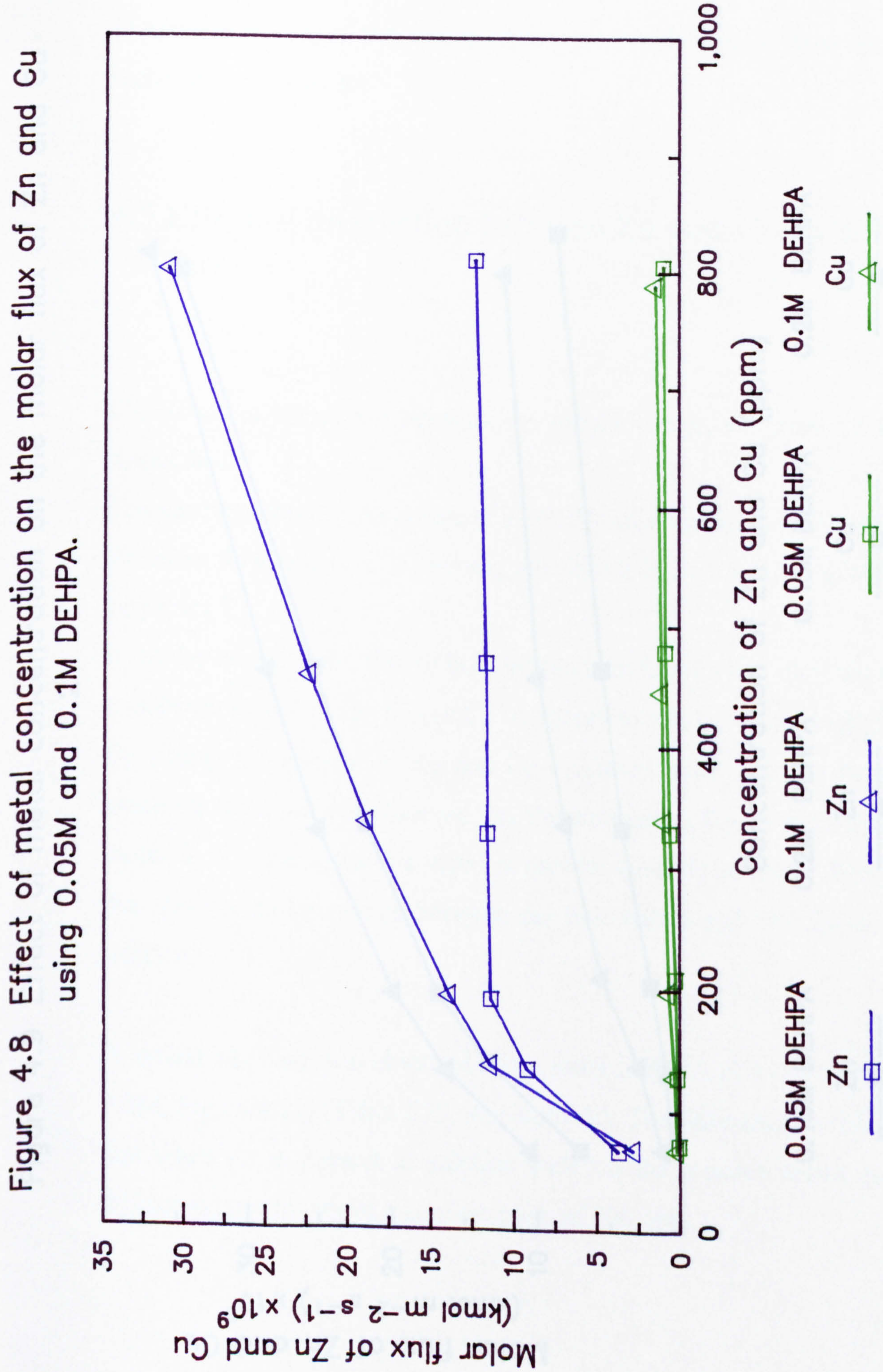
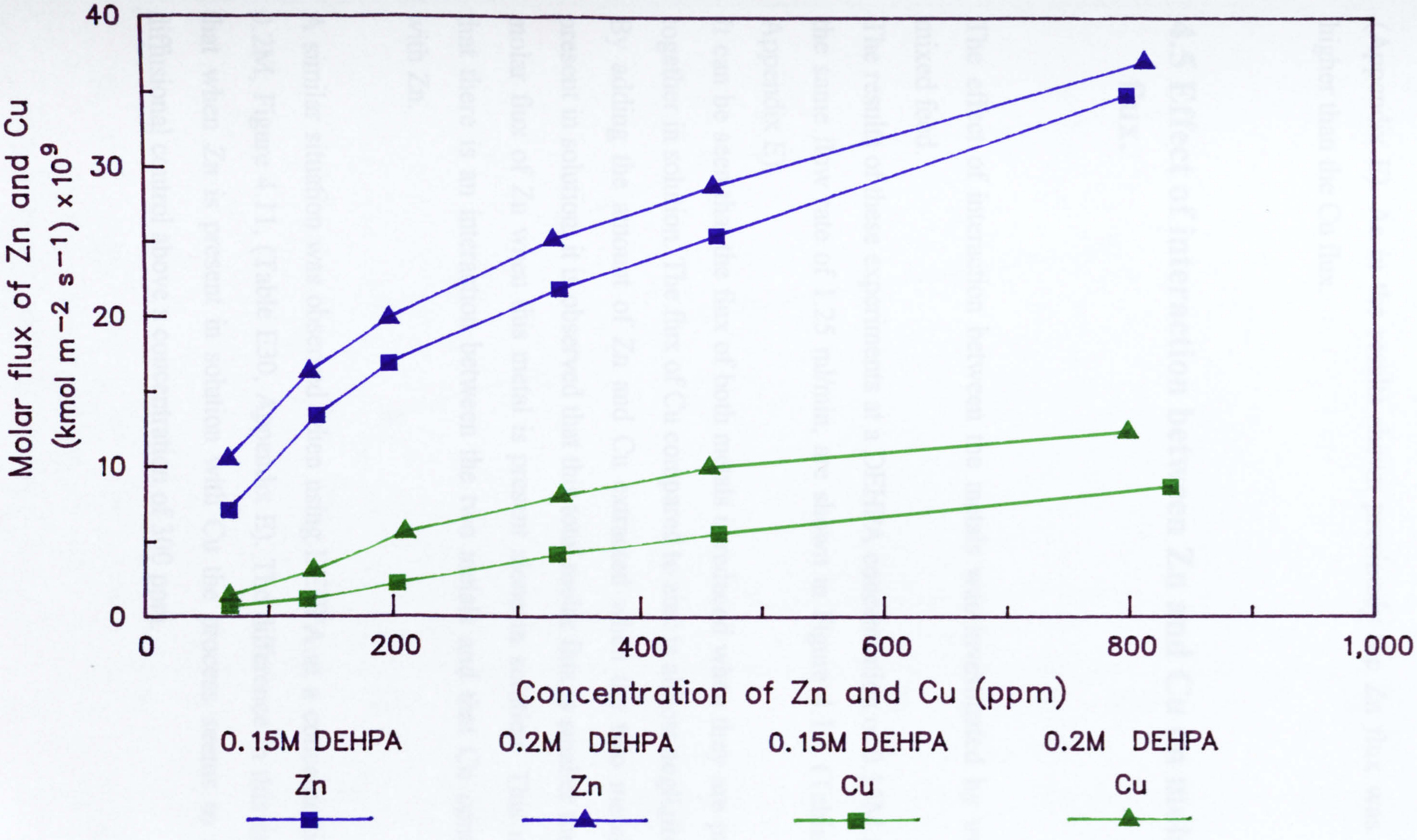


Figure 4.8 Effect of metal concentration on the molar flux of Zn and Cu using 0.05M and 0.1M DEHPA.

Figure 4.9 Effect of metal concentration on the molar flux of Zn and Cu using 0.15M and 0.2M DEHPA.



Di=0.6mm

Feed flow rate=1.25ml/min

(Appendix E). As in the results shown previously the Zn flux was much higher than the Cu flux.

4.5 Effect of interaction between Zn and Cu on molar flux.

The effect of interaction between the metals was investigated by using a mixed feed.

The results of these experiments at a DEHPA concentration of 0.15M and at the same flow rate of 1.25 ml/min, are shown in Figure 4.10, (Table E29, Appendix E).

It can be seen that the flux of both metals is reduced when they are present together in solution. The flux of Cu compared to zinc is almost negligible.

By adding the amount of Zn and Cu extracted when the two metals are present in solution, it is observed that this total molar flux is smaller than the molar flux of Zn when this metal is present alone in solution. This means that there is an interaction between the two metals and that Cu competes with Zn.

A similar situation was observed when using DEHPA at a concentration of 0.2M, Figure 4.11, (Table E30, Appendix E). The difference in this case is that when Zn is present in solution with Cu the process seems to reach diffusional control above a concentration of 300 ppm.

Figure 4.10 Effect of the interaction of Zn and Cu on the molar flux.

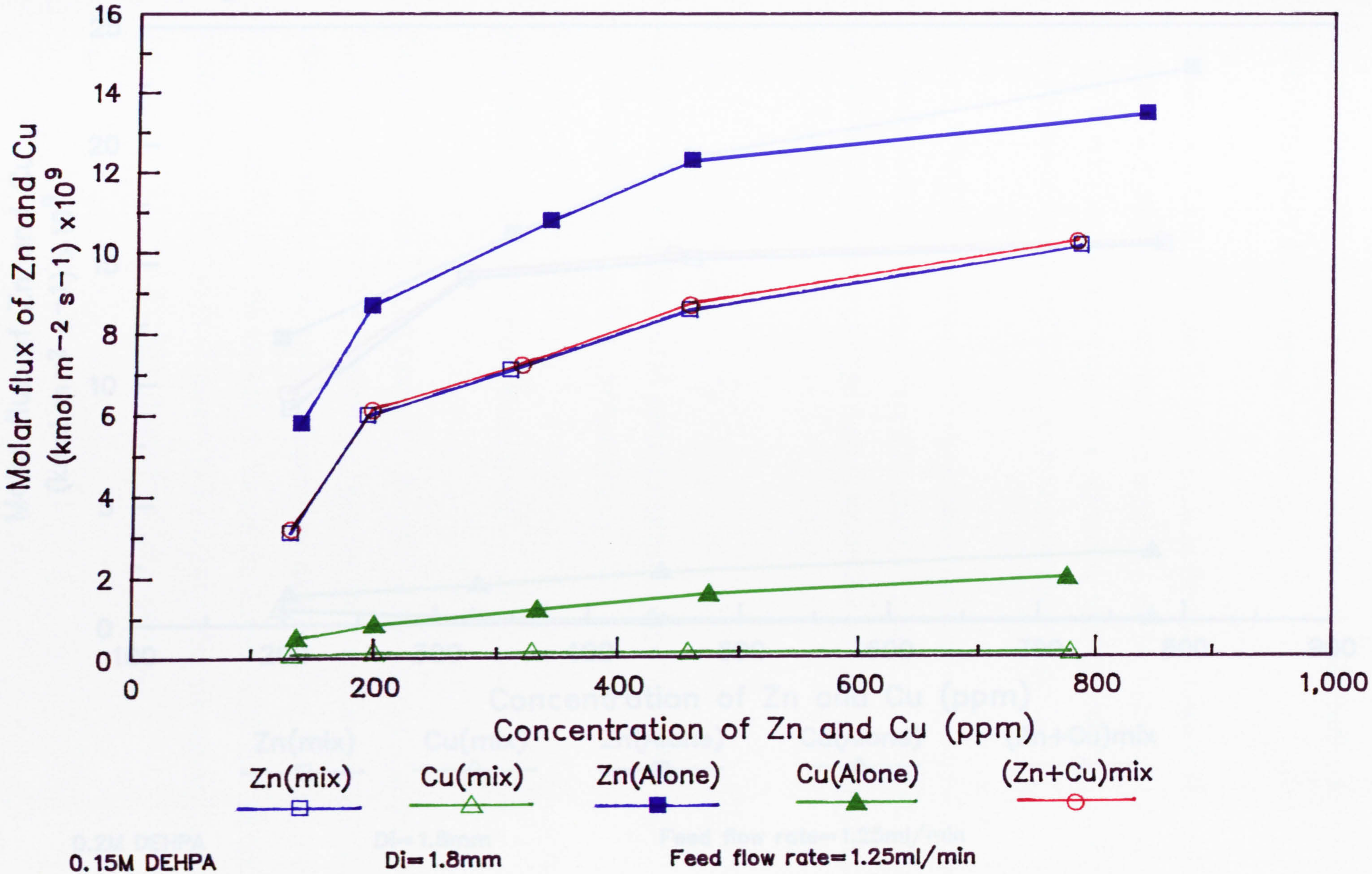
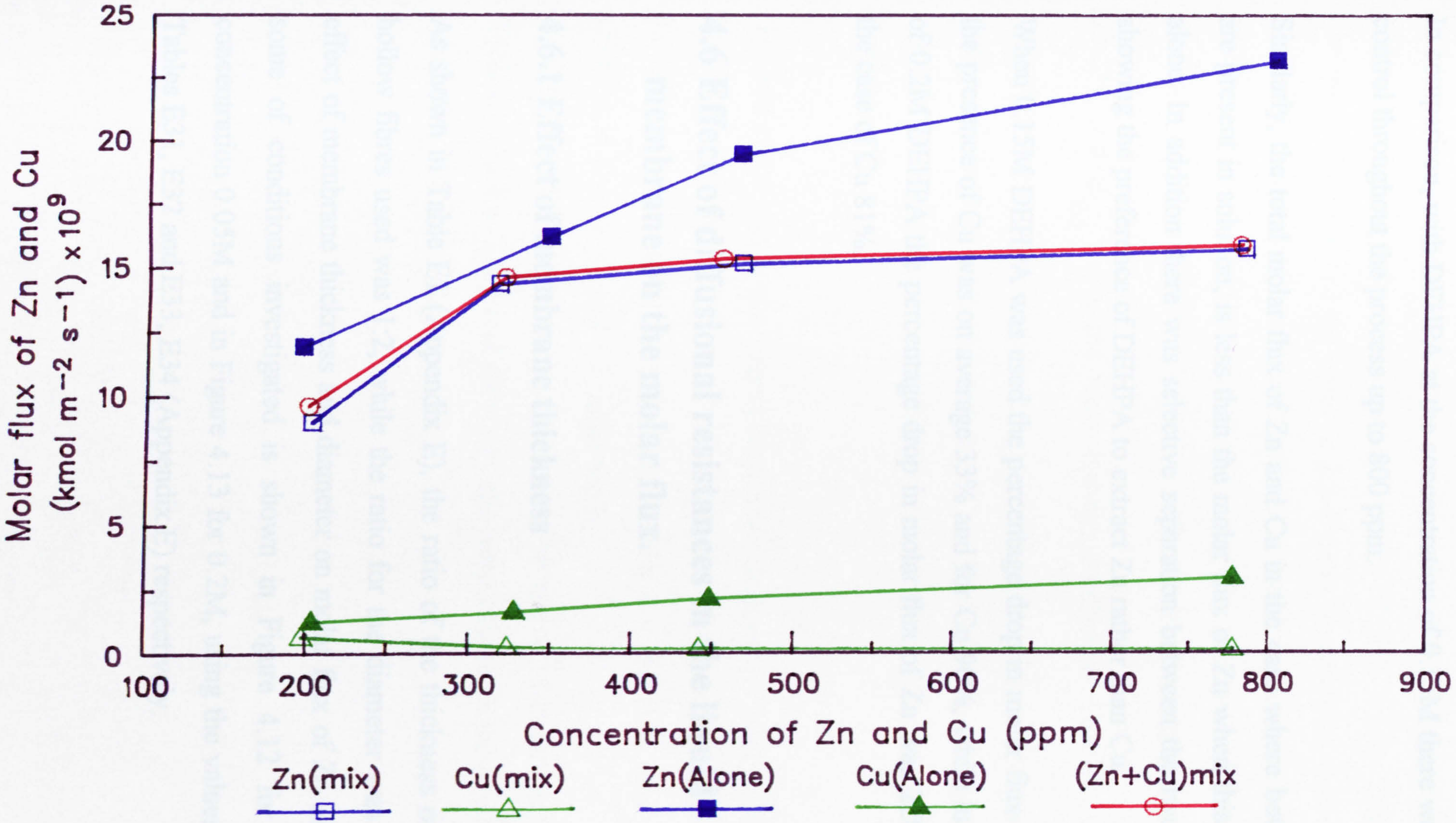


Figure 4.11 Effect of the interaction of Zn and Cu on the molar flux.



In comparison, with DEHPA at the concentration of 0.15M there was mixed control throughout the process up to 800 ppm.

Similarly, the total molar flux of Zn and Cu in the case where both metals are present in solution, is less than the molar flux of Zn when this metal is alone. In addition there was selective separation between the two metals, showing the preference of DEHPA to extract Zn rather than Cu.

When 0.15M DEHPA was used the percentage drop in molar flux of Zn, in the presence of Cu was on average 33% and for Cu 90%, while in the case of 0.2M DEHPA the percentage drop in molar flux of Zn was 22% and in the case of Cu 81%.

4.6 Effect of diffusional resistances in the liquid membrane on the molar flux.

4.6.1 Effect of membrane thickness

As shown in Table E1 (Appendix E), the ratio of the thickness of the two hollow fibres used was 1:2, while the ratio for the diameter was 1:3. The effect of membrane thickness and diameter on molar flux of Zn and Cu for some of conditions investigated is shown in Figure 4.12 for DEHPA concentration 0.05M and in Figure 4.13 for 0.2M, using the values given in Tables E31, E32 and E33, E34 (Appendix E) respectively.

As the flow rates are the same as for the larger fibre, the graphs show the effect of changing both, the Re number and the fibre thickness. The fluxes in the smaller fibre are of the order of 2.5-3 times greater than in the those in the 1.8mm diameter fibre. If there were only membrane control, the reaction in fibre thickness could not lead to such a large increase in molar flux.

In fact if the mass transfer coefficient in the membrane is given by equation (3.13), (i.e $K_{zo} = \frac{\mathcal{D}}{\delta}$), the mass transfer coefficient doubles when δ is halved, so membrane control can only justify an increase in R_z by a factor of 2.The influence of membrane resistance can be further analysed by plotting the interfacial flux R_z versus DEHPA concentration. This will be discussed in section 4.6.2.

The rest of the results concerning feed concentrations for both Zn and Cu, in the range of 67 ppm - 192 ppm and 192 ppm - 810 ppm, at a concentration of DEHPA of 0.05 M are shown in Tables 4.1 and 4.2, and for 0.2M DEHPA in Tables 4.7 and 4.8 respectively.

Results for DEHPA concentrations of 0.1M and 0.15M are presented in Tables 4.3 to 4.6. The trend shown by the results listed in these tables is the same as in that in the graphs.

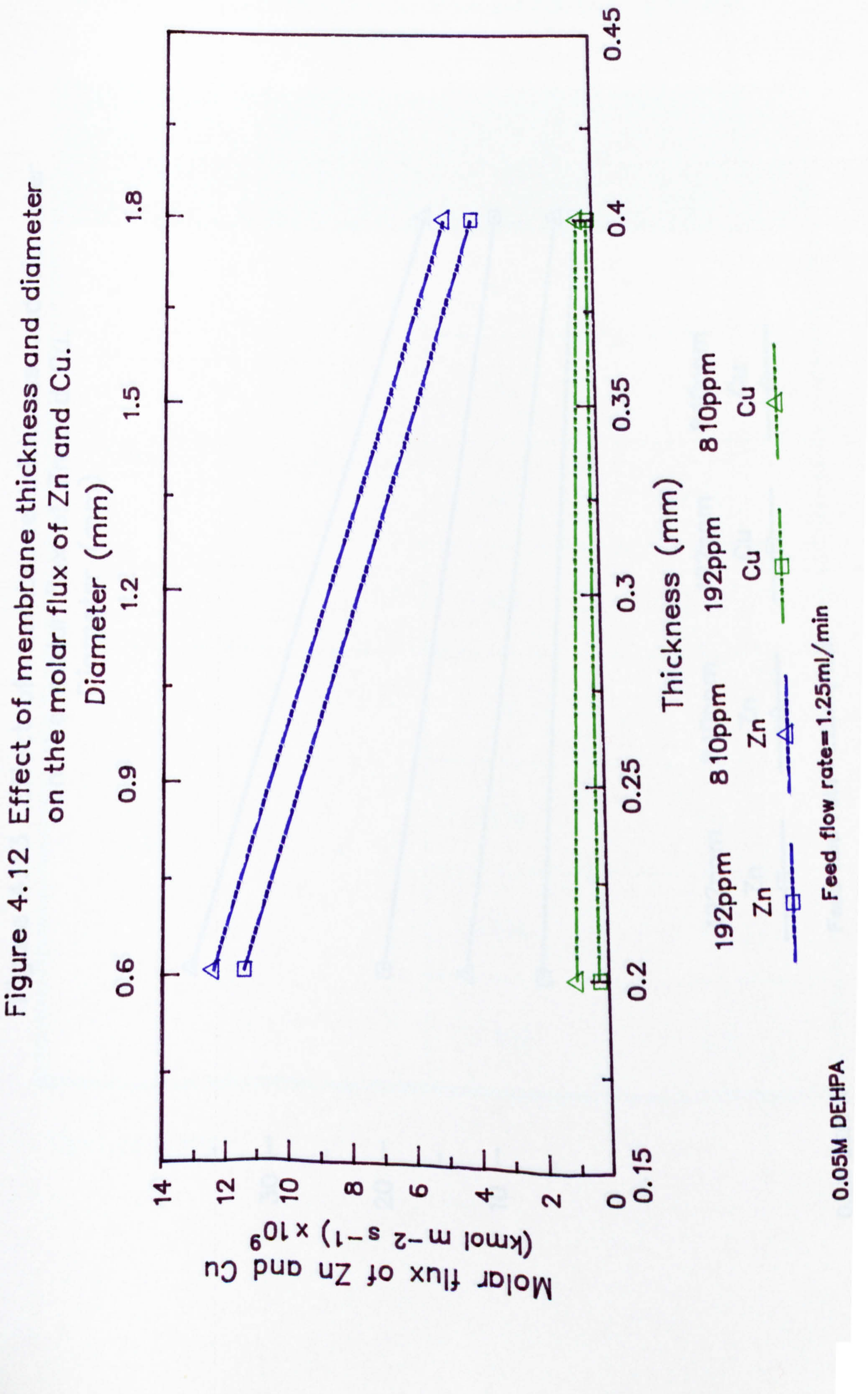


Figure 4.12 Effect of membrane thickness and diameter on the molar flux of Zn and Cu.

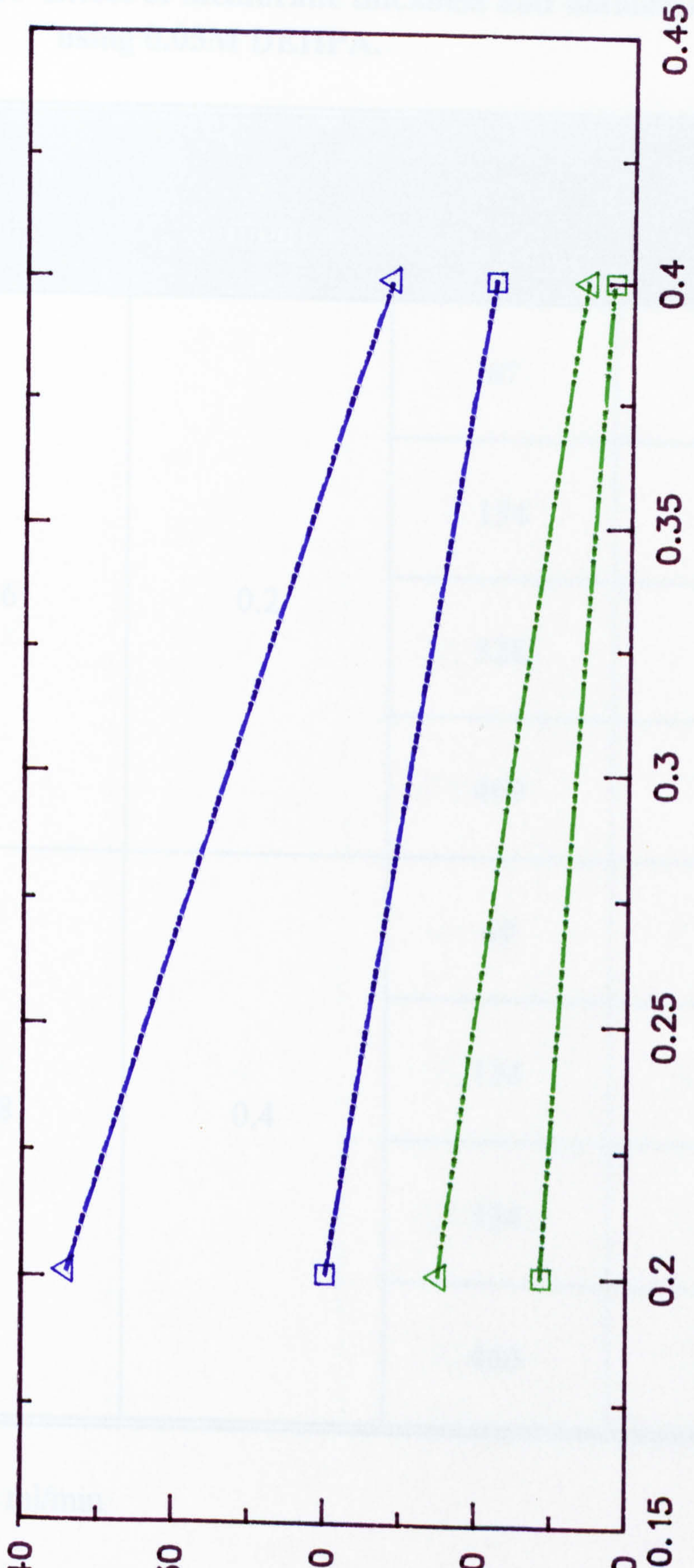


Figure 4.13 Effect of membrane thickness and diameter on the molar flux of Zn and Cu.

Table 4.1 Effect of membrane thickness and diameter on Zn flux, using 0.05M DEHPA.

Di (mm)	δ (mm)	[Zn] (ppm)	R_Z (x10^9) (kmol m^{-2} s^{-1})
0.6	0.2	67	3.7
		134	9.2
		328	11.6
		469	11.7
1.8	0.4	69	2.3
		134	3.6
		334	4.6
		460	4.8

Q_F=1.25 ml/min

TABLE 4.2 Effect of membrane thickness and diameter on Cu flux, using 0.05M DEHPA.

Di (mm)	δ (mm)	[Cu] (ppm)	Molar flux ($x10^9$) (kmol m^{-2} s^{-1})
0.6	0.2	72	0.09
		128	0.19
		329	0.63
		479	0.89
1.8	0.4	66	0.08
		142	0.12
		338	0.28
		462	0.34

Q_F=1.25 ml/min

TABLE 4.3 Effect of membrane thickness and diameter on Zn flux, using 0.1M DEHPA.

Di (mm)	δ (mm)	[Zn] (ppm)	R_Z (x10^9) (kmol m^{-2} s^{-1})
0.6	0.2	68	5.8
		137	11.4
		195	13.9
		337	18.9
		458	22.4
		800	31.1
1.8	0.4	67	2.4
		132	4.4
		199	6.3
		327	8.6
		455	10.4
		795	12.4

Q_F=1.25 ml/min

Table 4.4 Effect of membrane thickness and diameter on Cu flux, using 0.1M DEHPA.

Di (mm)	δ (mm)	[Cu] (ppm)	Molar flux (x10^9) (kmol m^{-2} s^{-1})
0.6	0.2	67	0.54
		134	0.91
		200	1.65
		338	3.11
		458	4.13
		810	6.42
1.8	0.4	68	0.19
		128	0.36
		198	0.71
		339	0.99
		445	1.11
		788	1.49

Q_F=1.25 ml/min

Table 4.5 Effect of membrane thickness and diameter on Zn flux, using 0.15M DEHPA.

Di (mm)	δ (mm)	[Zn] (ppm)	R_Z (x10^9) (kmol m^{-2} s^{-1})
0.6	0.2	67	7.1
		138	13.4
		196	16.9
		334	21.9
		463	25.5
		798	34.9
1.8	0.4	68	2.6
		138	5.8
		195	8.7
		341	10.8
		456	12.3
		840	13.5

Q_F=1.25 ml/min

Table 4.6 Effect of membrane thickness and diameter on Cu flux, using 0.15M DEHPA.

Di (mm)	δ (mm)	[Cu] (ppm)	Molar flux (x10^9) (kmol m^{-2} s^{-1})
0.6	0.2	68	0.74
		131	1.19
		203	2.24
		332	4.21
		464	5.62
		833	8.74
1.8	0.4	66	0.24
		136	0.48
		200	0.8
		333	1.16
		474	1.53
		775	1.93

Q_F=1.25 ml/min

Table 4.7 Effect of membrane thickness and diameter on Zn flux, using 0.2M DEHPA.

Di (mm)	δ (mm)	[Zn] (ppm)	R_z (x10^9) (kmol m^{-2} s^{-1})
0.6	0.2	66	10.5
		132	16.3
		329	25.2
		460	28.8
1.8	0.4	67	2.8
		133	5.8
		348	14.4
		465	15.2

Q_F=1.25 ml/min

Table 4.8 Effect of membrane thickness and diameter on Cu flux, using 0.2M DEHPA.

Di (mm)	δ (mm)	[Cu] (ppm)	Molar flux (x10^9) (kmol m^{-2} s^{-1})
0.6	0.2	68	1.41
		136	3.09
		335	8.11
		456	10.03
1.8	0.4	69	0.52
		139	0.8
		328	1.61
		448	2.12

Q_F=1.25 ml/min

4.6.2 Effect of DEHPA concentration on the molar flux of Zn and Cu, at different feed concentrations.

Figures 4.14 - 4.17 present the results of R_Z with respect to DEHPA concentration for both sizes of fibres, (Tables E35-E38, Appendix E).

As it can be observed the variation of the molar flux with the concentration of DEHPA increases with the metal concentration. At a low metal concentration (i.e 68 ppm) the flux does not change with DEHPA concentration. As the metal concentration is increased the variation of R_Z with DEHPA increases first but reaches a plateau in the high range of DEHPA concentration values, showing a switch of control from mixed to diffusional. However, at the highest concentration of metal used no plateau is observed, thus indicating that at this concentration there is no change to full diffusional control.

4.7 Effect of Re on extraction flux: Diffusional resistances in the feed phase.

As the change in fibre thickness cannot be obtained without changing the diameter, the effect of fibre thickness discussed in 4.6.1 could not be decoupled from the effect of Di if the flow rate were kept constant. Thus in order to investigate the effect of the hydrodynamic conditions alone on the molar flux the Re number was changed by changing the flow rate.

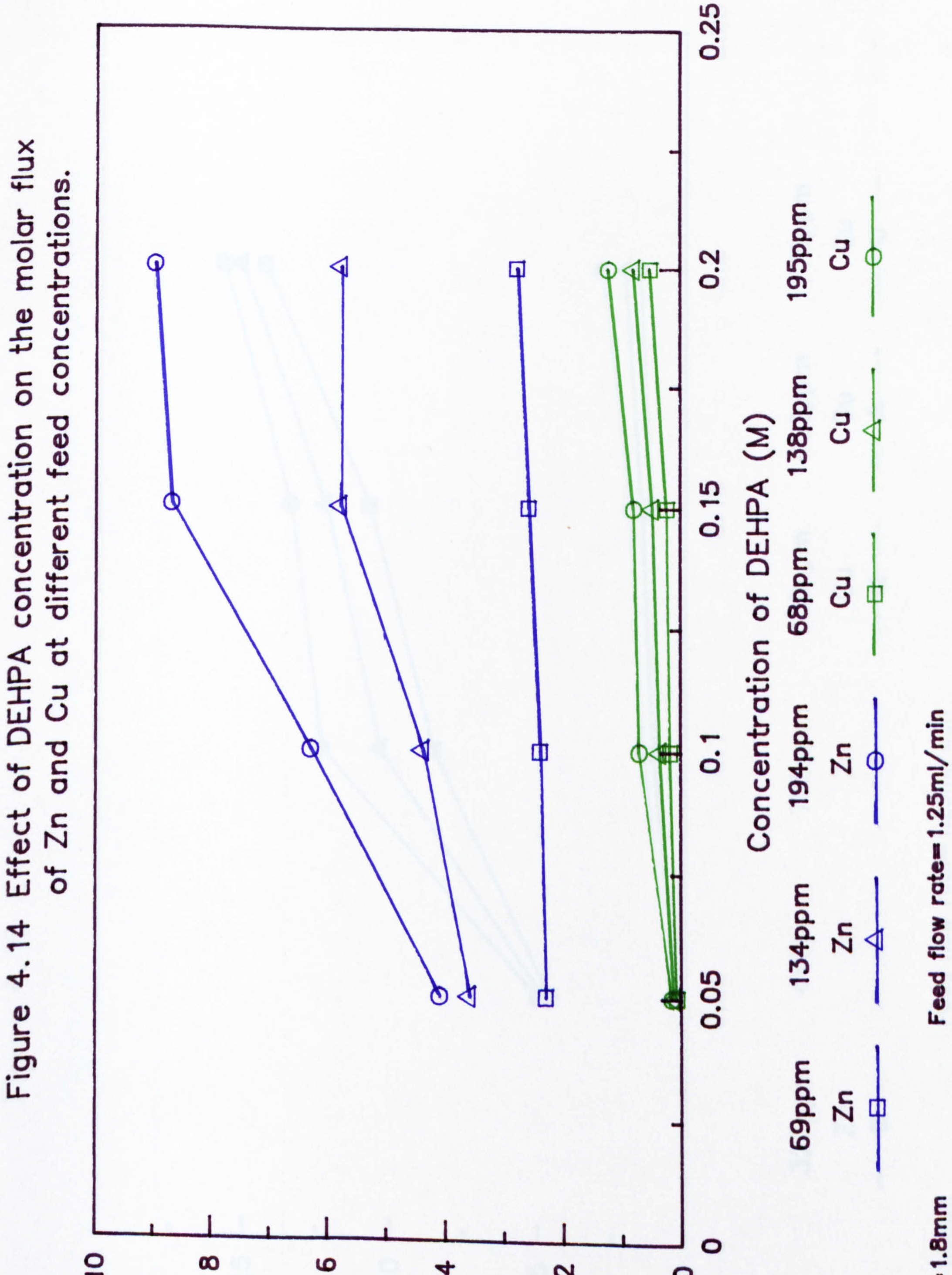
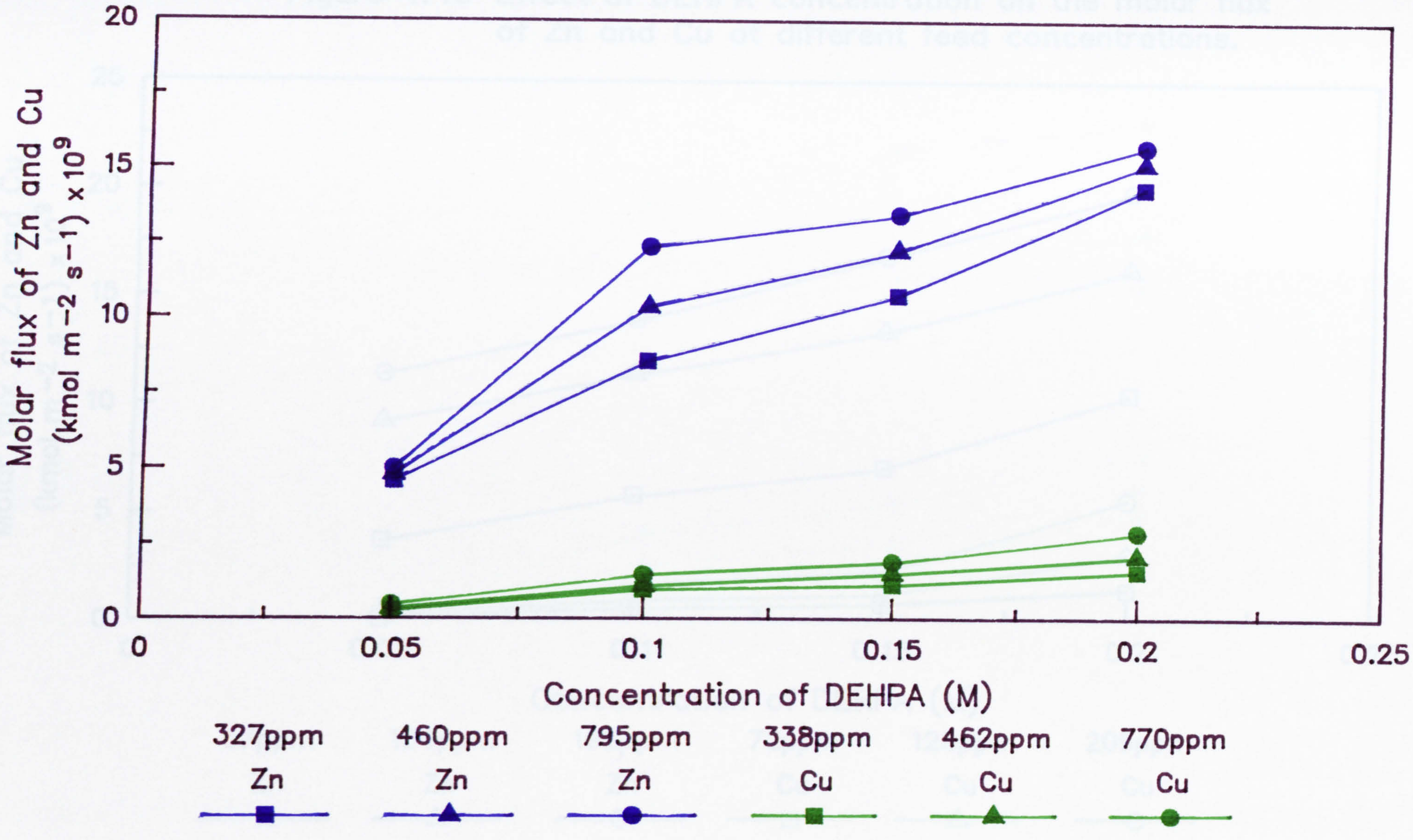


Figure 4.14 Effect of DEHPA concentration on the molar flux of Zn and Cu at different feed concentrations.

Figure 4.15 Effect of DEHPA concentration on the molar flux of Zn and Cu at different feed concentrations.



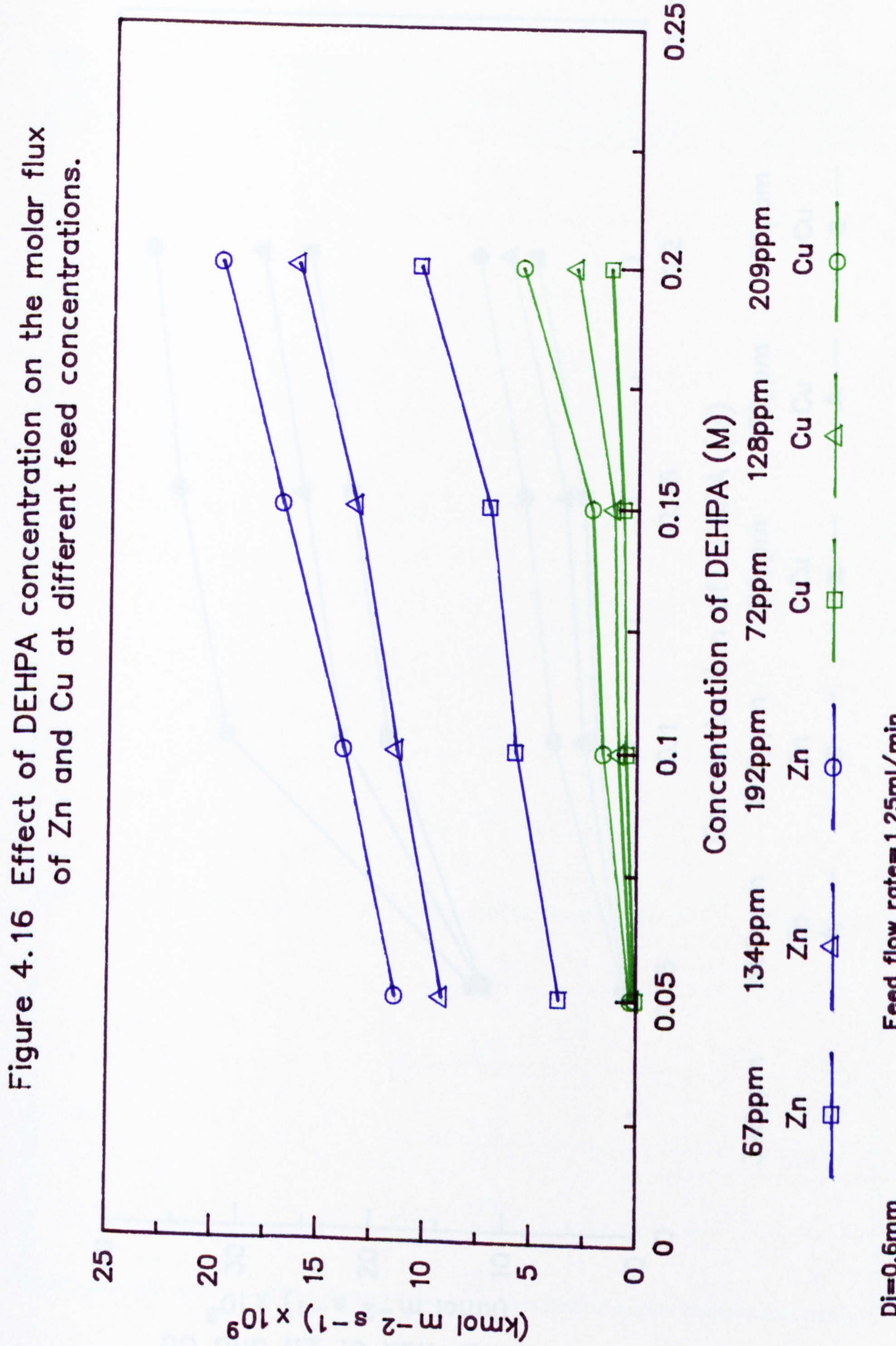


Figure 4.16 Effect of DEHPA concentration on the molar flux of Zn and Cu at different feed concentrations.

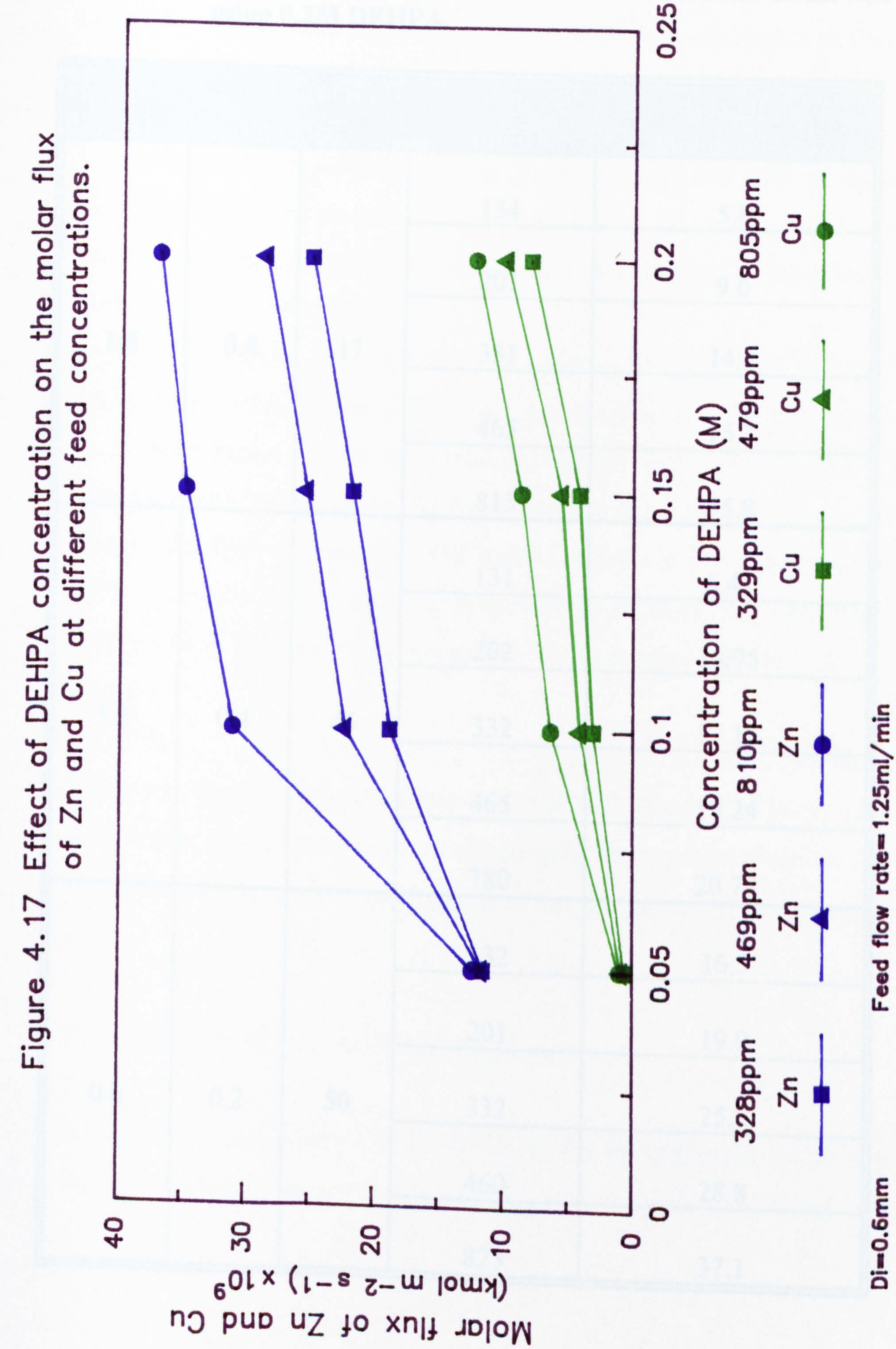


Figure 4.17 Effect of DEHPA concentration on the molar flux of Zn and Cu at different feed concentrations.

Table 4.9 Effect of Re number and membrane thickness on Zn flux using 0.2M DEHPA.

Di (mm)	δ (mm)	Re	[Zn] (ppm)	R_Z (x10^9) (kmol m^{-2} s^{-1})
1.8	0.4	17	134	5.8
			201	9.0
			331	14.4
			465	15.2
			815	15.8
1.8	0.4	45	131	6.41
			202	10.95
			332	17.19
			465	19.24
			780	20.78
0.6	0.2	50	132	16.3
			201	19.9
			332	25.2
			460	28.8
			825	37.1

Experiments were conducted in both fibres and results are shown in Figure 4.18 (Table E39, Appendix E), for the 1.8mm diameter fibre and Figure 4.19 (Table E40, Appendix E), for the 0.6mm diameter fibre.

For the large fibre, there is an increase in the extraction flux with Re up to a Reynolds number of about 40, which is steeper in the range of lower Re, and also for zinc concentrations of 330 ppm and above. The same trend is observed in the small fibre.

Figure 4.20 (Table E41, Appendix E) shows a comparison of results obtained in the two fibres at DEHPA concentration of 0.2M and different zinc concentration. Points connected by straight lines correspond to the same flow rate in both fibres. As can be seen in the figure the Re numbers change with fibre size and therefore direct comparison of results in the two fibres cannot be done in terms of flow rates. In addition, the mass transfer coefficients in the feed varies not only with Re number but also with fibre diameter.

Therefore, in order to compare the results in both fibres, first the length of the entrance regions have to be calculated using these values of the Re. Then the mass transfer coefficient in the feed can be estimated using equation 3.10.

4.7.1 Length of the entrance region

Assuming a typical value of 1.0×10^{-9} m^2/s for the diffusivity of the metal ion in the aqueous phase and a dynamic viscosity of 10^{-6} m^2/s for the

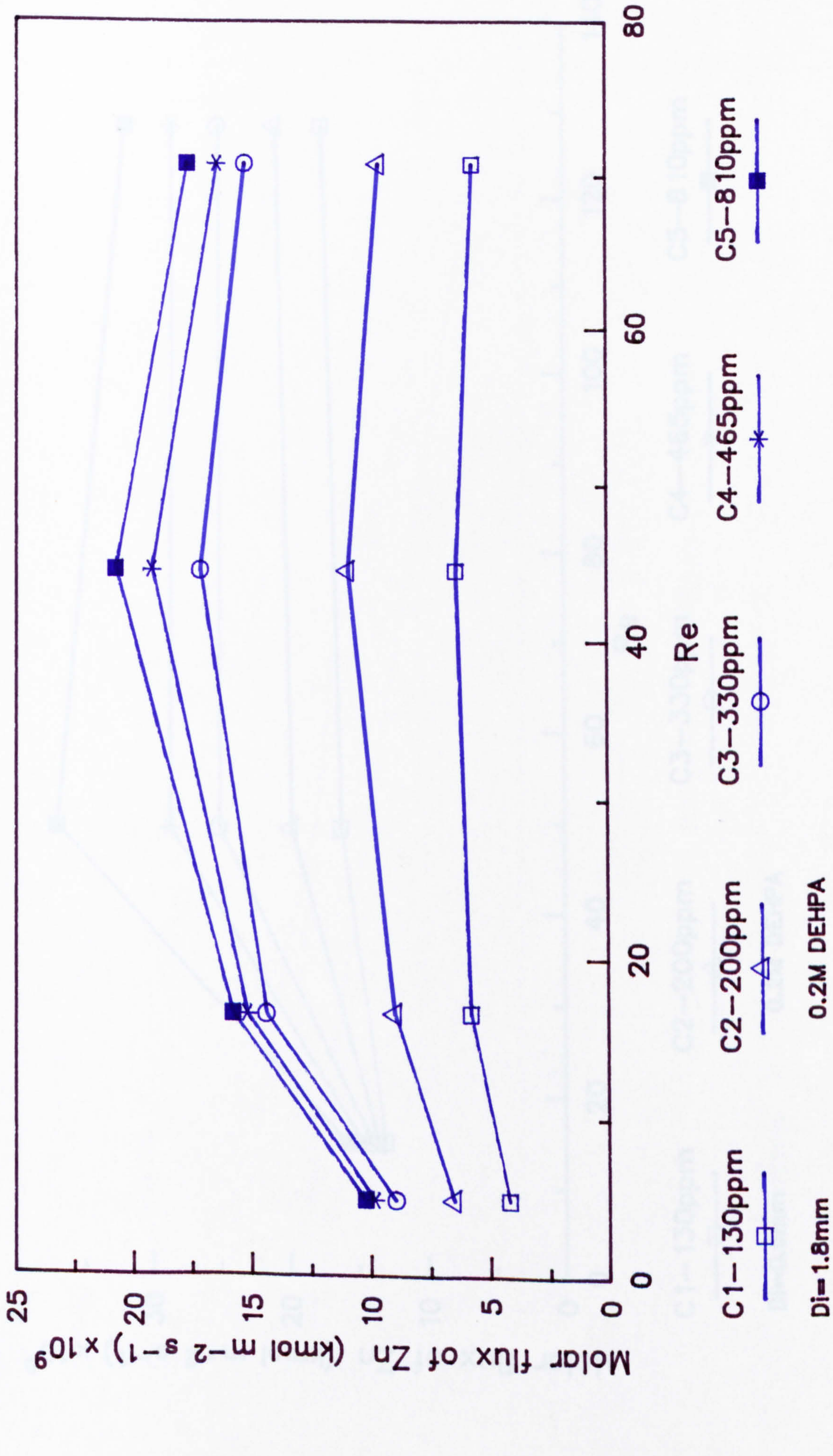


Figure 4.18 Effect of the Re number on the molar flux of Zn at different feed concentrations.

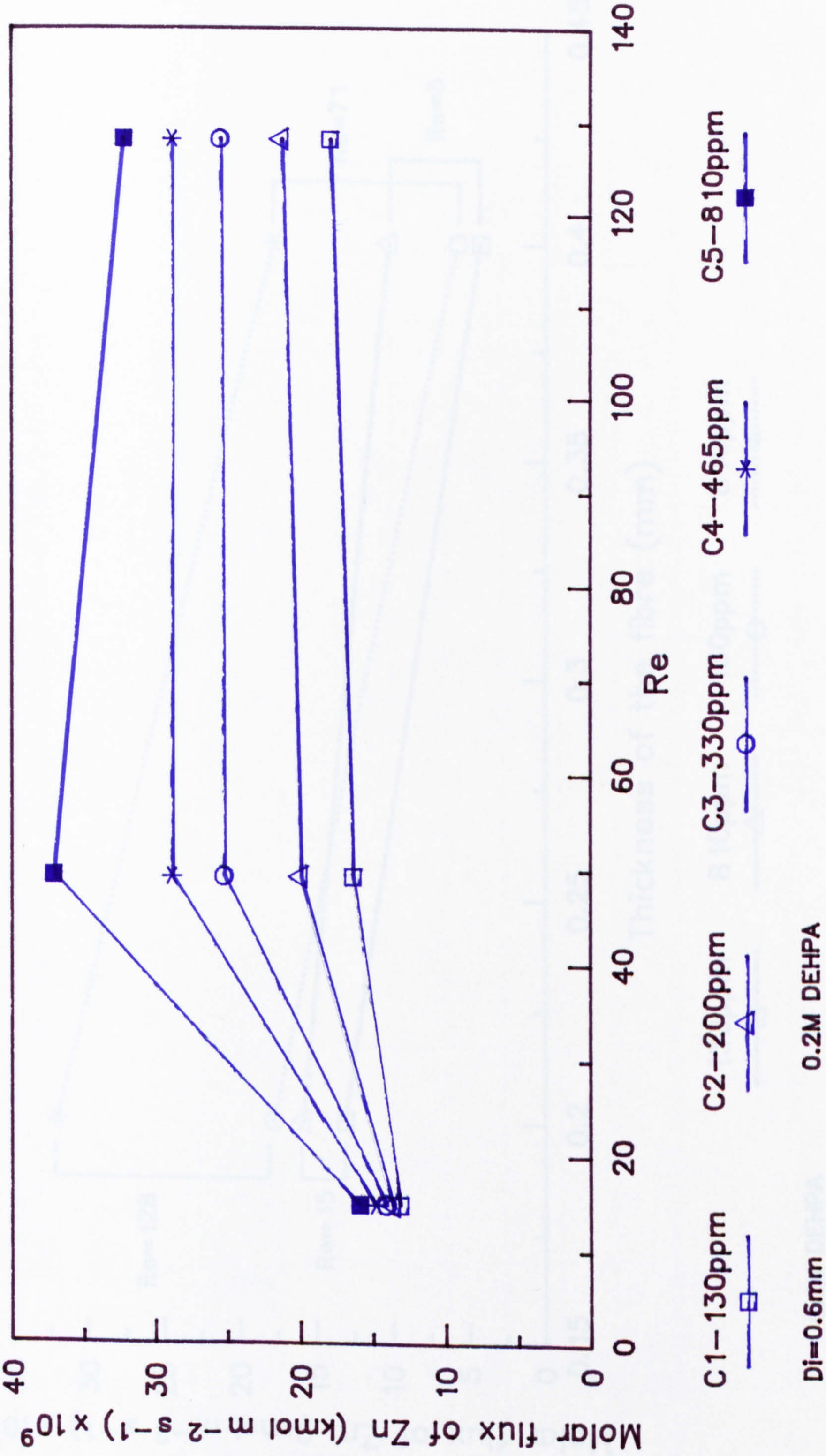


Figure 4.19 Effect of the Re number on the molar flux of Zn at different feed concentrations.

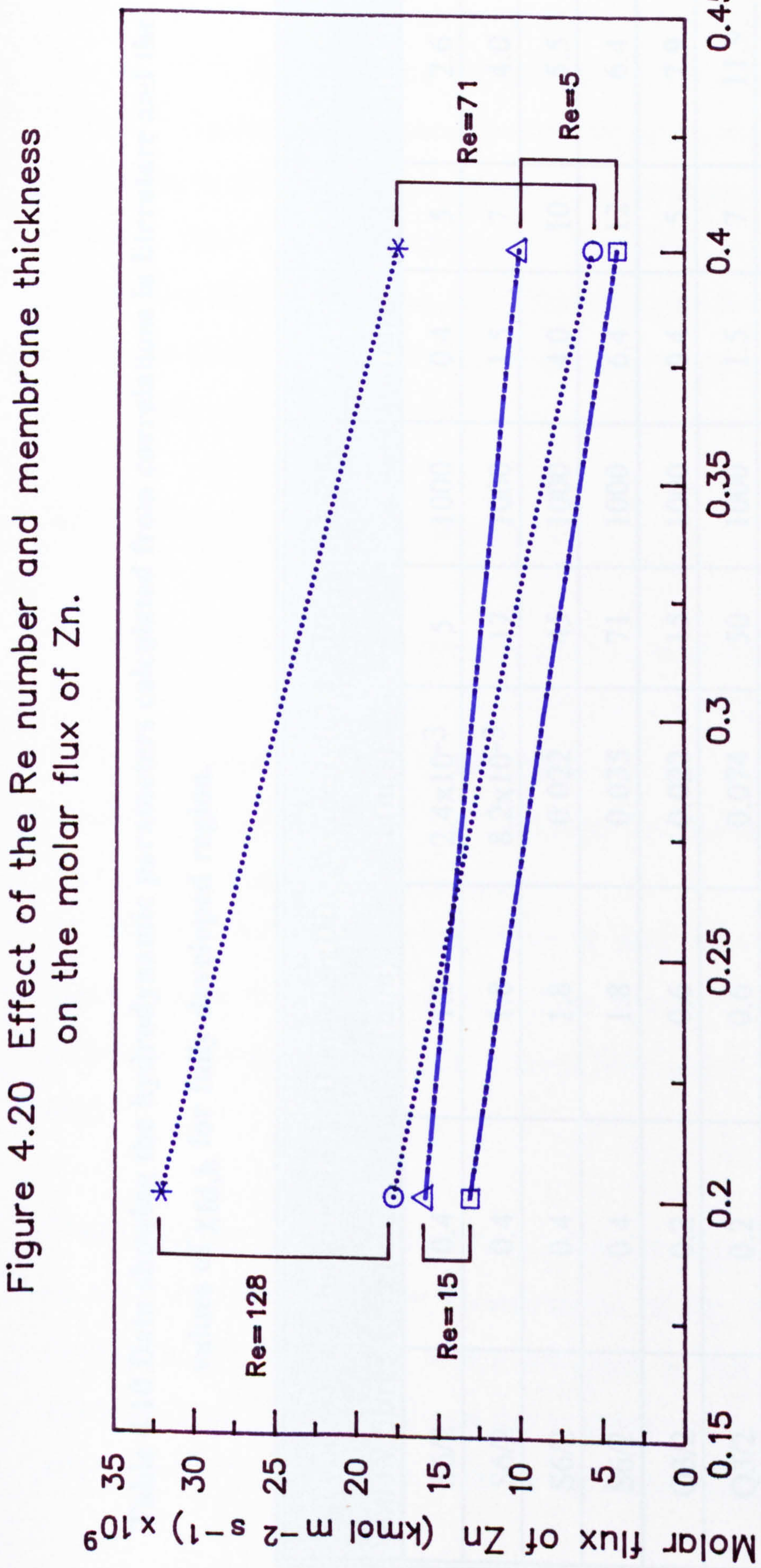


Figure 4.20 Effect of the Re number and membrane thickness on the molar flux of Zn.

Table 4.10 Data showing the hydrodynamic parameters calculated from correlations in literature and the values of $\chi_{fd,h}$ for fully developed region.

Type of hollow fibre	Thickness(δ) (mm)	Diameter(Di) (mm)	Velocity(u) (m/s)	Re	Sc	$\chi_{fd,h}$ (m)	Sh	$K_{z\alpha}(x10^6)$ (m/s)
S6/2	0.4	1.8	$2.4x10^{-3}$	5	1000	0.4	5	2.6
S6/2	0.4	1.8	$8.2x10^{-3}$	17	1000	1.5	7	4.0
S6/2	0.4	1.8	0.022	45	1000	4.0	10	5.5
S6/2	0.4	1.8	0.035	71	1000	6.4	12	6.4
Q3/2	0.2	0.6	0.022	15	1000	0.4	5	7.9
Q3/2	0.2	0.6	0.074	50	1000	1.5	7	11.9
Q3/2	0.2	0.6	0.19	128	1000	3.8	10	16.3

aqueous phase, the Sc number in the feed becomes 1000. Using this value of Sc, the fibre diameters and the different Re numbers, (using a value of $8.9x10^{-4}$ kg/ms for the viscosity of the aqueous solution; Weast, 1988-89), the values of the entrance length were calculated using Figure 3.4. These are listed in Table 4.10. The shortest of these entry lengths is 0.4m, which is longer than the length of the fibre. Therefore the flow in the fibre does not reach the fully developed regime under any of the experimental conditions used in this work.

4.7.2 Mass transfer coefficients

As all the fibre is in the entrance region, the mass transfer coefficient in the aqueous phase, ($K_{z\alpha}$), was calculated using Leveque equation, (equation 3.12) and listed in Table 4.10. While for the membrane mass transfer coefficient (K_{zo}), equation (3.13) indicates that the value of K_{zo} in the small fibre is twice that of the thicker one.

As can be seen in the table, there is only one value of $K_{z\alpha}$ that is approximately the same for the two fibres: $6.4x10^{-6}$ and $7.9x10^{-6}$ m/s which correspond to Re=71 in the Di=1.8mm fibre and Re=15 in the Di=0.6mm fibre.

Comparing the fluxes for these Re numbers in Figures 4.18 and 4.19, it can be seen that for the lowest concentration of Zn, the flux approximately doubles in the small fibre, which thickness is half of that of the 1.8mm diameter fibre. This may indicate that at those conditions the rate controlling step is diffusion in the membrane. At the highest zinc concentration the flux

in both fibres is approximately the same, thus indicating that the diffusional resistances in the membrane do not affect the molar flux.

4.7.3 Diffusion coefficients in the organic phase

As no experimental values were found, The (Wilke - Chang, 1955) equation was used to predict the diffusion coefficients of the organic species:

$$\frac{\mathcal{D}_{AB}\mu_B}{T} = \frac{7.4x10^{-12}\left(\phi M_B\right)^{0.5}}{V_B^{0.6}} \qquad (4.1)$$

Where,

$\mathcal{D}_{AB}$ =the mutual diffusion coefficient of solute A at very low concentrations in solute B, cm^2/s

M_B =the molecular weight of solvent B, g/mol

T =the temperature, K

μ_B =viscosity of solvent B, cp

V_B =molar volume of solute A at its normal boiling temperature, cm^3/mol.

ϕ =association factor of solvent B, dimensionless.

Values of V_B, the molar volume of the solute at the boiling point, were estimated from the data of Le Bas as reported in (Reid et.al., 1987).

(Wilke and Chang, 1955), recommended that ϕ be chosen as 1.0 for an unassociated liquid.

Values for $\mathcal{D}(m^2/s)$ were calculated for DEHPA containing species in n-dodecane. These values are tabulated in Table 4.11.

Values for viscosities of water and n-dodecane were obtained from Weast, (1988-1989) and Perry, (1984).

viscosity, $\mu_{water} = 0.8904$ cp

$\mu_{dodecane} = 1.35$ cp

solvent association factor, ϕ (n-dodecane) = 1.0

Molecular weight, $M_{dodecane} = 170.34$

T = 298 K

The mass transfer coefficient of organic zinc complex (K_{zo}), was estimated using the film theory, which establishes that the mass transfer coefficient is directly proportional to the molecular diffusivities. Therefore the ratio of the mass transfer coefficients is given by the equation

$$\frac{K_{zo}}{K_o} = \frac{\mathcal{D}_{zo}}{\mathcal{D}_o} \qquad (4.2)$$

Where,

K_{zo} = mass transfer coefficient of organic zinc complex, (m/s)

K_o = mass transfer coefficient of DEHPA, (m/s)

$\mathcal{D}_{zo}$ = Diffusivity of zinc complex, (m^2/s)

$\mathcal{D}_o$ = Diffusivity of DEHPA dimer, (m^2/s)

Table 4.11 Diffusion coefficients for organic species predicted by the Wilke - Chang relationship.

species	V_B ($m^3.kmol^{-1}$)	$\mathcal{D}x10^9$ ($m^2.s^{-1}$)
HR	422.9	0.566
$(HR)_2$	845.8	0.374
ZnR_2	858.4	0.370
ZnR_2HR	1281.7	0.291
$ZnR_2(HR)_2$	1704.2	0.245

4.8 Effect of No of hollow fibres on molar flux of Zn

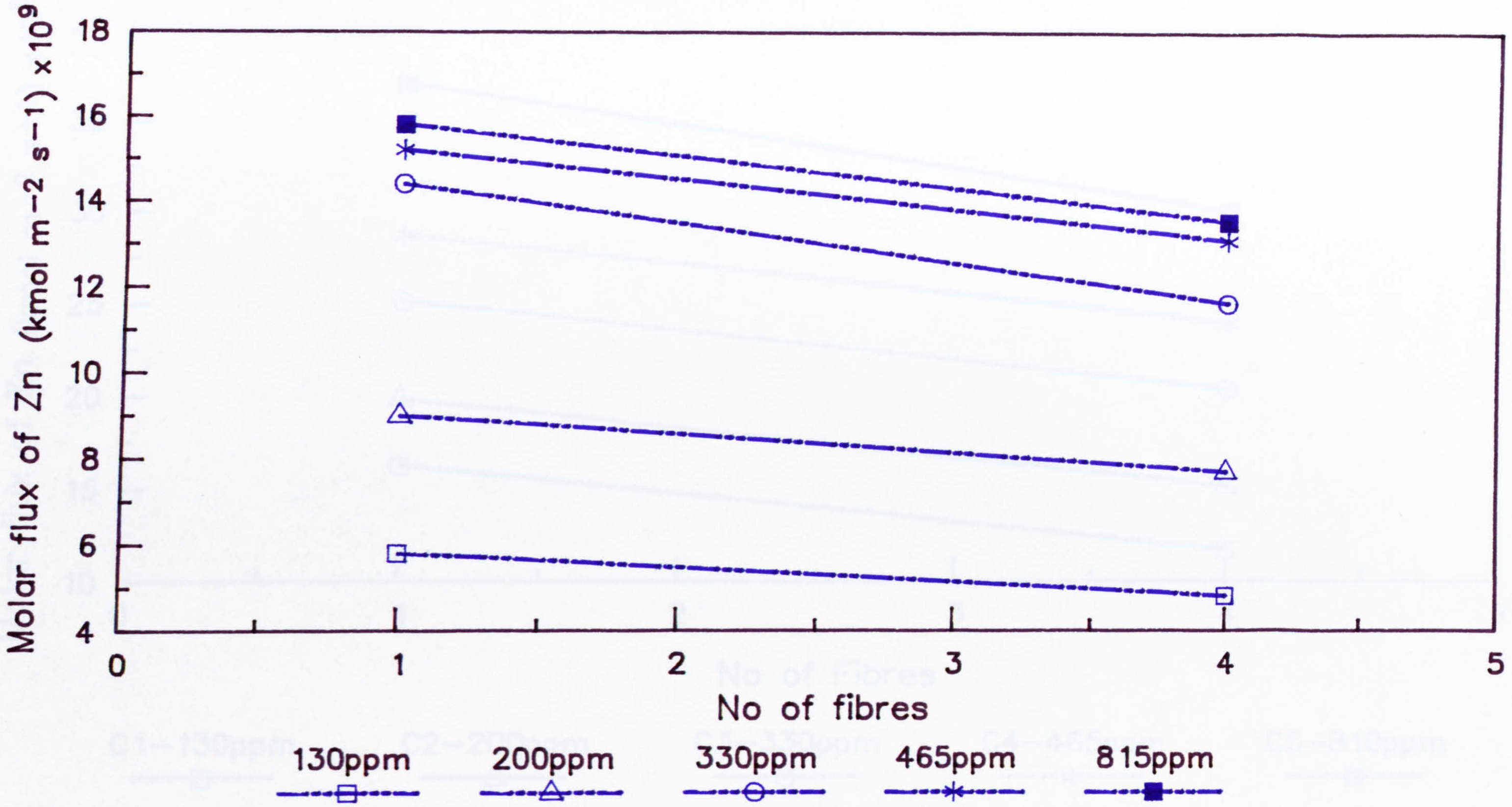
The effect of increasing the number of hollow fibres in the module was investigated in two bundles of four fibres of internal diameter 1.8mm and 0.6mm, Figures 4.21, 4.22 (Tables E42, E43, Appendix E) respectively. As it can be observed the flux in the two bundles is lower than in the corresponding single fibre module. This may be due to the change in the hydrodynamic conditions in the shell of the module, as the fibres are quite close and the higher concentration of metal ion in the strip phase. In this case the chemical and possibly also the diffusional resistances in the stripping phase are not negligible.

Figure 4.23 shows the effect of Zn concentration on the Zn flux in both bundles using 0.2M DEHPA. These results correspond to those shown in Figures 4.7 and 4.9 for the single fibre modules. The trend of the results is similar for the single fibre and the bundle, with smaller fluxes in the larger fibre and a plateau reached at a concentration of about 400 ppm in the fibre of Di=1.8 mm. This indicates that whatever the effect of the resistances in the stripping phase on the overall flux, the relative importance of the membrane and the feed resistances seem to remain unchanged.

4.9 Effect of pH on the separation of Zn and Cu

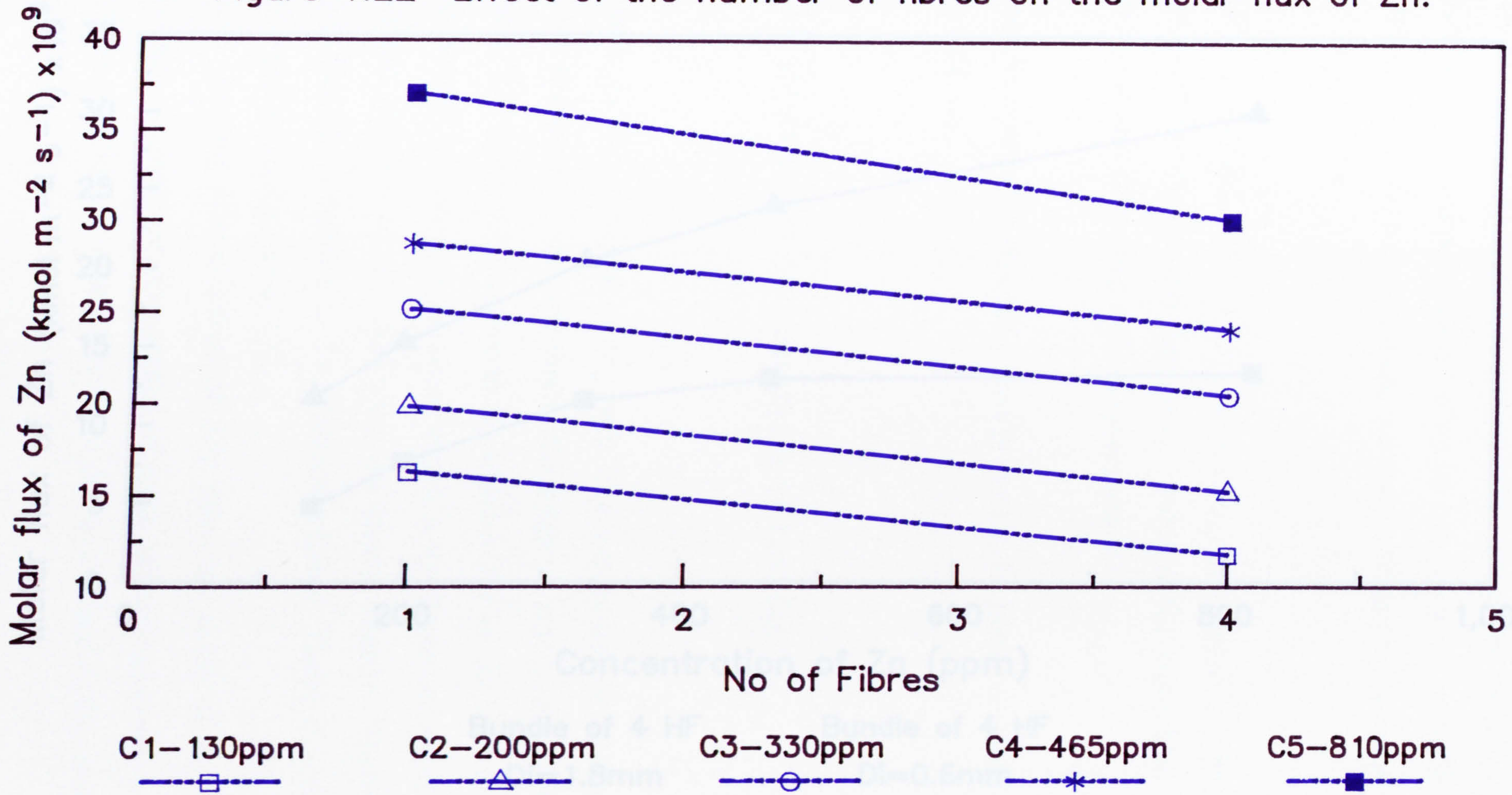
Experiments were carried out using Zn and Cu solutions at different concentration ratios keeping the Zn concentration constant. Results are shown in Figure 4.24, Figure 4.25 and Tables E45 and E46 in Appendix E.

Figure 4.21 Effect of the number of fibres on the molar flux of Zn.



Feed flow rate of a single fibre=1.25ml/min
Feed flow rate of the bundle=5.0ml/min
Di=1.8mm 0.2M DEHPA

Figure 4.22 Effect of the number of fibres on the molar flux of Zn.



Feed flow rate of a single fibre=1.25ml/min
Feed flow rate of the bundle=5.0ml/min
Di=0.6mm 0.2M DEHPA

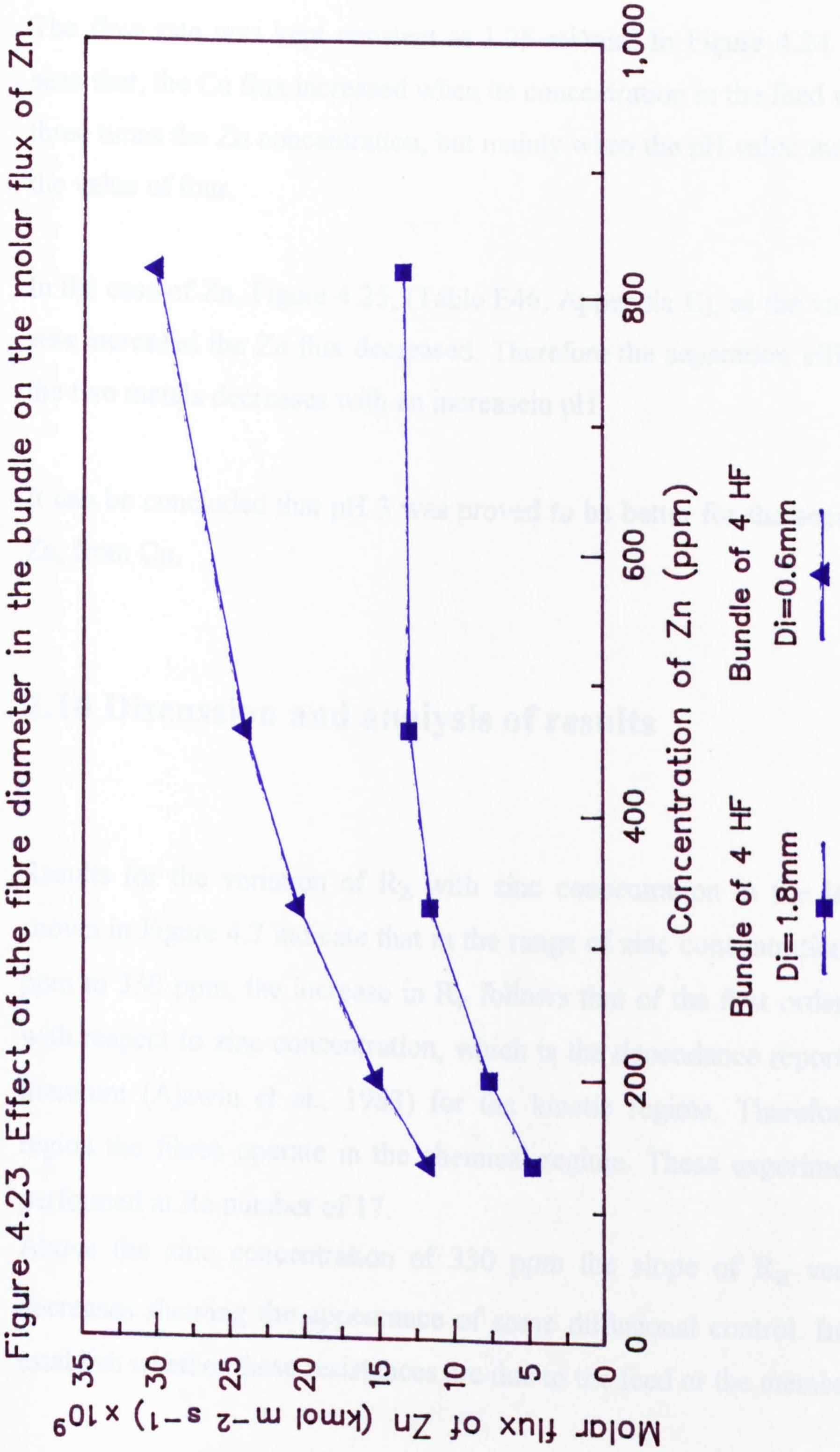


Figure 4.23 Effect of the fibre diameter in the bundle on the molar flux of Zn.

The flow rate was kept constant at 1.25 ml/min. In Figure 4.24 it can be seen that, the Cu flux increased when its concentration in the feed was about three times the Zn concentration, but mainly when the pH value increased to the value of four.

In the case of Zn, Figure 4.25, (Table E46, Appendix E), as the value of pH was increased the Zn flux decreased. Therefore the separation efficiency of the two metals decreases with an increasein pH.

It can be concluded that pH 3 was proved to be better for the separation of Zn, from Cu.

4.10 Discussion and analysis of results

Results for the variation of R_Z with zinc concentration in the large fibre shown in Figure 4.7 indicate that in the range of zinc concentration from 68 ppm to 330 ppm, the increase in R_Z follows that of the first order reaction with respect to zinc concentration, which is the dependance reported in the literature (Ajawin et al., 1983) for the kinetic regime. Therefore in this region the fibres operate in the chemical regime. These experiments were performed at Re number of 17.

Above the zinc concentration of 330 ppm the slope of R_Z versus $C_{Z\alpha}$ decreases showing the appearance of some diffusional control. In order to establish whether these resistances are due to the feed or the membrane, the

Figure 4.24 Effect of pH on the molar flux of Cu from a mixture with Zn.

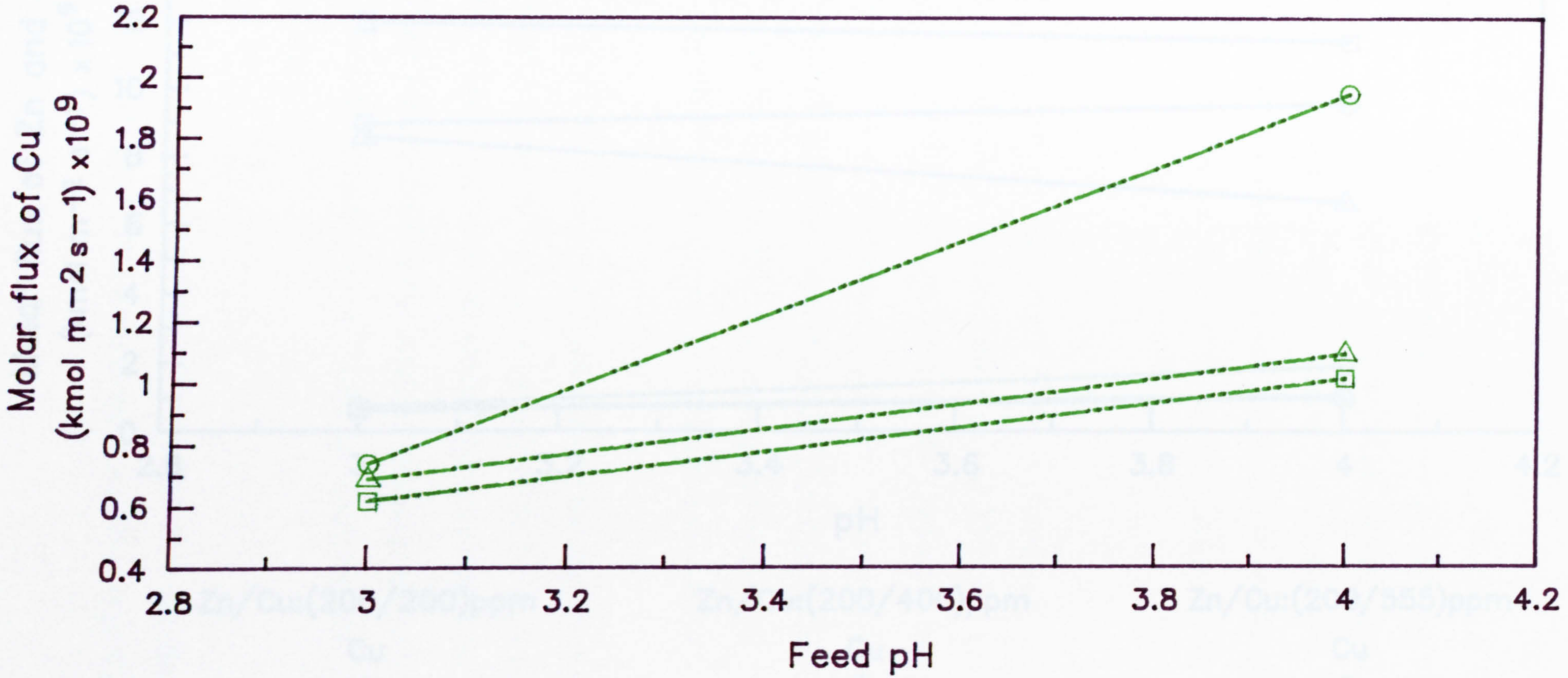
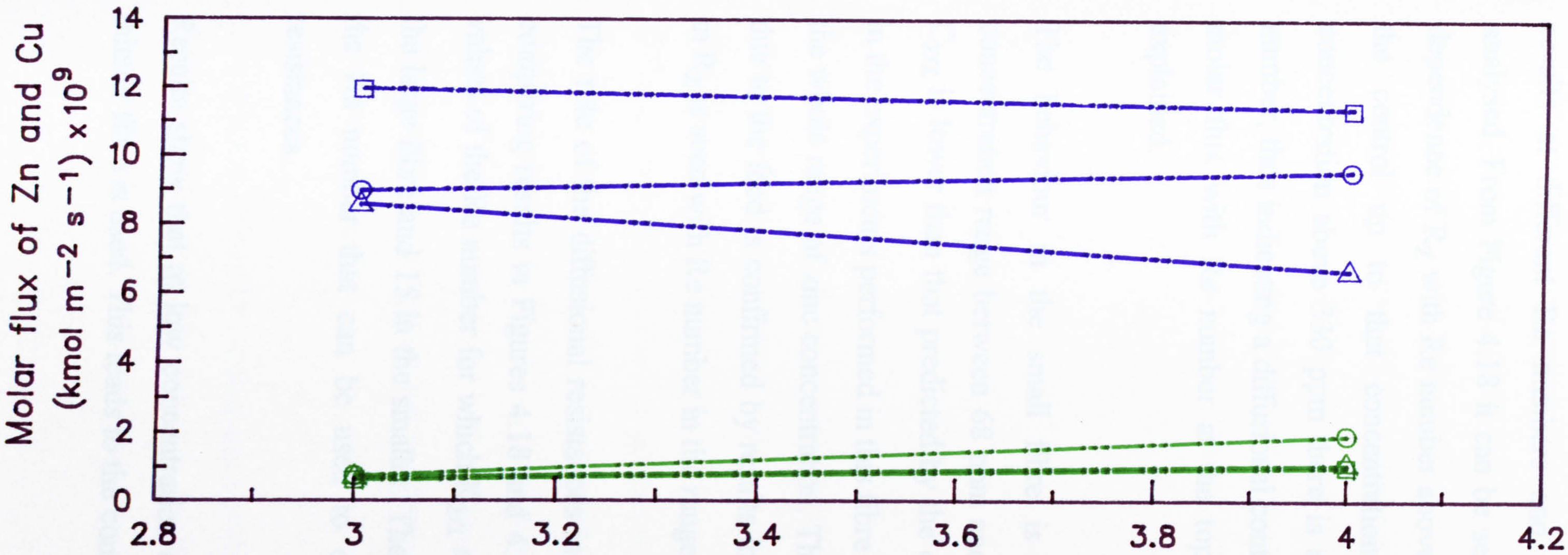


Figure 4.25 Effect of pH on the molar flux of Zn and Cu from a mixed feed.



results at different Re numbers and membrane thickness have to be analysed. From Figure 4.18 it can be seen that up to 330 ppm there is no dependence of R_Z with Re number above Re=17; this seems to confirm that the control up to that concentration is chemical; however at zinc concentration above 330 ppm there is an increase in molar flux with Re number, thus indicating a diffusional control in the feed. The decrease of the molar flux with Re number at the top range of Re number cannot be explained.

The behaviour in the small fibre is somehow different. In the zinc concentration range between 68 ppm and 330 ppm the increase in R_Z with $C_{Z\alpha}$ is lower than that predicted by the chemical kinetic control. Therefore in the experiments performed in this fibre there is some diffusional control in the whole range of zinc concentration. That part of this diffusional control is due to the feed is confirmed by results in Figure 4.19, in which an increase in R_Z is seen with Re number in the range between 15 and 50.

The role of the diffusional resistances in the membrane can be inferred by comparing results in Figures 4.18 and 4.19. As seen in Table 4.10the only values of the Re number for which $K_{Z\alpha}$ are close in both fibres is Re=71 in the large fibre and 15 in the smaller. Therefore these are the only values of the Re number that can be used to compare the effect of membrane resistances.

Results show that at low concentration of zinc the flux doubles when the thinner fibre is used. This leads to the conclusion that there is a predominant

membrane diffusional control. This is confirmed by Figure 4.16 in which R_Z is seen to increase with DEHPA concentration but at substantially less than the first order reaction predicts. However, at zinc concentrations higher than 330 ppm the thickness of the membrane does not seem to affect the flux. This may be due to the fact that in the smaller fibre the diffusional resistances in the feed may be predominant, as shown in Figure 4.19, in which it can be seen a steep change in R_Z with Re number in the region of Re=15.

4.11 Conclusions

From the analysis of the experimental results it can be concluded that the rate controlling mechanisms change with metal and DEHPA concentrations, fibre thickness and Re numbers.

Consequently, it is not easy to predict which are the controlling mechanisms by simple guide lines. A mathematical modelling of the kinetics of transfer that includes the different rate mechanisms may provide the information required for the scale-up of the process. A comparison between the mathematical model presented in Chapter 3 and the experimental results are reported in Chapter 5.

Comparison of bundle performance with that of single fibres shows that the flux decreases with the increase in the number of fibres. This can be attributed to a build up of resistances, chemical and diffusional, in the

stripping phase. However the dependence of flux on metal feed concentration is similar in both types of modules.

Regarding the separation of Zn and Cu from mixed feeds, it has been observed that there is interaction between the two metals which results in an overall decrease in the flux with respect to Zn flux obtained with a single feed. As the pH is increased the flux of Cu from mixed feeds increases while that of Zn decreases giving then a poorer separation ratio.

CHAPTER 5

COMPARISON OF EXPERIMENTAL AND PREDICTED RESULTS

In this chapter the interfacial fluxes of zinc are calculated using the model presented in Chapter 3 and they are compared with the experimental results.

Equation (3.9) was used in order to calculate the Zn flux. The mass transfer coefficients used in the simulation were calculated using equations 3.10, 3.12 and 4.2. Predicted values of α_{zo} at different $C_{z\alpha}$ values were used

together with the hydrodynamic and mass transfer parameters which have already been obtained for both types of fibres S6/2 and Q3/2. The values of the chemical reaction rate constants $k_{I\alpha}$ and $k'_{I\alpha}$ used were 3.95×10^{-6} and 2.96×10^{-5} m/s respectively, (Saeed, 1989), at Ionic strength, I=1.0 kmol/m^3 and 25°C. The values of mass transfer coefficients for the two fibres are listed in Tables G1 - G13, (Appendix G), as well as the values of α_o and α_{zo}. The predicted interfacial zinc flux, was calculated with equation (3.9) using the effective area of the fibre which is 0.75 of the total area according to MICRODYN technical data.

The concentration $C_{z\alpha}$ was taken as equal to that of the feed and assumed to remain constant along the fibre length since fully developed conditions are not reached in the fibre.

5.1 Experimental and predicted results using the S6/2 fibre.

Figure 5.1 (Table G1, Appendix G) shows the predicted and experimental values of the zinc flux at a concentration of DEHPA of 0.05M, which is the lowest one used. As it can be observed the experimental values reach a plateau above $C_{z\alpha}$=200 ppm and that plateau continues up to about 800 ppm. The predicted data seem to be in good agreement with the experimental ones at concentrations up to about 200 ppm, while above that value there is no indication of a plateau region in the predicted results, although the slope of the curve decreases with increasing concentration.

In Figures 5.2-5.4 (Tables G2 - G4, Appendix G), where the concentration of DEHPA are 0.1M, 0.15M, 0.2M respectively, it can be seen that there is good agreement between the experimental and predicted fluxes of zinc.

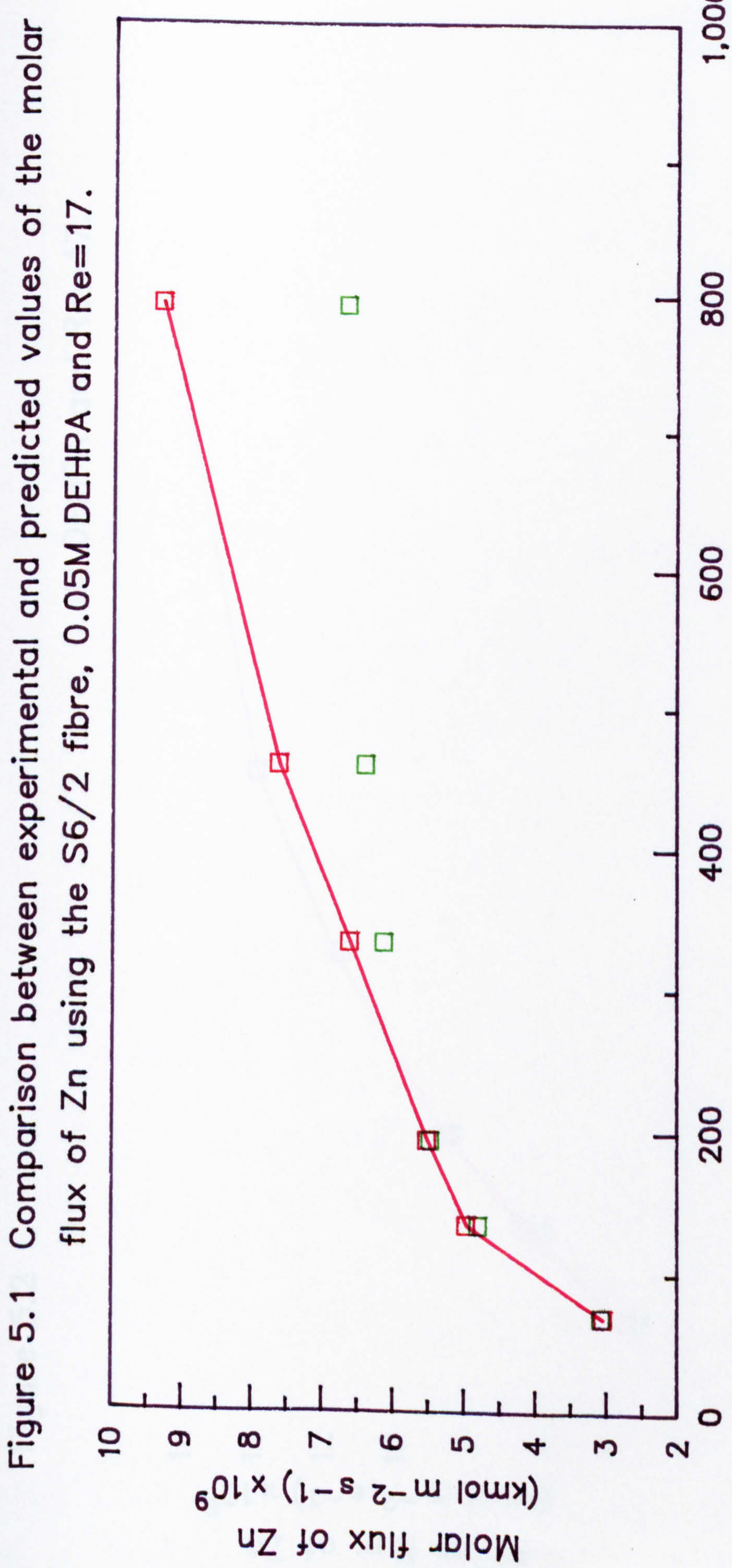


Figure 5.1 Comparison between experimental and predicted values of the molar flux of Zn using the S6/2 fibre, 0.05M DEHPA and Re=17.

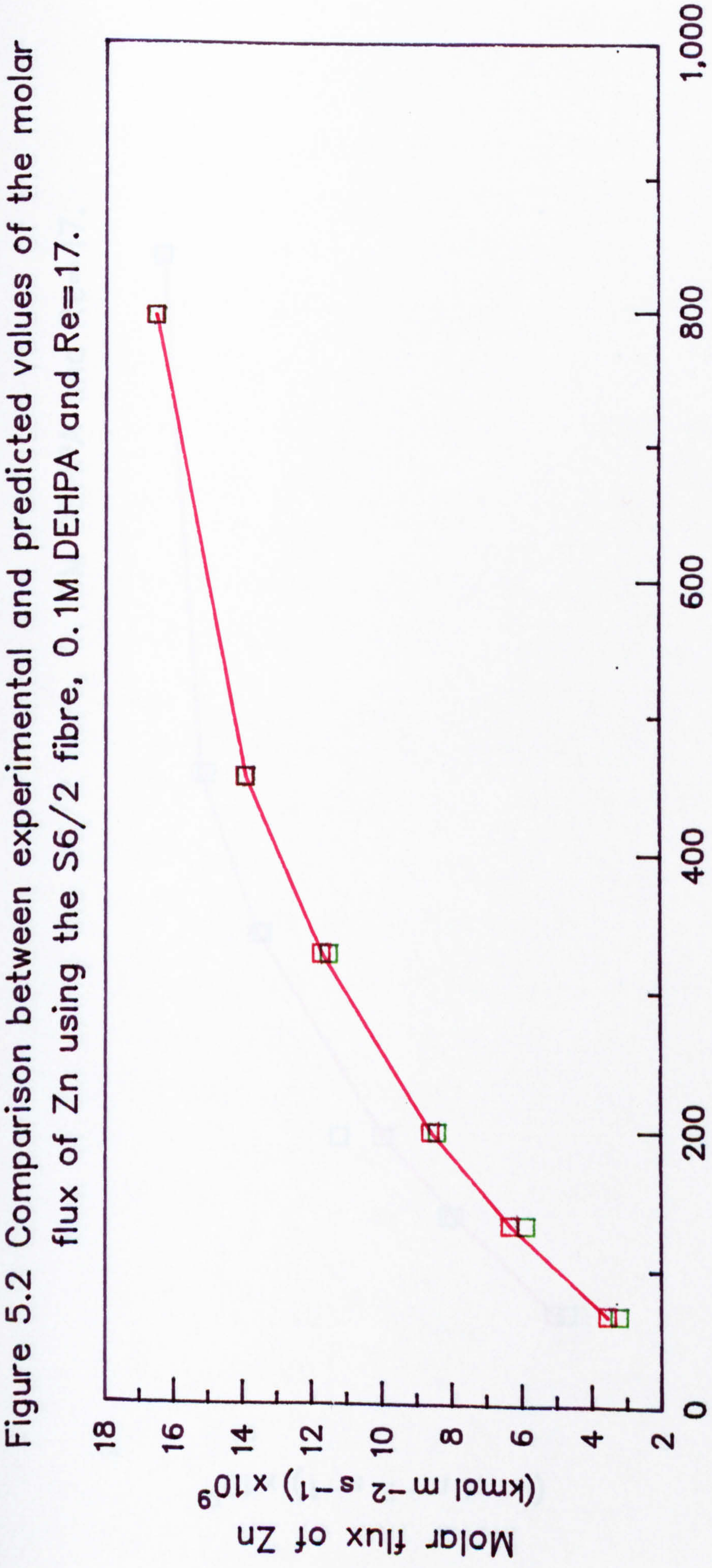


Figure 5.2 Comparison between experimental and predicted values of flux of Zn using the S6/2 fibre, 0.1M DEHPA and Re=17.

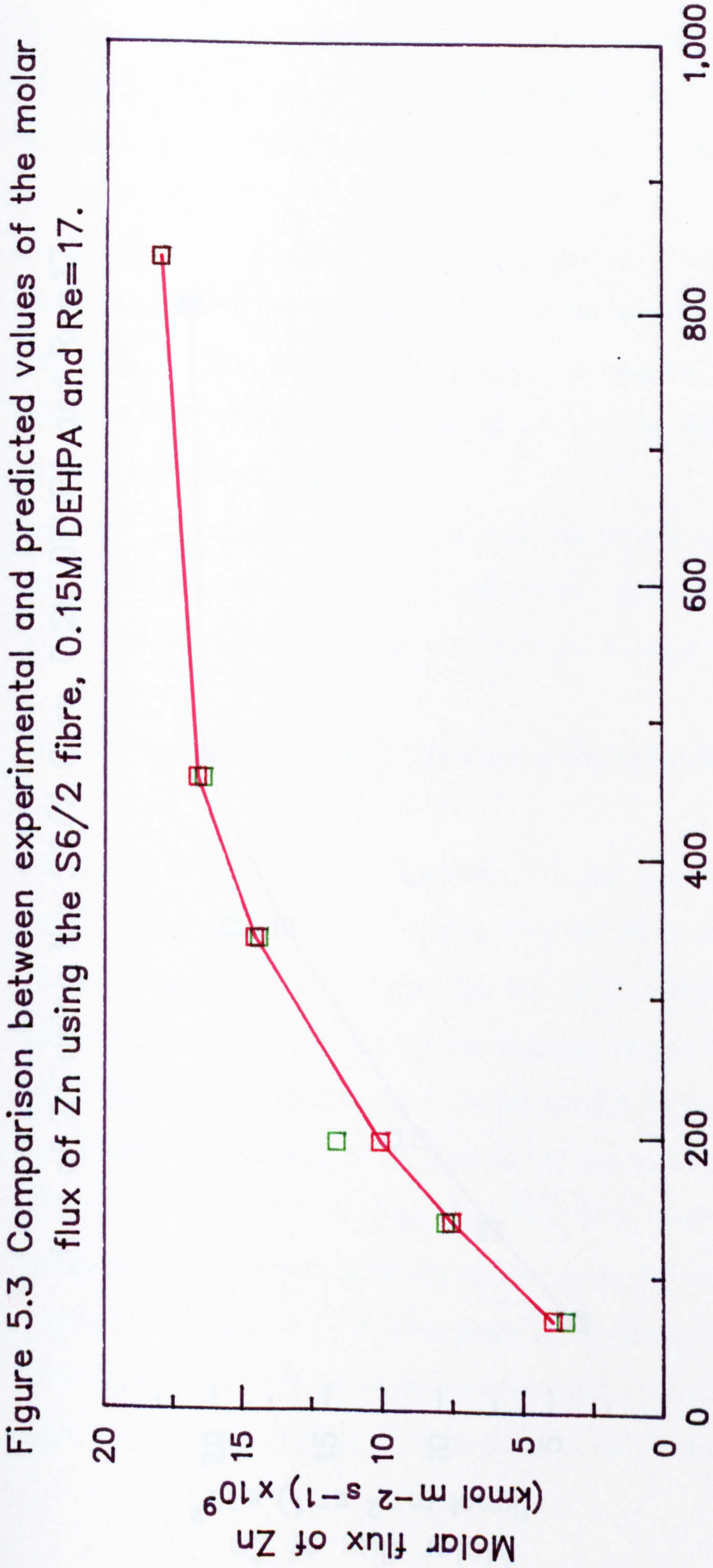
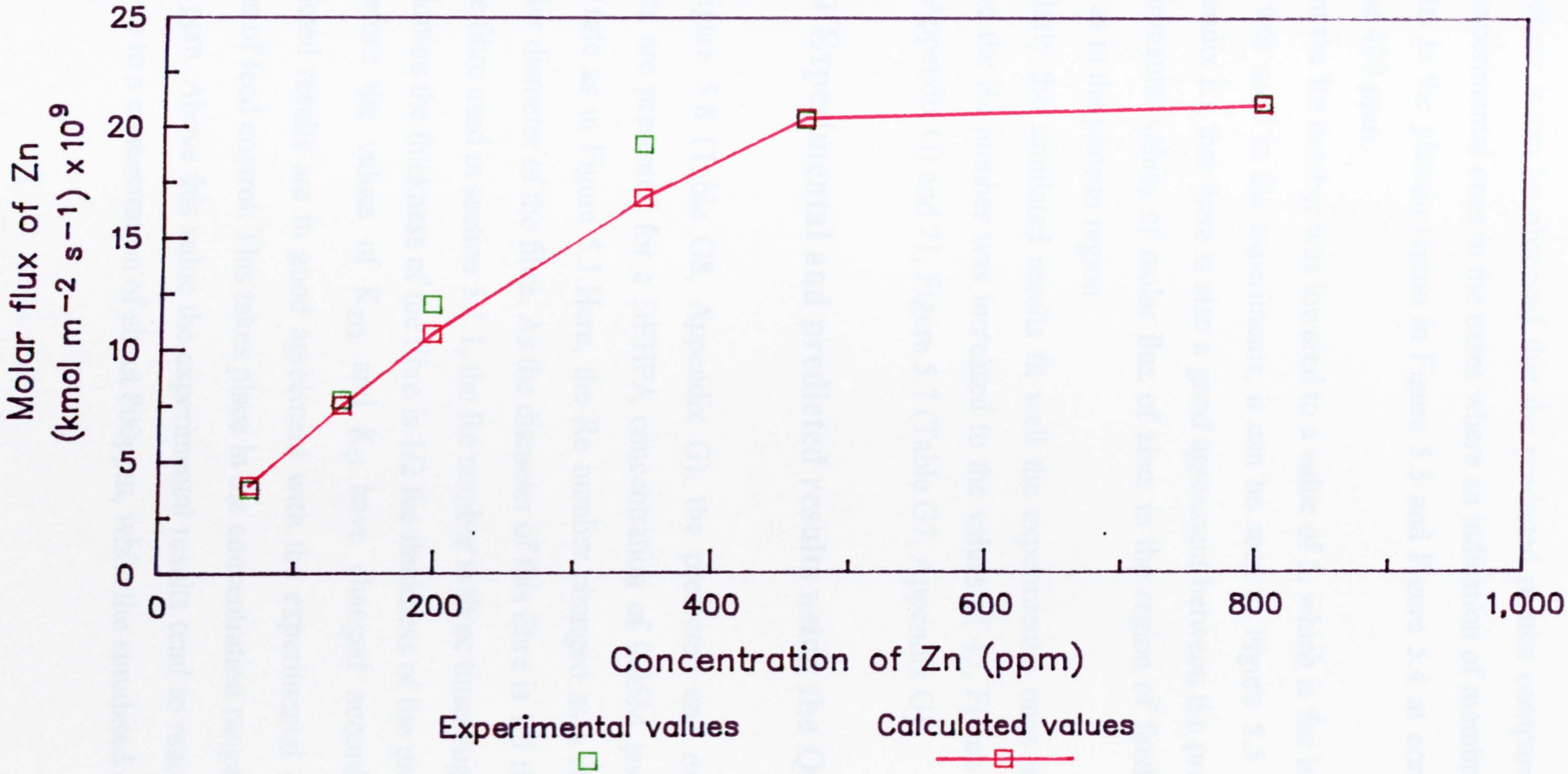


Figure 5.3 Comparison between experimental and predicted values of the molar flux of Zn using the S6/2 fibre, 0.15M DEHPA and Re=17.

Figure 5.4 Comparison between experimental and predicted values of the molar flux of Zn using the S6/2 fibre, 0.2M DEHPA and Re=17.



Moreover it can be observed that the predicted results compare well with the experimental ones in the cases where an indication of membrane control results in the plateau region in Figure 5.3 and Figure 5.4 at concentrations above 400 ppm.

When the Re number was lowered to a value of 5, which is the lowest value that was used in the experiments, it can be seen in Figure 5.5 (Table G5, Appendix E), that there is also a good agreement between the predicted and experimental values of molar flux of zinc, in the region of feed control as well as in the plateau region.

Similarly the simulated results fit well the experimental ones in the cases where the Re number was increased to the values of 45, Figure 5.6 (Table G6, Appendix G) and 71, Figure 5.7 (Table G7, Appendix G).

5.1.1 Experimental and predicted results using the Q3/2 fibre.

In Figure 5.8 (Table G8, Appendix G), the predicted and experimental results are presented for a DEHPA concentration of 0.05M and the same flow rate as in Figure 5.1.Here, the Re number changed as a result of the smaller diameter of the fibre. As the diameter of this fibre is 1/3 the diameter of the fibre used in section 5.1.1, the Re number is three times higher, 50.

In addition the thickness of the fibre is 1/2 the thickness of the previous one. Therefore the values of $K_{z\alpha}$ and K_o have changed accordingly. The predicted results are in good agreement with the experimental ones in the region of feed control. This takes place in the concentration range from (67 - 200) ppm. Above this value the experimental results tend to reach a plateau right up to a concentration of about 800ppm, while the simulated data do

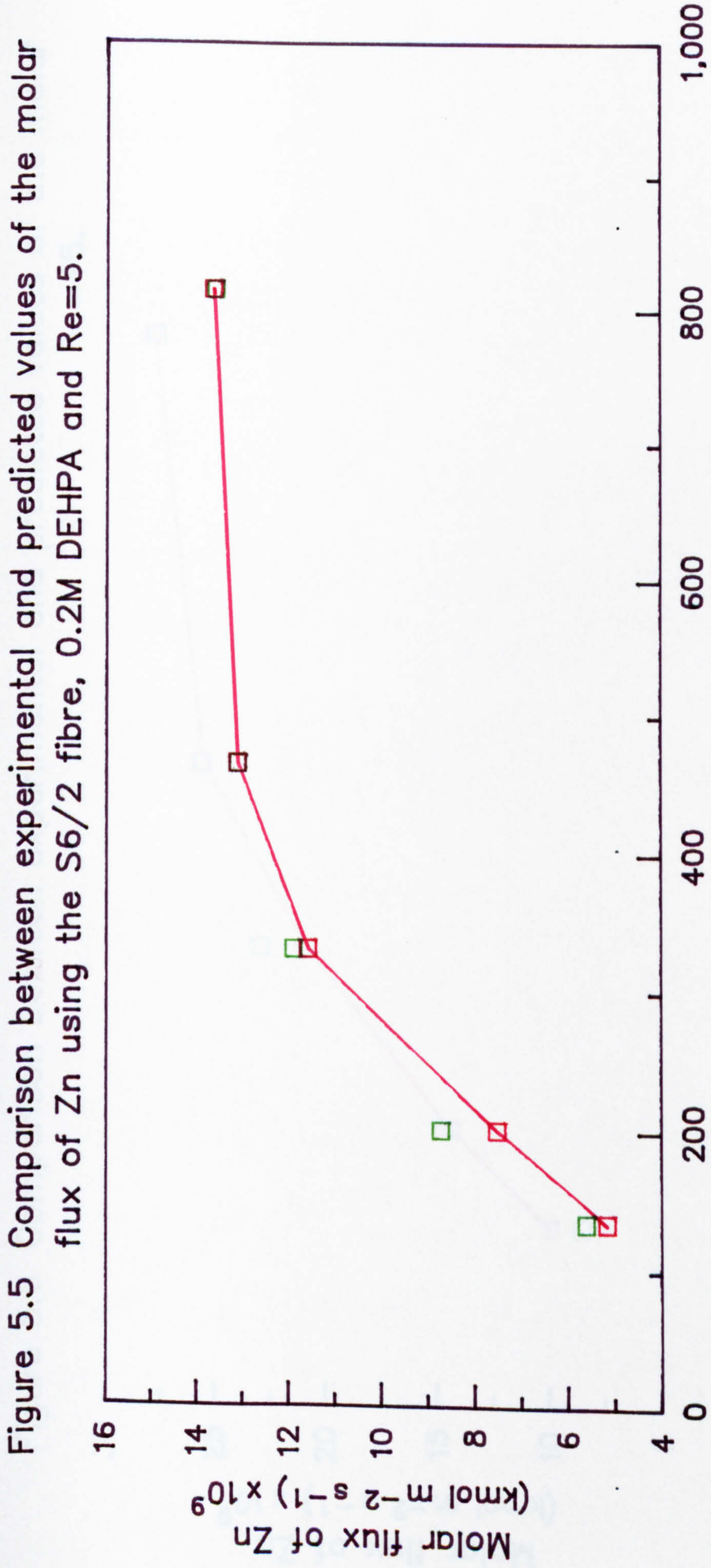


Figure 5.5 Comparison between experimental and predicted values of molar flux of Zn using the S6/2 fibre, 0.2M DEHPA and Re=5.

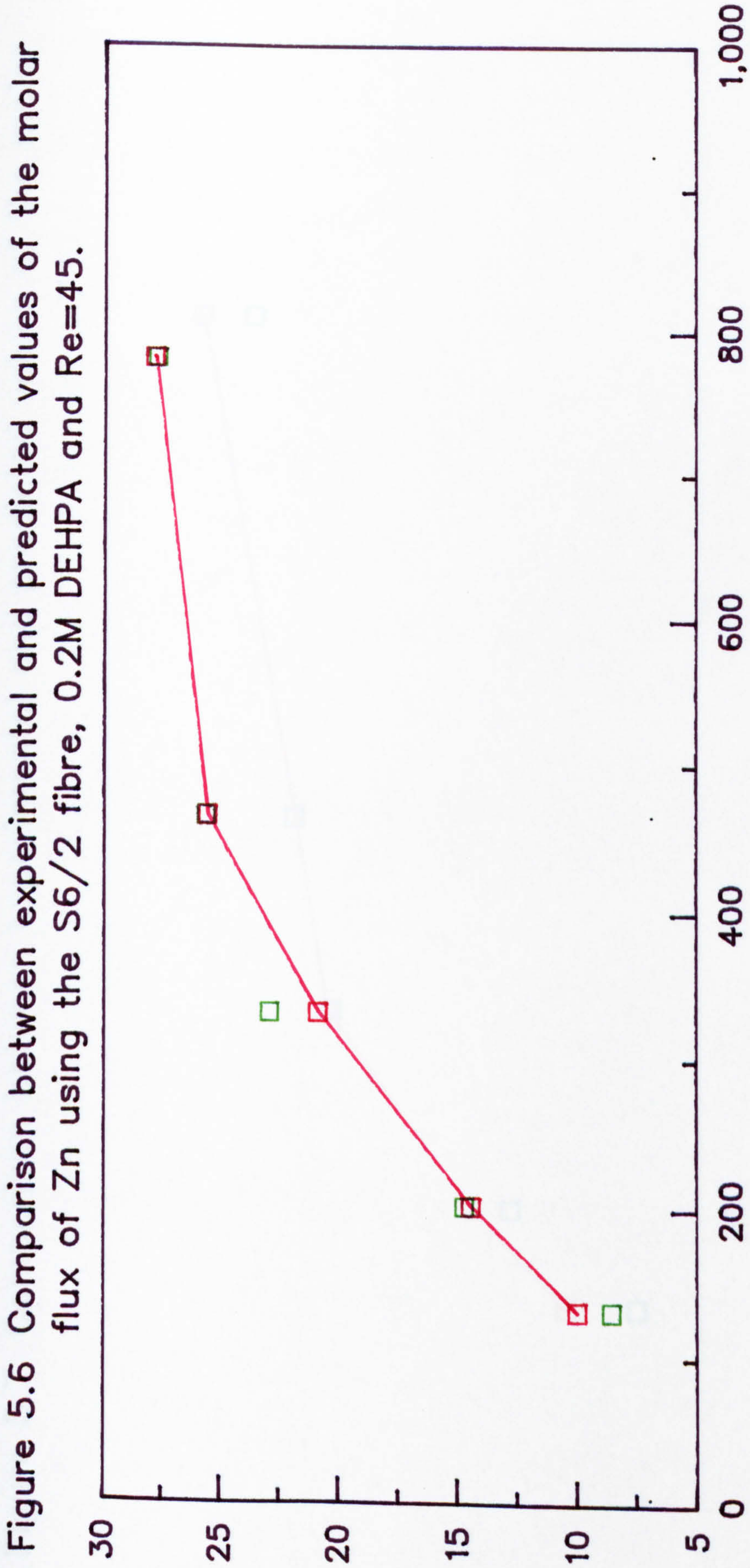


Figure 5.6 Comparison between experimental and predicted values of the flux of Zn using the S6/2 fibre, 0.2M DEHPA and Re=45.

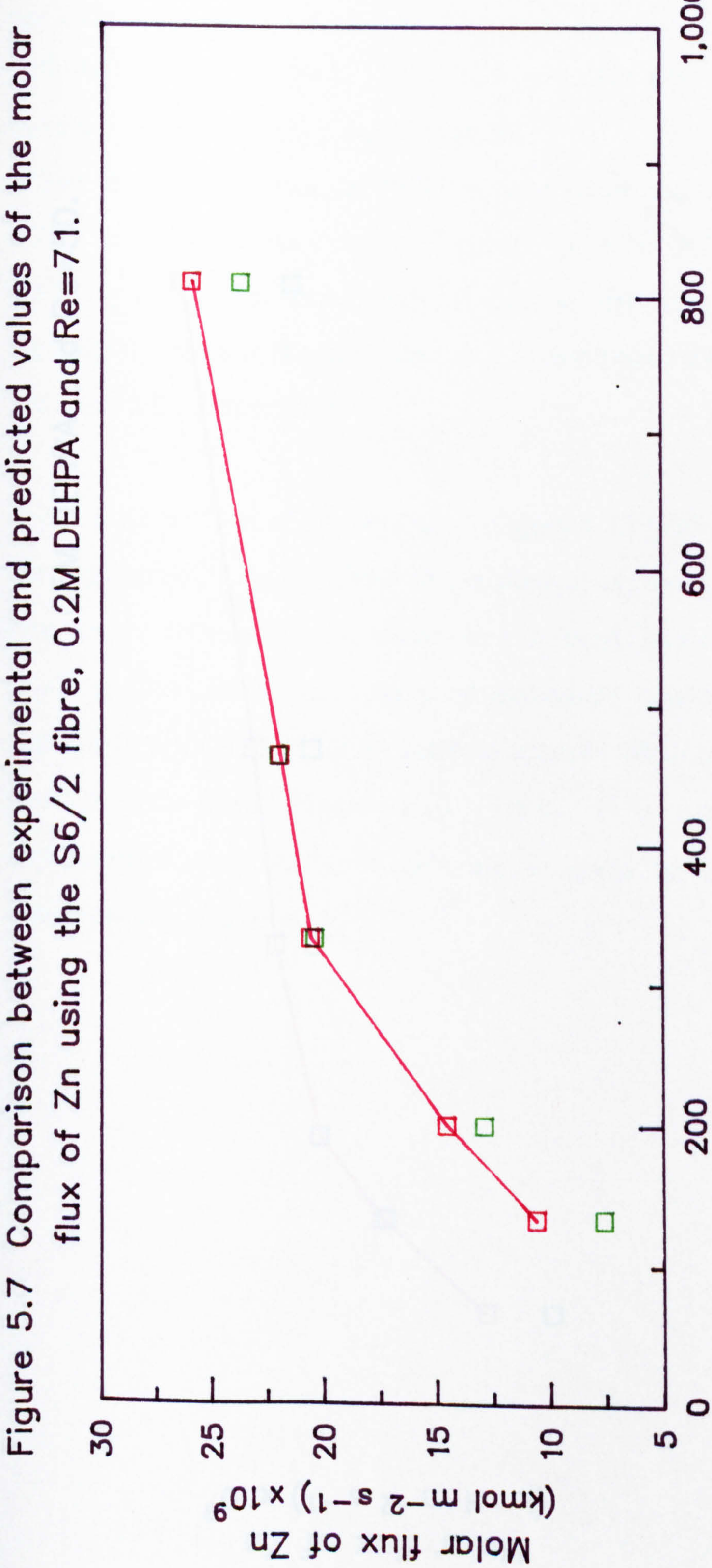


Figure 5.7 Comparison between experimental and predicted values of the molar flux of Zn using the S6/2 fibre, 0.2M DEHPA and Re=71.

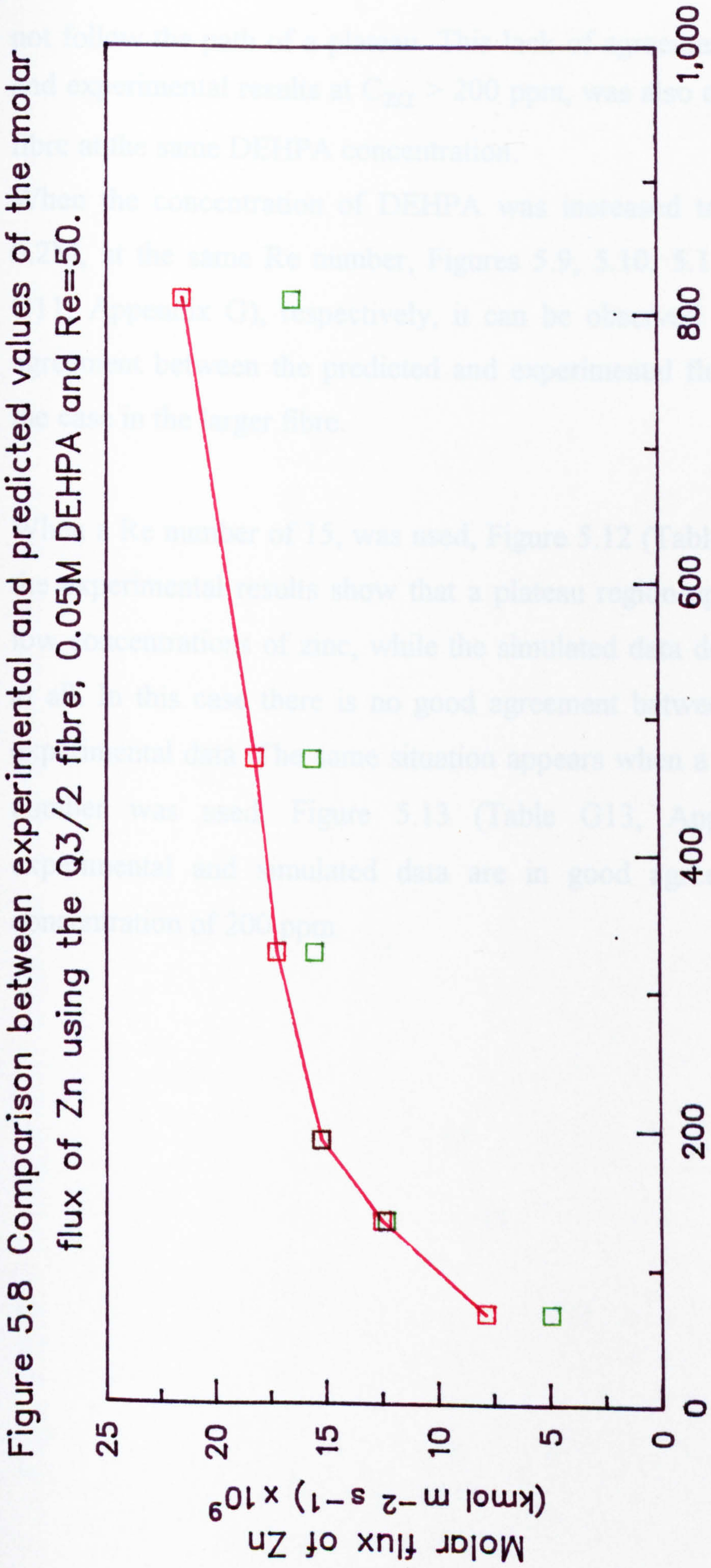


Figure 5.8 Comparison between experimental and predicted values of the molar flux of Zn using the Q3/2 fibre, 0.05M DEHPA and Re=50.

not follow the path of a plateau. This lack of agreement between predicted and experimental results at $C_{z\alpha} > 200$ ppm, was also observed in the larger fibre at the same DEHPA concentration.

When the concentration of DEHPA was increased to 0.1M, 0.15M, and 0.2M, at the same Re number, Figures 5.9, 5.10, 5.11, (Tables G9, G10, G11, Appendix G), respectively, it can be observed that there is a good agreement between the predicted and experimental fluxes. This again was the case in the larger fibre.

When a Re number of 15, was used, Figure 5.12 (Table G12, Appendix G), the experimental results show that a plateau region appears right from the low concentrations of zinc, while the simulated data do not show a plateau at all. In this case there is no good agreement between the simulated and experimental data. The same situation appears when a high value of the Re number was used, Figure 5.13 (Table G13, Appendix G), but the experimental and simulated data are in good agreement up to a feed concentration of 200 ppm.

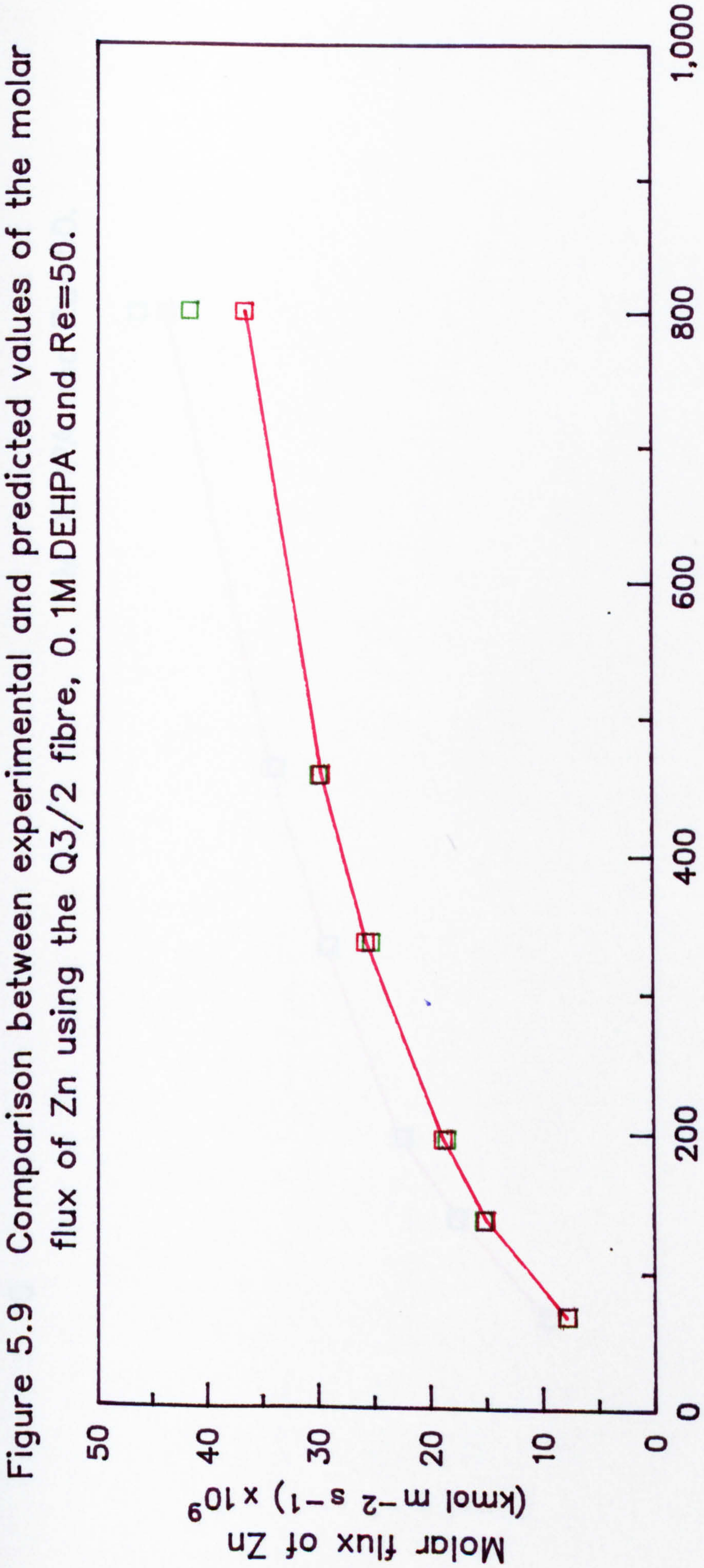


Figure 5.9 Comparison between experimental and predicted values of the molar flux of Zn using the Q3/2 fibre, 0.1M DEHPA and Re=50.

Figure 5.10 Comparison between experimental and predicted values of the molar flux of Zn using the Q3/2 fibre, 0.15M DEHPA and Re=50.

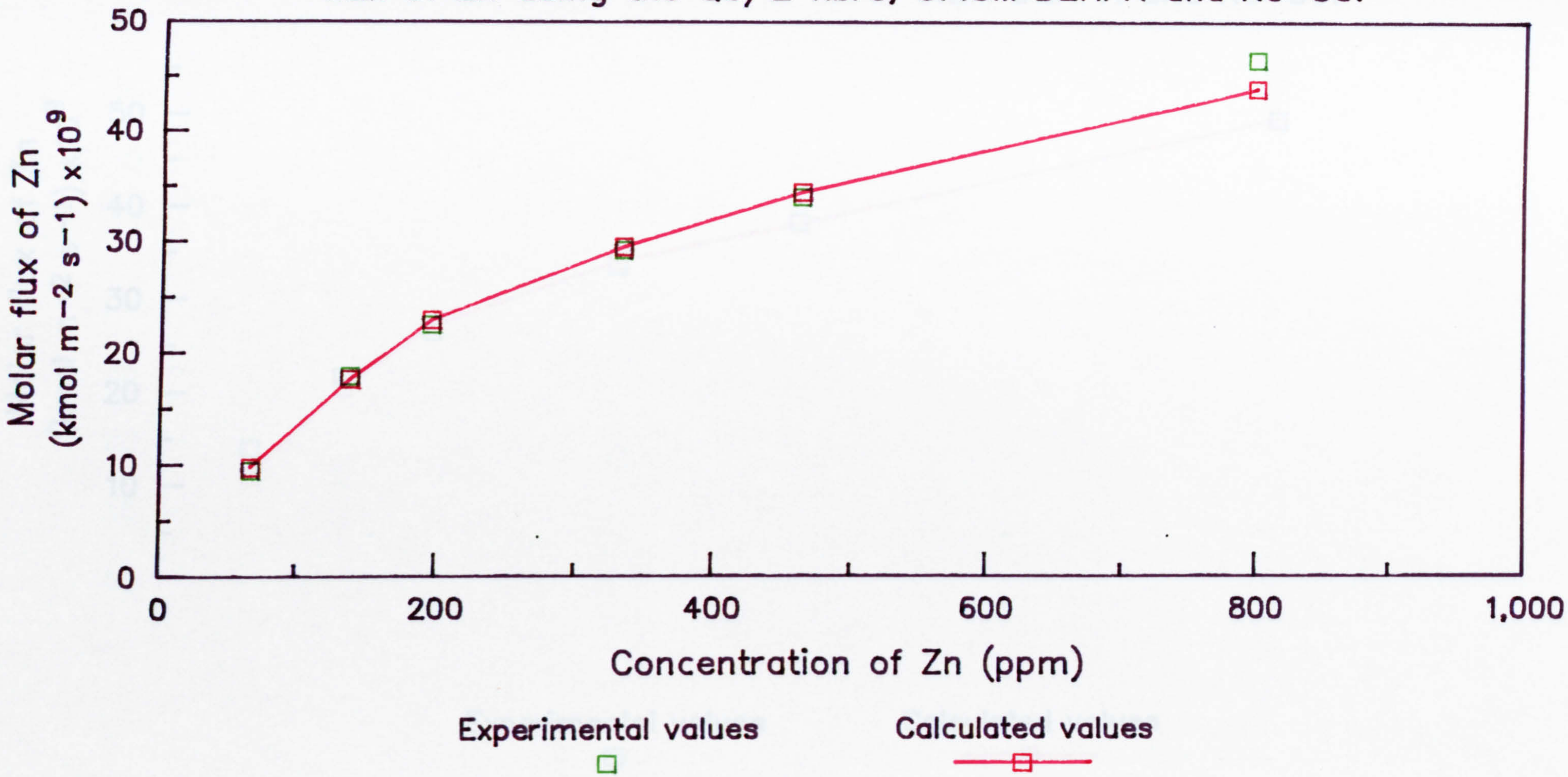
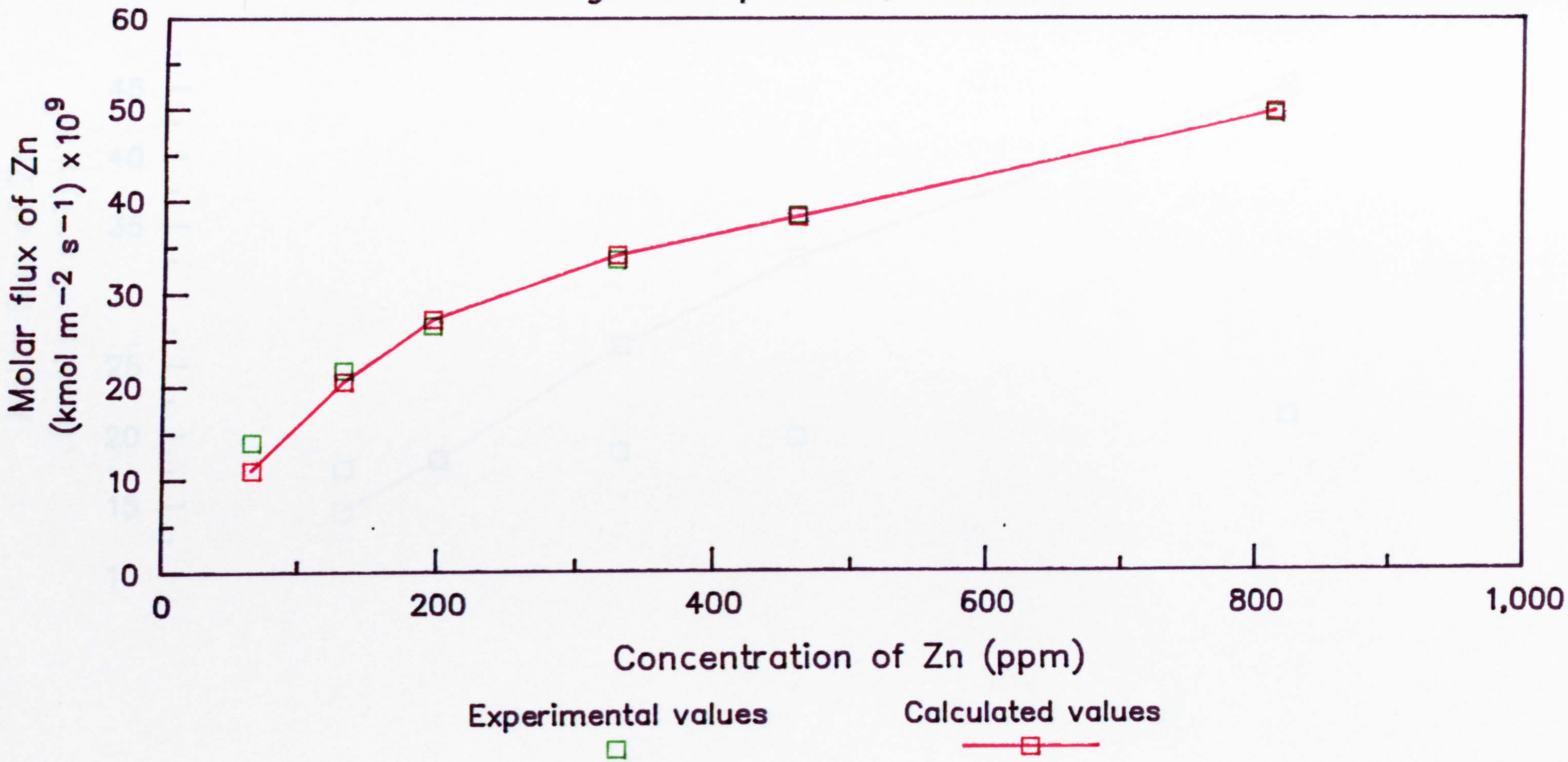


Figure 5.11 Comparison between experimental and predicted values of the molar flux of Zn using the Q3/2 fibre, 0.2M DEHPA and Re=50.



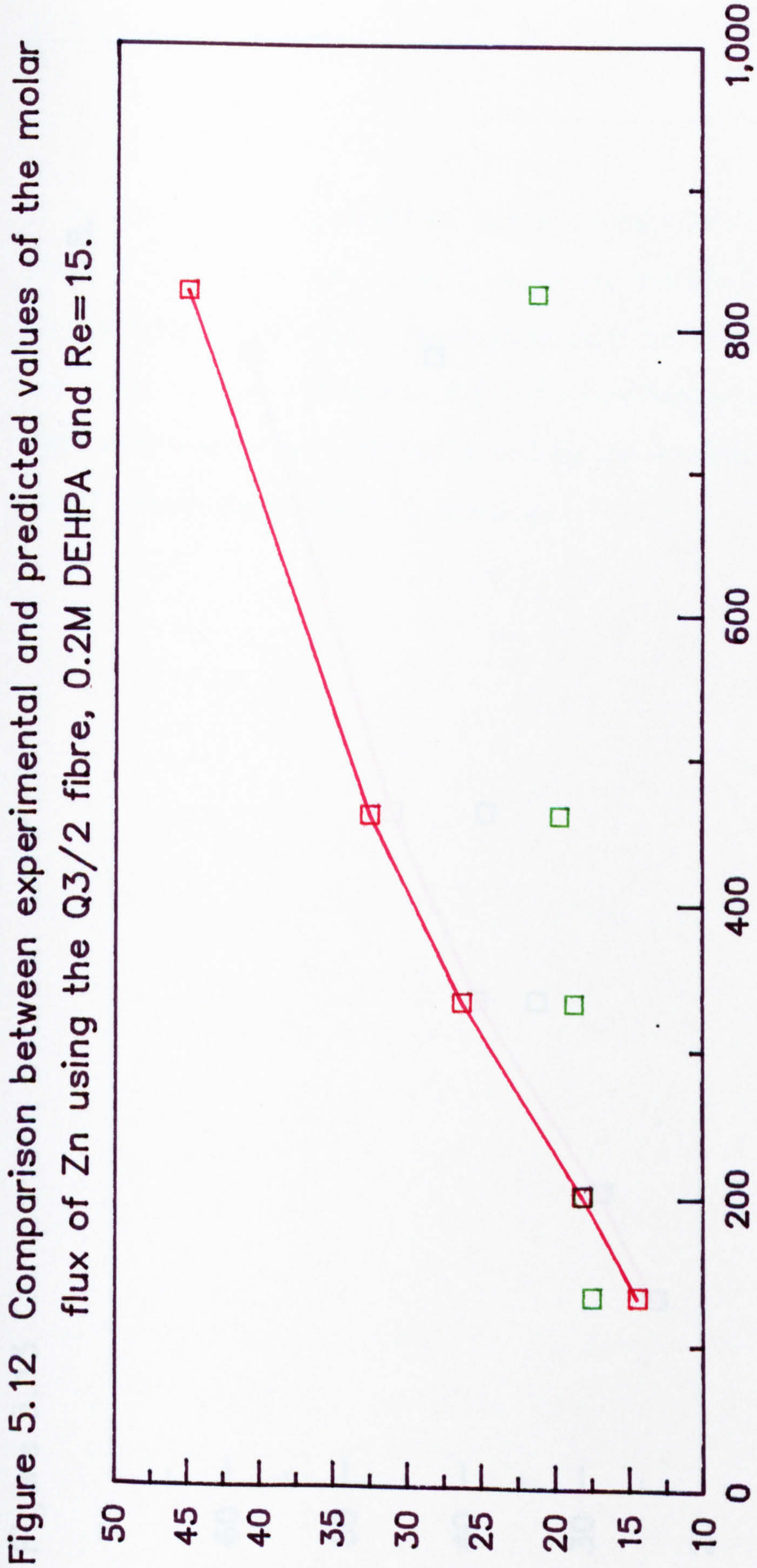
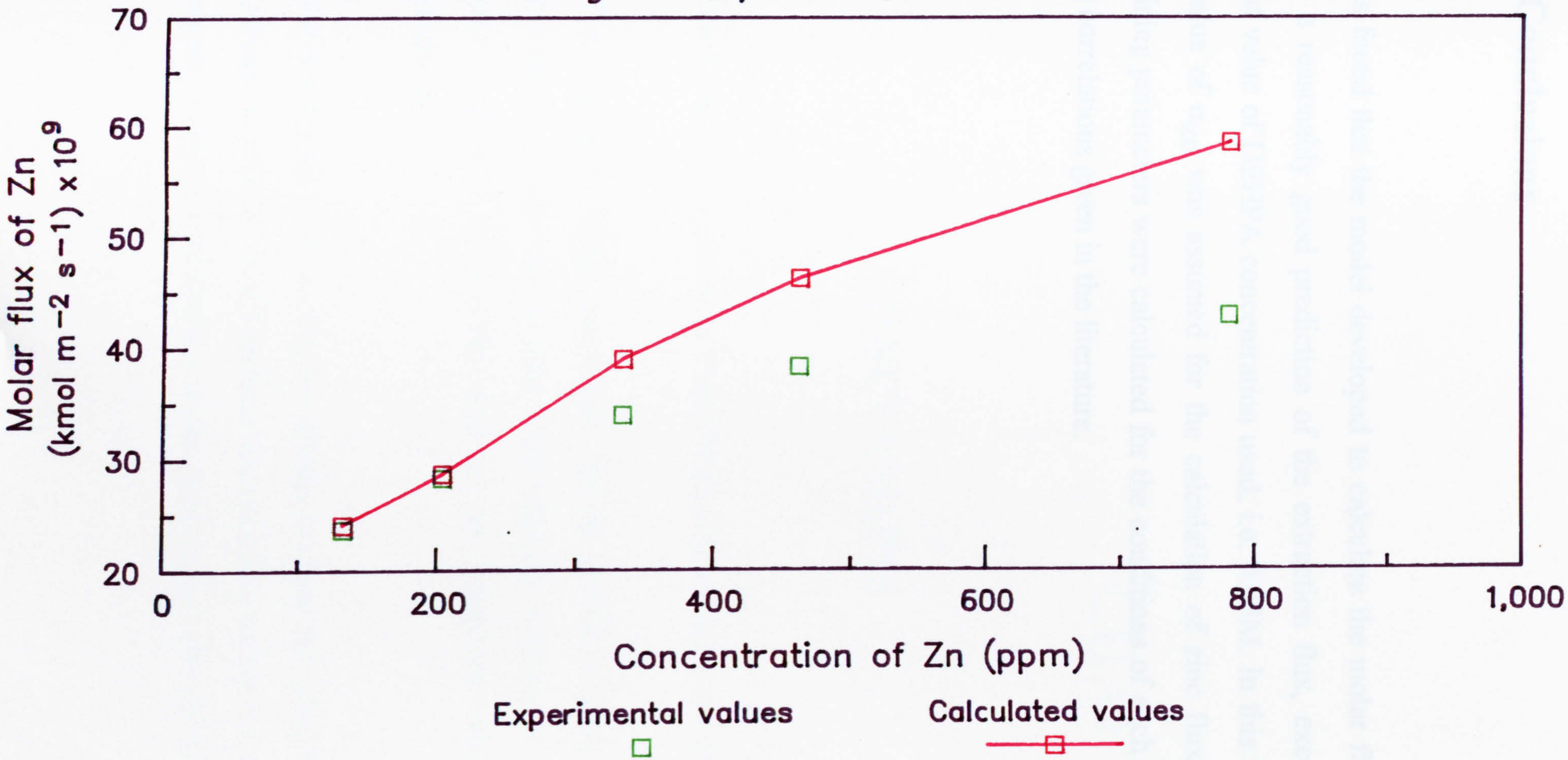


Figure 5.12 Comparison between experimental and predicted values of the molar flux of Zn using the Q3/2 fibre, 0.2M DEHPA and Re=15.

Figure 5.13 Comparison between experimental and predicted values of the molar flux of Zn using the Q3/2 fibre, 0.2M DEHPA and Re=128.



5.2 Conclusions

It was found that the model developed to calculate the molar flux of zinc, gives a reasonably good prediction of the extraction flux, except for the lowest value of DEHPA concentration used, i.e. 0.05M. In this model only the value of α_{zo} was assumed for the calculation of zinc flux, while the remaining parameters were calculated for the conditions of each experiment using correlations given in the literature.

CHAPTER 6

CONCLUSIONS

The main conclusions that have been obtained from this work are:

(1) The supported liquid membrane can be successfully applied to the extraction of zinc and copper from aqueous sulphate solutions using di(2-ethylhexyl) phosphoric acid as an extractant dissolved in n-dodecane.

(2) An interaction between the two metals is observed when they are both present in solution which reduces the total flux below the value for zinc alone. A selective separation of zinc over copper was obtained at pH 3.

(3) The main rate controlling mechanisms of the process are:

(i) aqueous film diffusion

(ii) interfacial chemical reaction

(iii) membrane diffusion

Their relative importance of each of them depends on the concentration of the feed solution, the hydrodynamic parameters, the thickness of the membrane and the concentration of the extractant. As the predominant resistance varies with experimental conditions, it cannot be predicted without the help of a mathematical model.

(4) An equation for calculation of the zinc flux was developed for the Zn - DEHPA system which includes the resistances listed above:

$$R_z = k_{I\alpha} \frac{\left(C_{z\alpha} - \frac{R_z}{K_{z\alpha}}\right)\left(\alpha_o - 1.7\frac{R_z}{K_o}\right)}{\left(C_H + 2\frac{R_z}{K_H}\right)}$$

$$-k'_{I\alpha} \frac{\left(\alpha_{zo} + \frac{R_z}{K_{zo}}\right)\left(C_H + 2\frac{R_z}{K_H}\right)}{\left(\alpha_o - 1.7\frac{R_z}{K_o}\right) + 0.75\left(\alpha_o - 1.7\frac{R_z}{K_o}\right)^{1/2}}$$

The diffusion coefficients, hydrodynamic parameters and mass transfer coefficients are calculated from reported correlations, in a simulation programme that included the kinetic parameters for the forward and reverse reactions.

The agreement between the experimental results and the results predicted by the model was in general good, except for those at Re=15 and Re=128, for DEHPA 0.2M in which the fit is poor at zinc concentrations above 200 ppm.

CHAPTER 7

FUTURE WORK

The major uncertainty in the use of supported liquid membranes for industrial separation processes remains on the little information presently available on supported liquid membrane stability. Some results have been obtained on the life - time of supported liquid membranes ranging from a few days to several months, (Pearson, 1983; Danesi, 1984-85). Further

studies should be carried out to obtain a deeper insight onto the basic phenomena which control the stability of supported liquid membranes.

Further work using long fibres should be carried out in order to study the effect of the entrance region. Experiments with a module with a substantially larger number of fibres should be carried out in order to investigate the hydrodynamic effects on extraction flux.

The mathematical model should be improved to allow for axial variations of concentrations and for the resistance that may build up on the stripping interface due to an increase in the concentration of metal in the strippate.

A sensitivity analysis of the model presented here with respect to parameters predicted from independent correlations such as diffusivity and mass transfer coefficients, may indicate whether the poor agrrement between experimental and predicted results is due to the errors inherent in these correlations.

APPENDIX A

Methods for the determination of DEHPA

A number of methods are available for the determination of DEHPA. These methods involve titration, infrared spectroscopy, and vapor chromatography.

Titration

The technical grade di (2-ethylhexyl) phosphoric acid (DEHPA) may contain up to 4vol% of impurities, mainly mono (2-ethylhexyl) phosphoric acid (MEHPA) plus a small amount of metal ions, mainly Fe^{3+}. A slight yellowish colour is an indication of the presence of Fe^{3+}.

To determine the relative amounts of DEHPA and MEHPA, a method employing colourimetric titration may be used.

The method is fast, convenient and is carried out as follows.

1. Dissolve approximately 0.5 ml of the extractant in 100 ml of a 3:1 mixture of ethanol and distilled water in a 250 ml conical flask.

2. Add a few drops of the mixed indicator bromocresol blue and methyl red (0.2% and 0.1% in alcohol). The solution appears red in colour.

3. Slowly add a 0.1 M NaOH solution from a burette to the extractant solution. The first end-point at about pH 5 is reached when the red colour just disappears. A faint green colour may be observed.This end-point corresponds to the neutralisation of the first, stronger hydrogen ion, hence the combined concentration of DEHPA and MEHPA.

4. Add a few drops of phenolphthalein indicator to the solution. Add the NaOH solution dropwise until the colour changes from green to violet. This second end-point at about pH 9 corresponds to the second, weaker hydrogen ion of MEHPA.

If the total volume of NaOH solution added up to the first and second end-point are V1' and V2' respectively then the percentage of MEHPA in the extractant is given by

$$\% \text{ MEHPA} = \frac{(V_2' - V_1')}{V_1'} \times 100$$

Infrared Spectroscopy (IR)

In this method, the IR absorption of DEHPA is measured between 3.8 and 3.95 microns. By comparison with the absorption obtained with a standard curve, the amount of DEHPA present in the unknown sample can be

determined. This method can be used in the plant to determine the amount of active extractant in the organic phase. The presence of a neutral organic phosphate phase modifier does not interfere. The organic phase is washed with 10 per cent caustic to remove any metallic ions that might be complexed by the extractant. The DEHPA is reformed by containing with hydrochloric acid or sulfuric acid. Following washing with water, the purified organic phase is dried with calcium chloride and the IR absorption is measured. The amount of absorption is compared to a standard curve.

Vapor Phase Chromatography (VPC)

Because of its low volatility, DEHPA can not be determined direct by VPC. It can be determined indirectly, however, through its volatile derivatives. One such method developed by Oak Ridge for the detection of dibutyl phosphate should be applicable, Kibbey et al., (1968).

This method involves the methylation of alkyl phosphoric acid with diazomethane. The methylated products are then analyzed by gas chromatography. Silane derivatives of DEHPA can also be prepared and their concentration determined by VPC. By this method, concentrations as low as 100 ppm of DEHPA can be determined.

APPENDIX B

Purification of D2EHPA

The following procedure removes both metal ions and MEHPA from the impure extractant. It is suitable for purifying fairly large quantities of sample and gives a good yield. A purity of better than 99% can usually be obtained. The method is based on the fact that the sodium salt of MEHPA is soluble in aqueous Na_2CO_3 while that of DEHPA is not.

1. Put 200 ml of 100 g/l aqueous Na_2CO_3 solution in a 500 ml separating funnel.

2. Add 100 ml of the extractant to the funnel carefully, about 20 ml at a time. Swirl the mixture gently after each addition until the formation of gaseous product (CO_2) has subsided before adding the next 20 ml.

3. After all 100 ml of the extractant has been added, add another 100 ml of Na_2CO_3 solution to the mixture. The funnel with its contents should then be shaken lightly and the gaseous product released often. Repeat this brief shaking several times until no more CO_2 is formed, i.e. all the organic acids have reacted. The mixture can then be shaken vigorously.

4. Leave the mixture to stand overnight. Two layers of liquid should result. Discard the lower, aqueous phase as well as any (white or yellow) precipitate at the interface.

5. If a significant amount of precipitate has been observed at the previous stage, it may be advisable to add 100 ml of fresh Na_2CO_3 solution to the remaining organic layer. Shake the mixture well and repeat step 4. Step 4 and 5 may be repeated as many times as required. Usually, however, no more than three washings with Na_2CO_3 solution should be necessary.

6. To the organic layer which is the sodium salt of DEHPA, slowly add 100 ml of 2M H_2SO_4, swirling gently. Some more gaseous product may be formed due to entrained Na_2CO_3. Add a further 100 ml of H_2SO_4, shake well and allow to stand for 1-2 hours. Discard the aqueous layer and repeat this stage twice.

7. To remove entrained H_2SO_4, add 200 ml of distilled water to the organic acid. Swirl the mixture gently, allow the phases to separate then discard the aqueous layer. Repeat 2-3 times.

8. Finally, centrifuge the organic acid for 4-6 hours to separate entrained water droplets. The resulting organic phase should be clear and colourless.

APPENDIX C

Determination of the Composition and Ionic Strength of the Aqueous Phase in the Extraction Process.

The continuous phase is an aqueous solution of Na_2SO_4, $ZnSO_4$, and H_2SO_4 where the concentration of Na_2SO_4 is much larger than the concentration of either of the other two solutes. It can be assumed that Na_2SO_4 completely dissociates and that the amount of undissociated H_2SO_4 is negligible. However, incomplete dissociation of the bisulphate ion, HSO_4^-, and $ZnSO_4$ are taken into account.

The ionic strength, I, is defined by the following equation

$$I = \frac{1}{2} \sum_{i=1}^{n} C_i z_i^2 \qquad (1)$$

where C_i and z_i are the molar concentration and ionic charge of the species i respectively. Thus, for the system under consideration,

$$2I = [Na^+] + 4[Zn^{2+}] + [H^+] + [HSO_4^-] + 4[SO_4^{2-}] \qquad (2)$$

Where the square brackets denote the actual concentration of the specified ion in the solution.

Writing $M_{H_2SO_4}$, $M_{SO_4^{2-}}$ and C_{zt} for the formal concentration of the H_2SO_4, the formal total sulphate concentration and formal concentration of $ZnSO_4$ respectively, it can be shown that

$$\left[H^+\right] = 2M_{H_2SO_4} - \left[HSO_4^-\right] \tag{3}$$

$$\left[SO_4^{2-}\right] = M_{SO_4^{2-}} - \left[HSO_4^-\right] - \left[ZnSO_4\right] \tag{4}$$

$$\left[Na^+\right] = 2\left(M_{SO_4^{2-}} - M_{H_2SO_4} - C_{zt}\right) \tag{5}$$

and

$$\left[Zn^{2+}\right] = C_{zt} - \left[ZnSO_4\right] \tag{6}$$

Substituting equations (3),(4),(5) and (6) into equation (2) gives

$$I = 3M_{SO_4^{2-}} + [Zn^{2+}] - 2[HSO_4^-] - 3[ZnSO_4] \qquad (7)$$

$M_{SO_4^{2-}}$ is a known quantity. In order to calculate the ionic strength the values of $[HSO_4^-]$ and $[Zn^{2+}]$ must be estimated from the dissociation equilibrium of bisulphate ion and zinc sulphate. The values of bisulphate ion dissociation quotient, Q1, defined by the equation

$$Q1 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \qquad (8)$$

and dissociation constant of zinc sulphate is given by

$$K_{Zn} = \frac{[Zn^{2+}][SO_4^{2-}]}{[ZnSO_4]} \qquad (9)$$

Baes (1957) reported the values of dissociation quotient of bisulphate ion, Q1, for the system sodium sulphate-sulphuric acid, as a function of total sulphate concentration. His results shows that at constant total sulphate concentration, Q1 is nearly constant as the composition is changed, even though the accompanying change in ionic strength is considerable. Hence, his data can be represented by the following equation:

$$Q1 = 0.021388 + 0.3864M_{SO_4^{2-}} - 0.2764M^2_{SO_4^{2-}} + 0.2361M^3_{SO_4^{2-}} \quad (10)$$

Assuming that the presence of zinc sulphate does not affect the above equilibrium relation, Baes (1957) values can be used for the calculation of dissociation quotient, Q1. Substitution of equations (3) and (4) into equation (8) yields a quadratic equation in $\left[HSO_4^-\right]$:

$$\left[HSO_4^-\right]^2 - \left(M_{SO_4^{2-}} + 2M_{H_2SO_4} + Q1\right)\left[HSO_4^-\right] + 2M_{SO_4^{2-}}M_{H_2SO_4} = 0 \quad (11)$$

The roots are given by

$$\left[HSO_4^-\right]=\frac{1}{2}\left(M_{SO_4^{2-}}+2M_{H_2SO_4}+Q1\right)$$

$$\pm\frac{1}{2}\left(\sqrt{\left(M_{SO_4^{2-}}+2M_{H_2SO_4}+Q1\right)^2-8M_{H_2SO_4}M_{SO_4^{2-}}}\right) \quad (12)$$

Since it is also known that

$$\left[HSO_4^-\right]<M_{H_2SO_4}\ll M_{SO_4^{2-}} \quad (13)$$

only the negative square-root in equation (12) gives a feasible value for $\left[HSO_4^-\right]$.

As the value of dissociation constant of zinc sulphate, K_{Zn}, (Smith and Martell, 1976) is known, substitution of equations (4) and (6) into equation (9) also yields a quadratic equation in $\left[Zn^{2+}\right]$:

$$\left[Zn^{2+}\right]^2+\left(M_{SO_4{}^{2-}}-\left[HSO_4{}^-\right]-C_{zt}+K_{Zn}\right)\left[Zn^{2+}\right]-K_{Zn}C_{zt}=0 \tag{14}$$

The roots are given by

$$\left[Zn^{2+}\right]=-\frac{1}{2}\left(M_{SO_4{}^{2-}}-\left[HSO_4{}^-\right]-C_{zt}+K_{Zn}\right)$$

$$\pm\frac{1}{2}\left(\sqrt{\left(M_{SO_4{}^{2-}}-\left[HSO_4{}^-\right]-C_{zt}+K_{Zn}\right)^2+4K_{Zn}C_{zt}}\right) \tag{15}$$

only the positive square-root in equation (15) gives a feasible value for $\left[Zn^{2+}\right]$.

To summarize, the algorithm for calculating the ionic strength, $\left[H^+\right]$ or pH and $\left[Zn^{2+}\right]$ from known concentrations of Na_2SO_4, $ZnSO_4$ and H_2SO_4 is as follows:

(1) Calculate $M_{SO_4^{2-}}$ from known concentrations of the solutes.

(2) Calculate Q1 from equation (10).

(3) Calculate $\left[HSO_4^-\right]$ from equation (12).

(4) Calculate $\left[SO_4^{2-}\right]$ from equation (4).

(5) Calculate $\left[Zn^{2+}\right]$ from equation (15).

(6) Calculate $\left[ZnSO_4\right]$ from equation (6).

(7) Calculate I and $\left[H^+\right]$ from equations (7) and (3) or (8) respectively.

If, on the other hand, the value of $M_{H_2SO_4}$ which will give a certain pH is required, the same algorithm may be used iteratively using guessed values of $M_{H_2SO_4}$.

APPENDIX D

Di (2-Ethylhexyl) Phosphoric Acid (DEHPA)

Di (2-ethylhexyl) phosphoric acid is a mobile, amber colored liquid that is insoluble in water and miscible with most organic solvents.

Physical properties

Molecular Weight.....322.43

Appearance.....clear liquid

Wt per ml at 20 ^{0}C .....0.972 to 0.976g

Freezing Point.....sets to glass below -60 ^{0}C

Viscosity at 20 ^{0}C 53cps

Density at 20 ^{0}C.....0.974 g/cm^3

Refractive Index, η_D 20 ^{0}C.....1.443 to 1.444

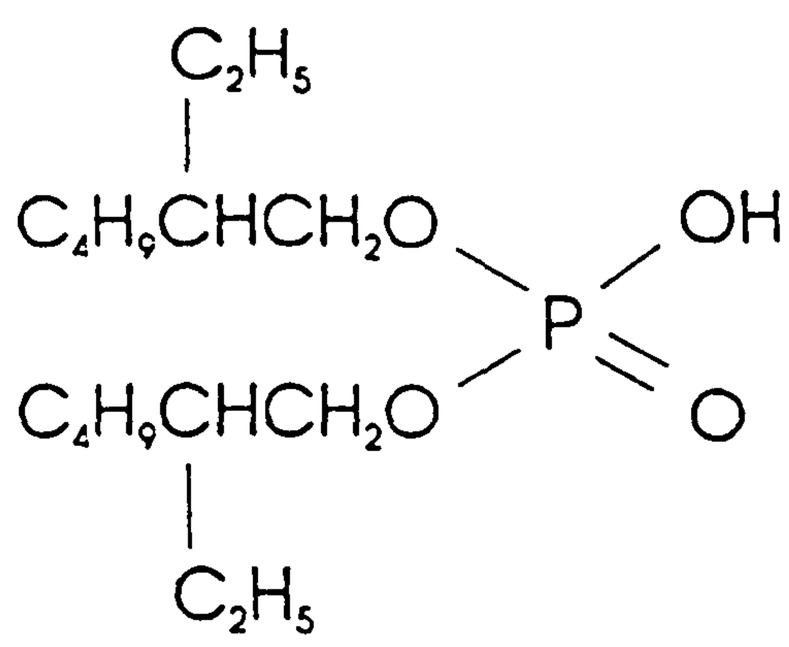
Solubility at 20 ^{0}C.

in water.....<0.01% by weight

water in.....2.4% by weight

Flash Point, Cleveland open cup (ASTM Method D92).....385 ^{0}F. (a)

(a) Determined on typical commercial material



DEHPA Chemical structure

Dodecane: $C_{12}H_{26}$ [b]

Molecular Weight 170.34

Density (g/cc) ..... $0.7487^{20/4}$

Refractive Index, η_D 20 ^{0}C 1.4216

Boiling Point / Range (^{0}C) 91.5-216.3

Freezing / Melting Point (^{0}C) ..... -9.6

Solubility: Alcohol, Ether, Acetone, Chloroform.

(b) Data from C.R.C. Handbook of Chemistry and Physics. 69th Edition.
Editor R.C. Weast. C.R.C. Press Inc.,
Florida (1988-1989).

APPENDIX E

Table E1 Characteristics of the fibres used in this experimental work

	Type of fibre	
	S6/2	Q3/2
Inside diameter of the fibre i.d. (mm)	1.8	0.6
Outsider diameter of the fibre o.d. (mm)	2.6	1
Thickness of the membrane δ(mm)	0.4	0.2
Pore size (μm)	0.2	0.2

75% void polypropylene Hollow fibre

MICRODYN
D- 42289 WUPPERTAL
GERMANY

Internal area of S6/2 fibre: 1.98×10^{-3} m^2
External area of S6/2 fibre: 2.86×10^{-3} m^2
Internal area of Q3/2 fibre: 6.6×10^{-4} m^2
External area of Q3/2 fibre: 1.1×10^{-3} m^2

Table E2 Experimental conditions under which Zn was extracted using DEHPA and an S6/2 type of fibre.

Di (mm)	δ (mm)	u(x10^3) (m/s)	Re	DEHPA (M)	[Zn] (ppm)	Run No
1.8	0.4	8.2	17	0.05	69	1-2
				0.05	134	3-4
				0.05	194	5-6
				0.05	334	7-8
				0.05	460	9-10
				0.05	793	11-12
				0.1	67	13-14
				0.1	132	15-16
				0.1	199	17-18
				0.1	327	19-20
				0.1	455	21-22
				0.1	795	23-24
				0.15	68	25-26
				0.15	138	27-28
				0.15	195	29-30
				0.15	341	31-32
				0.15	456	33-34
				0.15	840	35-36
				0.2	67	37-38
				0.2	133	39-40
				0.2	197	41-42
				0.2	348	43-44
				0.2	465	45-46
				0.2	803	47-48

Table E3 Experimental conditions under which Zn was extracted using DEHPA and a Q3/2 type of fibre.

Di (mm)	δ (mm)	u (m/s)	Re	DEHPA (M)	[Zn] (ppm)	Run No
0.6	0.2	0.073	50	0.05	67	49-50
				0.05	134	51-52
				0.05	192	53-54
				0.05	328	55-56
				0.05	469	57-58
				0.05	810	59-60
				0.1	68	61-62
				0.1	137	63-64
				0.1	195	65-66
				0.1	337	67-68
				0.1	458	69-70
				0.1	800	71-72
				0.15	67	73-74
				0.15	138	75-76
				0.15	196	77-78
				0.15	334	79-80
				0.15	463	81-82
				0.15	798	83-84
				0.2	66	85-86
				0.2	132	87-88
				0.2	196	89-90
				0.2	329	91-92
				0.2	460	93-94
				0.2	813	95-96

Table E4 Experimental conditions under which Cu was extracted using DEHPA and an S6/2 type of fibre.

Di (mm)	δ (mm)	u(x10^3) (m/s)	Re	DEHPA (M)	[Cu] (ppm)	Run No
1.8	0.4	8.2	17	0.05	66	97-98
				0.05	142	99-100
				0.05	202	101-102
				0.05	338	103-104
				0.05	462	105-106
				0.05	770	107-108
				0.1	68	109-110
				0.1	128	111-112
				0.1	198	113-114
				0.1	339	115-116
				0.1	445	117-118
				0.1	788	119-120
				0.15	66	121-122
				0.15	136	123-124
				0.15	200	125-126
				0.15	333	127-128
				0.15	474	129-130
				0.15	775	131-132
				0.2	69	133-134
				0.2	139	135-136
				0.2	204	137-138
				0.2	328	139-140
				0.2	448	141-142
				0.2	778	143-144

Table E5 Experimental conditions under which Cu was extracted using DEHPA and a Q3/2 type of fibre.

Di (mm)	δ (mm)	u (m/s)	Re	DEHPA (M)	[Cu] (ppm)	Run No
0.6	0.2	0.073	50	0.05	72	145-146
				0.05	128	147-148
				0.05	209	149-150
				0.05	329	151-152
				0.05	479	153-154
				0.05	805	155-156
				0.1	67	157-158
				0.1	134	159-160
				0.1	200	161-162
				0.1	338	163-164
				0.1	458	165-166
				0.1	810	167-168
				0.15	68	169-170
				0.15	131	171-172
				0.15	203	173-174
				0.15	332	175-176
				0.15	464	177-178
				0.15	833	179-180
				0.2	68	181-182
				0.2	136	183-184
				0.2	209	185-186
				0.2	335	187-188
				0.2	456	189-190
				0.2	798	191-192

Table E6 Experimental conditions investigating possible interaction effects between Zn and Cu.

Di (mm)	δ (mm)	u(x10^3) (m/s)	Re	DEHPA (M)	[Zn] and [Cu] Mixed solution (ppm)		Run No
1.8	0.4	8.2	17	0.15	130	132	193-194
				0.15	193	200	195-196
				0.15	309	329	197-198
				0.15	456	457	199-200
				0.15	785	778	201-202
				0.2	203	198	203-204
				0.2	317	324	205-206
				0.2	467	442	207-208
				0.2	785	778	209-210

Table E7 Experimental conditions investigating the pH effect on molar flux of Zn and Cu.

Di (mm)	δ (mm)	u(x10^3) (m/s)	Re	DEHPA (M)	[Zn] and [Cu] Mixed solution (ppm)		pH	Run No
1.8	0.4	8.2	17	0.2	197	405	3	211-212
				0.2	198	555	3	213-214
				0.2	202	198	4	215-216
				0.2	198	390	4	217-218
				0.2	195	540	4	219-220

Table E8 Experimental conditions investigating the effect of Re on the molar flux of Zn.

Di (mm)	δ (mm)	u (m/s)	DEHPA (M)	[Zn] (ppm)	Re	Run No
1.8	0.4	$2.4x10^{-3}$	0.2	134	5	221-222
1.8	0.4	$2.4x10^{-3}$	0.2	201	5	223-224
1.8	0.4	$2.4x10^{-3}$	0.2	331	5	225-226
1.8	0.4	$2.4x10^{-3}$	0.2	465	5	227-228
1.8	0.4	$2.4x10^{-3}$	0.2	815	5	229-230
1.8	0.4	0.022	0.2	131	45	231-232
1.8	0.4	0.022	0.2	202	45	233-234
1.8	0.4	0.022	0.2	332	45	235-236
1.8	0.4	0.022	0.2	465	45	237-238
1.8	0.4	0.022	0.2	780	45	239-240
1.8	0.4	0.035	0.2	133	71	241-242
1.8	0.4	0.035	0.2	200	71	243-244
1.8	0.4	0.035	0.2	333	71	245-246
1.8	0.4	0.035	0.2	464	71	247-248
1.8	0.4	0.035	0.2	810	71	249-250
0.6	0.2	0.022	0.2	132	15	251-252
0.6	0.2	0.022	0.2	201	15	253-254
0.6	0.2	0.022	0.2	332	15	255-256
0.6	0.2	0.022	0.2	460	15	257-258
0.6	0.2	0.022	0.2	825	15	259-260
0.6	0.2	0.19	0.2	132	128	261-262
0.6	0.2	0.19	0.2	204	128	263-264
0.6	0.2	0.19	0.2	334	128	265-266
0.6	0.2	0.19	0.2	462	128	267-268
0.6	0.2	0.19	0.2	780	128	269-270

Table E9 Experimental conditions investigating the behaviour of two bundles of fibres and the effect on Zn molar flux.

Di (mm)	δ (mm)	Q_F (ml/min)	DEHPA (M)	Conc. of Zn, using a bundle of 4 fibres (ppm)	Run No
1.8	0.4	5	0.2	134	271-272
		5	0.2	199	273-274
		5	0.2	334	275-276
		5	0.2	465	277-278
		5	0.2	817	279-280
0.6	0.2	5	0.2	131	281-282
		5	0.2	199	283-284
		5	0.2	329	285-286
		5	0.2	463	287-288
		5	0.2	821	289-290

Table E10 Data used for the calibration of the peristaltic pump for the feed flowrate.

%	V (cm^3)	t (min)	Q (cm^3/min)
10	10	13	0.77
20	17.5	10	1.75
30	23.5	8.5	2.76
40	45	12	3.75
50	57.5	12	4.79
60	66	11.3	5.84
70	68	10	6.8
80	82	10.3	7.96
90	96	11	8.73
99	19.5	2	9.75

Table E11 Data used for the calibration of the peristaltic pump for the strip flow rate.

%	V (cm^3)	t (min)	Q (cm^3/min)
5	7	14	0.5
10	13	9	1.44
20	21.5	6.5	3.31
30	31	6	5.17
40	46	6.5	7.08
50	48	5.5	8.73
60	75	7	10.71
70	70	5.5	12.73
80	59	4	14.75
90	76	4.5	16.89
95	89	5	17.8

Table E12 Data from a typical run, lasted for five hours using Zn and Cu, by employing S6/2 and Q3/2 type of fibres.

	Molar flux; (kmol m^{-2} s^{-1}) x 10^9			
Time (H)	Zn (S6/2)	Zn (Q3/2)	Cu (S6/2)	Cu (Q3/2)
0.5	8	29.19	0.74	9.25
1.0	15.58	37.10	2.93	12.41
1.5	15.63	37.17	2.94	12.39
2.0	15.59	37.17	2.92	12.42
2.5	15.75	37.09	2.93	12.38
3.0	15.63	37.10	2.94	12.44
3.5	15.66	37.17	2.92	12.42
4.0	15.88	37.09	2.93	12.40
4.5	16.12	37.10	2.94	12.39
5.0	16.28	37.07	2.93	12.40

Flow Rate: 1.25ml/min
DEHPA: 0.2M

Table E13 Effect of concentration on Zn flux using 0.05M DEHPA and S6/2 type of fibre.

Feed concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (kmol m^{-2} s^{-1}) x 10^9
69	2.3
134	3.6
194	4.1
334	4.6
460	4.8
793	5.0

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E14 Effect of concentration on Zn flux using 0.1M DEHPA and S6/2 type of fibre.

Feed concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (kmol m^{-2} s^{-1}) x 10^9
67	2.4
132	4.4
199	6.3
327	8.6
455	10.4
795	12.4

Q_F = 1.25 ml/min
Q_S = 2.4 ml/min

Table E15 Effect of concentration on Cu flux using 0.05M DEHPA and S6/2 type of fibre.

Feed concentration, (ppm)	Molar flux, (kmol m^{-2} s^{-1}) x 10^9
66	0.08
142	0.12
202	0.16
338	0.28
462	0.34
770	0.48

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E16 Effect of concentration on Cu flux using 0.1M DEHPA and S6/2 type of fibre.

Feed concentration, (ppm)	Molar flux, (kmol m^{-2} s^{-1}) x 10^9
68	0.19
128	0.36
198	0.71
339	0.99
445	1.11
788	1.49

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E17 Effect of concentration on Zn flux using 0.15M DEHPA and S6/2 type of fibre.

Feed concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (kmol m^{-2} s^{-1}) x 10^9
68	2.6
138	5.8
195	8.7
341	10.8
456	12.3
840	13.5

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E18 Effect of concentration on Zn flux using 0.2M DEHPA and S6/2 type of fibre.

Feed concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (kmol m^{-2} s^{-1}) x 10^9
67	2.8
133	5.8
197	9.0
348	14.4
465	15.2
803	15.8

Q_F = 1.25 ml/min
Q_S = 2.4 ml/min

Table E19 Effect of concentration on Cu flux using 0.15M DEHPA and S6/2 type of fibre.

Feed concentration, (ppm)	Molar flux, (kmol m^{-2} s^{-1}) x 10^9
66	0.24
136	0.48
200	0.80
333	1.16
474	1.53
775	1.93

Q_F = 1.25 ml/min
Q_S = 2.4 ml/min

Table E20 Effect of concentration on Cu flux, using 0.2M DEHPA and S6/2 type of fibre.

Feed concentration, (ppm)	Molar flux, (kmol m^{-2} s^{-1}) x10^9
69	0.52
139	0.80
204	1.24
328	1.61
448	2.12
778	2.93

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E21 Effect of concentration on Zn flux, using 0.05M DEHPA and Q3/2 type of fibre.

Feed concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (kmol m^{-2} s^{-1}) x 10^9
67	3.7
134	9.2
192	11.4
328	11.6
469	11.7
810	12.4

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E22 Effect of concentration on Zn flux, using 0.1M DEHPA and Q3/2 type of fibre.

Feed concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (kmol m^{-2} s^{-1}) x10^9
68	5.8
137	11.4
195	13.9
337	18.9
458	22.4
800	31.1

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E23 Effect of concentration on Cu flux, using 0.05M DEHPA and Q3/2 type of fibre.

Feed concentration, (ppm)	Molar flux, (kmol m^{-2} s^{-1}) x 10^9
72	0.09
128	0.19
209	0.30
329	0.63
479	0.89
805	1.01

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E24 Effect of concentration on Cu flux, using 0.1M DEHPA and Q3/2 type of fibre.

Feed concentration, (ppm)	Molar flux, (kmol m^{-2} s^{-1}) x 10^9
67	0.54
134	0.91
200	1.65
338	3.11
458	4.13
810	6.42

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E25 Effect of concentration on Zn flux, using 0.15M DEHPA and Q3/2 type of fibre.

Feed concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (kmol m^{-2} s^{-1}) x 10^9
67	7.1
138	13.4
196	16.9
334	21.9
463	25.5
798	34.9

Q_F = 1.25 ml/min

Q_S = 2.4 ml/min

Table E26 Effect of concentration on Zn flux, using 0.2M DEHPA and Q3/2 type of fibre.

Feed concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (kmol m^{-2} s^{-1}) x 10^9
66	10.5
132	16.3
196	19.9
329	25.2
460	28.8
813	37.1

Q_F = 1.25 ml/min
Q_S = 2.4 ml/min

Table E27 Effect of concentration on Cu flux, using 0.15M DEHPA and Q3/2 type of fibre.

Feed concentration, (ppm)	Molar flux, (kmol m^{-2} s^{-1}) x 10^9
68	0.74
131	1.19
203	2.24
332	4.21
464	5.62
833	8.74

Q_F = 1.25 ml/min
Q_S = 2.4 ml/min

Table E28 Effect of concentration on Cu flux, using 0.2M DEHPA and Q3/2 type of fibre.

Feed concentration, (ppm)	Molar flux, (kmol m^{-2} s^{-1}) x 10^9
68	1.41
136	3.09
209	5.62
335	8.11
456	10.03
798	12.41

Q_F = 1.25 ml/min
Q_S = 2.4 ml/min

Table E29 Interaction and the effect on Zn and Cu flux, when the two metals are present in solution, using 0.15M DEHPA and S6/2 type of fibre.

Concentration $C_{z\alpha}$ (ppm)		Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})		Concentration $C_{z\alpha}$ (ppm)		Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})	
Zn Alone	Cu Alone	Zn Alone	Cu Alone	Zn (mix)	Cu (mix)	Zn (mix)	Cu (mix)
138	136	5.8	0.48	130	132	3.1	0.07
195	200	8.7	0.80	193	200	6.0	0.11
341	333	10.8	1.16	309	329	7.1	0.11
456	474	12.3	1.53	456	457	8.6	0.098
840	775	13.5	1.93	785	778	10.2	0.081

Q_F=1.25 ml/min
Q_S=2.4 ml/min
Feed pH:3.0

Table E30 Interaction and the effect on Zn and Cu flux, when the two metals are present in solution, using 0.2M DEHPA and S6/2 type of fibre.

Concentration $C_{z\alpha}$ (ppm)		Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})		Concentration $C_{z\alpha}$ (ppm)		Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})	
Zn Alone	Cu Alone	Zn Alone	Cu Alone	Zn (mix)	Cu (mix)	Zn (mix)	Cu (mix)
197	204	11.94	1.24	203	198	9.0	0.62
348	328	16.25	1.61	317	324	14.4	0.22
465	448	19.48	2.12	467	442	15.2	0.15
803	778	23.21	2.93	785	778	15.8	0.11

Q_F=1.25 ml/min
Q_S=2.4 ml/min
Feed pH:3.0

Table E31 Effect of membrane thickness on Zn flux, using 0.05M DEHPA.

	Molar flux, R_Z ($x10^9$) (kmol m^{-2} s^{-1})	
Membrane thickness (mm)	**Feed concentration**	
	192	810
0.2	11.4	12.4
0.4	4.1	5.0

Q_F=1.25 ml/min
Q_S=2.4 ml/min

Table E32 Effect of membrane thickness on Cu flux, using 0.05M DEHPA.

	Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})	
Membrane thickness (mm)	**Feed concentration**	
	192	810
0.2	0.3	1.01
0.4	0.16	0.48

Q_F=1.25 ml/min
Q_S=2.4 ml/min

Table E33 Effect of membrane thickness on Zn flux, using 0.2M DEHPA.

	Molar flux, R_Z (x10^9) (kmol m^{-2} s^{-1})	
Membrane thickness (mm)	**Feed concentration**	
	192	810
0.2	19.9	37.1
0.4	9.0	15.8

Q_F=1.25 ml/min
Q_S=2.4 ml/min

Table E34 Effect of membrane thickness on Cu flux, using 0.2M DEHPA.

	Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})	
Membrane thickness (mm)	**Feed concentration**	
	192	810
0.2	5.62	12.41
0.4	1.24	2.93

Q_F=1.25 ml/min
Q_S=2.4 ml/min

Table E35 Effect of DEHPA concentration on Zn flux, at different feed concentrations, using S6/2 type of fibres.

Concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})	DEHPA Concentration (M)
69	2.3	0.05
134	3.6	0.05
194	4.1	0.05
334	4.6	0.05
460	4.8	0.05
793	5.0	0.05
67	2.4	0.1
132	4.4	0.1
199	6.3	0.1
327	8.6	0.1
455	10.4	0.1
795	12.4	0.1
68	2.6	0.15
138	5.8	0.15
195	8.7	0.15
341	10.8	0.15
456	12.3	0.15
840	13.5	0.15
67	2.8	0.2
133	5.8	0.2
197	9.0	0.2
348	14.4	0.2
465	15.2	0.2
803	15.8	0.2

Q_F=1.25 ml/min
Q_S=2.4 ml/min

Table E36 Effect of DEHPA concentration on Cu flux, at different feed concentrations, using S6/2 type of fibre.

Concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})	DEHPA Concentration (M)
66	0.08	0.05
142	0.12	0.05
202	0.16	0.05
338	0.28	0.05
462	0.34	0.05
770	0.48	0.05
68	0.19	0.1
128	0.36	0.1
198	0.71	0.1
339	0.99	0.1
445	1.11	0.1
788	1.49	0.1
66	0.24	0.15
136	0.48	0.15
200	0.80	0.15
333	1.16	0.15
474	1.53	0.15
775	1.93	0.15
69	0.52	0.2
139	0.80	0.2
204	1.24	0.2
328	1.61	0.2
448	2.12	0.2
778	2.93	0.2

Q_F=1.25 ml/min
Q_S=2.4 ml/min

Table E37 Effect of DEHPA concentration on Zn flux, at different feed concentrations, using Q3/2 type of fibre.

Concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})	DEHPA Concentration (M)
67	3.7	0.05
134	9.2	0.05
192	11.4	0.05
328	11.6	0.05
469	11.7	0.05
810	12.4	0.05
68	5.8	0.1
137	11.4	0.1
195	13.9	0.1
337	18.9	0.1
458	22.4	0.1
800	31.1	0.1
67	7.1	0.15
138	13.4	0.15
196	16.9	0.15
334	21.9	0.15
463	25.5	0.15
798	34.9	0.15
66	10.5	0.2
132	16.3	0.2
196	19.9	0.2
329	25.2	0.2
460	28.8	0.2
813	37.1	0.2

Q_F=1.25 ml/min
Q_S=2.4 ml/min

Table E38 Effect of DEHPA concentration on Cu flux, at different feed concentrations, using Q3/2 type of fibre.

Concentration, $C_{z\alpha}$ (ppm)	Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})	DEHPA Concentration (M)
72	0.09	0.05
128	0.19	0.05
209	0.30	0.05
329	0.63	0.05
479	0.89	0.05
805	1.01	0.05
67	0.54	0.1
134	0.91	0.1
200	1.65	0.1
338	3.11	0.1
458	4.13	0.1
810	6.42	0.1
68	0.74	0.15
131	1.19	0.15
203	2.24	0.15
332	4.21	0.15
464	5.62	0.15
833	8.74	0.15
68	1.41	0.2
136	3.09	0.2
209	5.62	0.2
335	8.11	0.2
456	10.03	0.2
798	12.41	0.2

Q_F=1.25 ml/min
Q_S=2.4 ml/min

Table E39 Effect of Re number on Zn flux, using 0.2M DEHPA and S6/2 type of fibre.

Re	Molar flux, R_Z (x10^9) (kmol m^{-2} s^{-1})				
	Feed concentrations				
	130ppm	200ppm	330ppm	465ppm	810ppm
5	4.2	6.54	8.96	9.84	10.23
17	5.8	9.0	14.4	15.2	15.8
45	6.41	10.95	17.19	19.24	20.78
71	5.71	9.65	15.3	16.5	17.75

Table E40 Effect of Re number on Zn flux, using 0.2M DEHPA and Q3/2 type of fibre.

	Molar flux, R_Z ($x10^9$) (kmol m^{-2} s^{-1})				
Re	**Feed concentrations**				
	130ppm	200ppm	330ppm	465ppm	810ppm
15	13.11	13.58	14.01	14.76	15.87
50	16.3	19.9	25.2	28.8	37.1
128	17.8	21.17	25.4	28.71	32.08

Table E41 Comparison between low and high Re number on the effect of Zn flux, using 0.2M DEHPA with S6/2 type of fibre.

Membrane thickness (mm)	Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1}) At Re=5 and 15		Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1}) At Re=71 and 128	
	Feed concentration		Feed concentration	
	130	810	130	810
0.2	13.11	15.87	17.8	32.08
0.4	4.2	10.23	5.71	17.75

Table E42 Effect of a bundle of four fibres of S6/2 type, on Zn flux, using 0.2M DEHPA.

	Molar flux, R_Z ($x10^9$) (kmol m^{-2} s^{-1})				
No of fibres	**Feed concentration**				
	130ppm	200ppm	330ppm	465ppm	815ppm
1	5.8	9.0	14.4	15.2	15.8
4	4.81	7.71	11.64	13.11	13.55

Table E43 Effect of a bundle of four fibres of Q3/2 type, on Zn flux, using 0.2M DEHPA.

	Molar flux, R_z ($x10^9$) (kmol m^{-2} s^{-1})				
No of fibres	**Feed concentration**				
	130ppm	200ppm	330ppm	465ppm	815ppm
1	16.3	19.9	25.2	28.8	37.1
4	11.78	15.26	20.54	24.13	30.19

Table E44 Comparison between two bundles of four fibres and the effect on Zn flux, using 0.2M DEHPA.

	Molar flux, R_Z ($x10^9$) (kmol m^{-2} s^{-1})	
Feed concentration (ppm)	**Bundle of 4 fibres Type S6/2**	**Bundle of 4 fibres Type Q3/2**
134	4.81	11.78
199	7.71	15.26
329	11.64	20.54
463	13.11	24.13
820	13.55	30.19

Q_F=5 ml/min
Q_S=9.25 ml/min

Table E45 Effect of pH on Cu flux, when the metal is present in solution with Zn, using 0.2M DEHPA and S6/2 type of fibre.

pH	Molar flux, R_z (x10^9) (kmol m^{-2} s^{-1})		
	Feed concentration of Cu(a)		
	200ppm	400ppm	555ppm
3.0	0.62	0.69	0.74
4.0	1.02	1.1	1.95

(a) Copper was present in mixture with Zn

Table E46 Effect of pH on Zn and Cu flux, when the two metals are present in solution, using 0.2M DEHPA and S6/2 type of fibre.

	Molar flux, R_Z, (kmol m^{-2} s^{-1}) x 10^9					
pH	**Feed concentration of Zn and Cu present in solution**					
	200ppm Zn	200ppm Cu	200ppm Zn	400ppm Cu	200ppm Zn	555ppm Cu
3.0	11.94	0.62	8.55	0.69	8.97	0.74
4.0	11.41	1.02	6.69	1.1	9.61	1.95

APPENDIX F

A Computer program for the calculation of R_Z using equation 3.9, developed for both forward and reverse reaction together with a flowchart are include in this appendix.

```
Function Iterate(kia, ksia, kza, kh, ch, ko, kzo, ao, azo, cza)
'##################################################################
'
' This function was written in Microsoft Visual Basic for the
' calculation of implicite equations (implemented: flux of zinc in a
' supported liquid membrane process.
'
' At the beginning, 10 initial values are being set up. Using them
' in the formula, 10 values on the left side of the equation are
' attained. The two values left and right of the target value are
' kept for next run and 8 values in between of them are
' generated. With this new set, the next pair of values, in between
' of which the target value is situated, will be determined. "i" is
' the number of sets that are generated while getting closer to the
' target value, i.e. the higher i is, the more precise the target
' value will be.
'
' An error message will be generated if the target value is not
' within the range of the initial set of values.
'
'##################################################################
```

```
'set initial values for rza
Static rza(1 To 10)                    'dimensions two arrays
Static rz(1 To 10)
i = 0                                  'mark for degree of precision
rza(1) = 0.0000001                     'initial first value of rza
For m = 2 To 10
   rza(m) = rza(1) / (10 ^ (m - 1))
Next m


'calculate rz-values
10
i = i + 1
For n = 1 To 10


   t = ao - 1.7 * rza(n) / ko


   If t <= 0 Then
      rz(n) = 0
      Else
rz(n) = kia * (cza * 0.001 / 65.4 - rza(n) / kza) * (ao - 1.7 * rza(n) / ko)
        / (ch + 2 * rza(n) / kh) - ksia * (azo + rza(n) / kzo) * (ch + 2 *
        rza(n) / kh) / (ao - 1.7 * rza(n) / ko + 0.75 * (ao - 1.7 * rza(n) /
        ko) ^ 0.5)
```

```
End If
    If n = 1 Then
    GoTo 15
End If

If rz(n) = 0 Then
    GoTo 15                         'next n
    Else
    If (rz(n) - rza(n)) * (rz(n - 1) - rza(n - 1)) < 0 Then
        rza(1) = rza(n - 1)
        rza(10) = rza(n)

If i = 4 Then
    GoTo 20                 'output

    Else

        For k = 2 To 9
        rza(k) = rza(1) + (rza(10) - rza(1)) * (k / 10)
        Next k
            GoTo 10
        End If
Else
GoTo 15                             'next n
```

```
    End If
End If
15
Next n

Iterate = "input error!"              'output if target value is not
GoTo 25                               'within the initial rza range

'output
20
Iterate = (rza(1) + rza(10)) / 2      'output mean value

25
End Function.
```

LEGEND

rza(n)=value to be input into equation as R_Z

rz(n) =value to be calculated with the equation (=R_Z)

i =steps parameter for adjusting degree of precision

t =argument in square root (for check: ≥0)

Iterate=final value for R_Z to be output into spreadsheet

k,m,n =running variables

kia =$k_{I\alpha}$

cza =$C_{z\alpha}$

kza =$K_{z\alpha}$

ao =α_o

ko =K_o

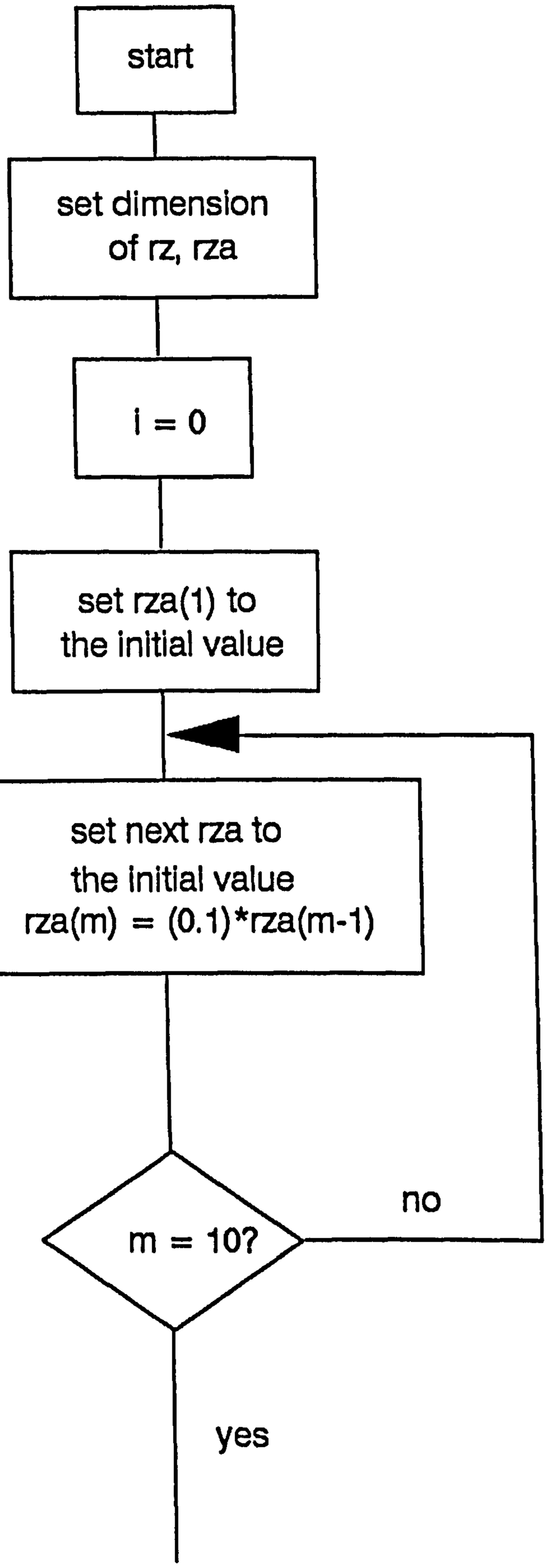
ch =C_H

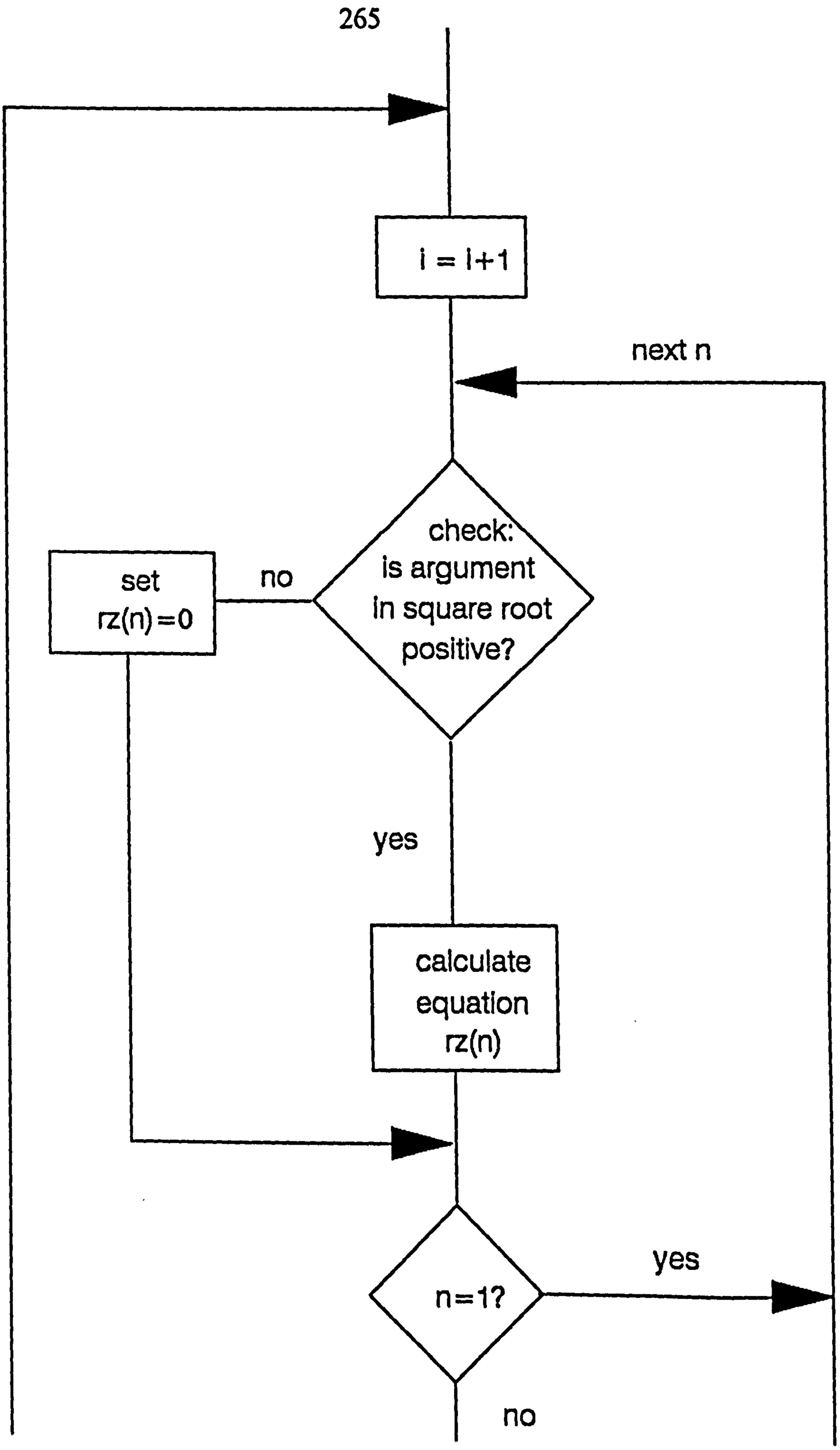
kh =K_H

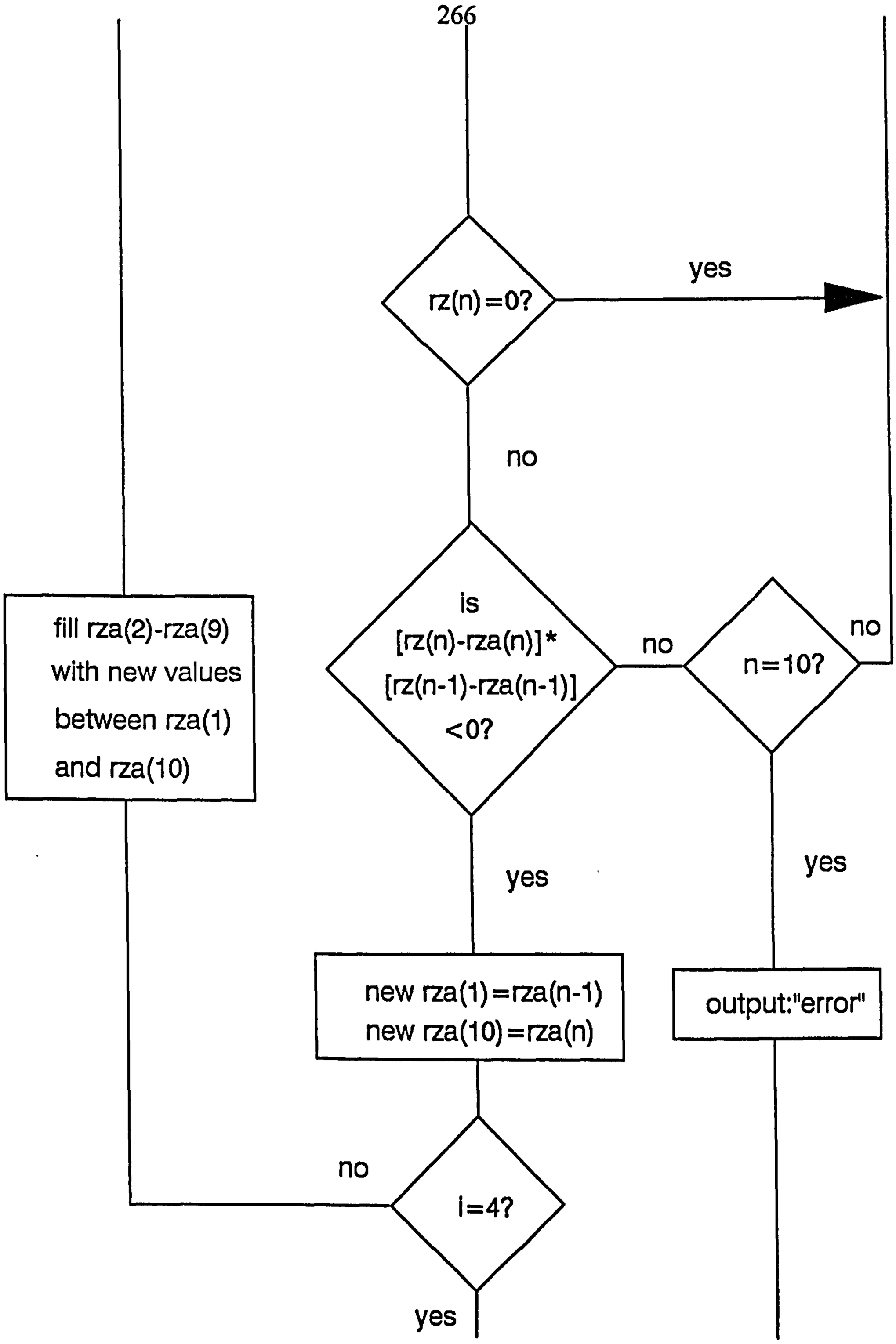
ksia =$k'_{I\alpha}$

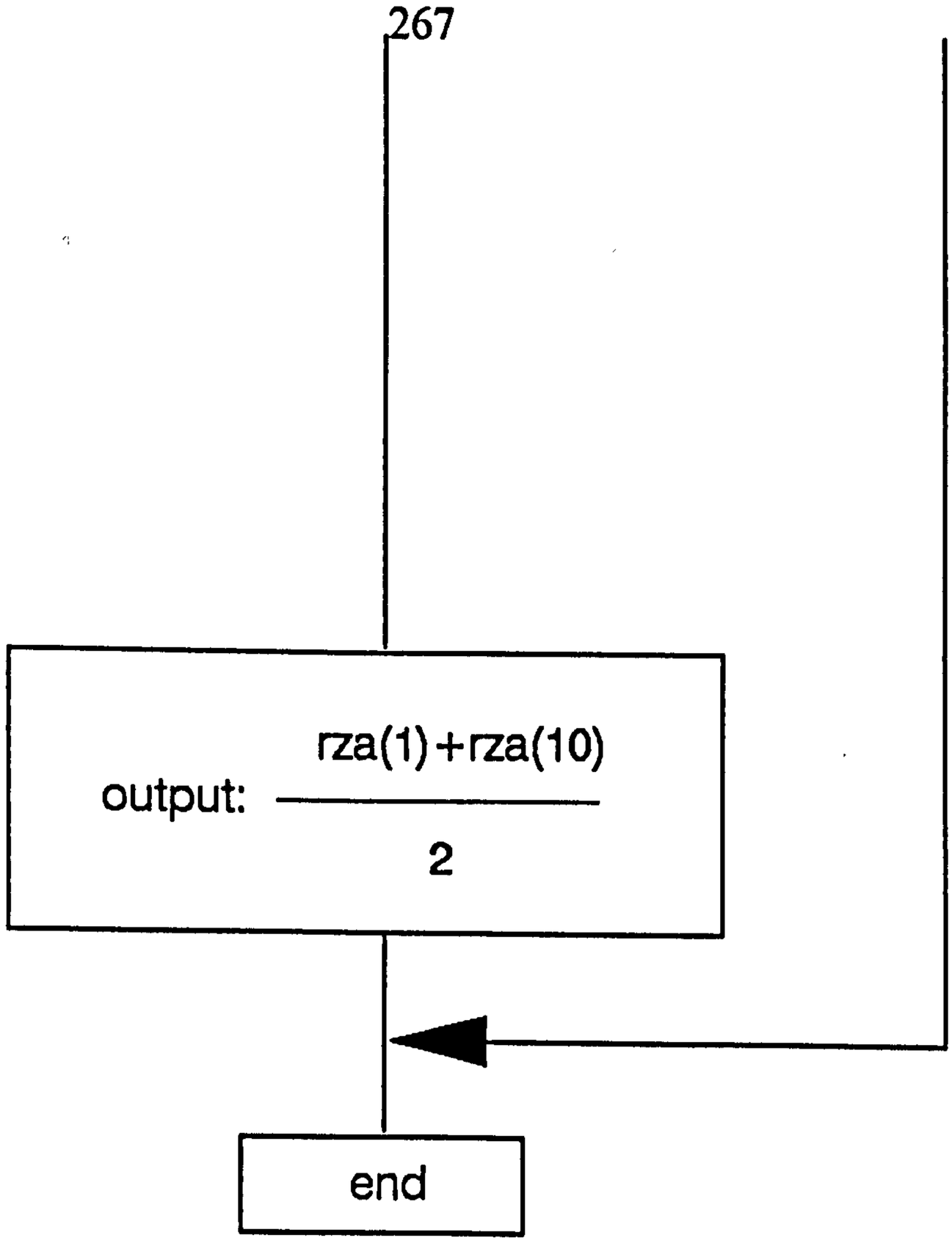
azo =α_{zo}

kzo =K_{zo}


start
set dimension
of rz, rza
i = 0
set rza(1) to
the initial value
set next rza to
the initial value
rza(m) = (0.1)*rza(m-1)
m = 10?
no
yes


265
i = i+1
next n
check:
is argument
in square root
positive?
no
set
rz(n)=0
yes
calculate
equation
rz(n)
n=1?
yes
no


266
rz(n)=0?
yes
no
is
[rz(n)-rza(n)]*
[rz(n-1)-rza(n-1)]
<0?
no
n=10?
no
fill rza(2)-rza(9)
with new values
between rza(1)
and rza(10)
yes
new rza(1)=rza(n-1)
new rza(10)=rza(n)
output:"error"
no
I=4?
yes


output: rza(1)+rza(10) / 2
end

APPENDIX G

Experimental and predicted results on molar flux of Zn, using equation (3.9) are represented in this appendix.

Table G1 Comparison between experimental and predicted values of molar flux of Zn,using S6/2 type of fibre,0.05M DEHPA and Re=17.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	3.96E-06	
K_H (m/s)	3.96E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	9.35E-07	
K_{zo} (m/s)	6.65E-07	
α_o (kmol/m^3)	3.20E-02	
α_{zo} (kmol/m^3)	0.013-0.045	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
69	3.04	3.07
134	4.96	4.80
194	5.51	5.47
334	6.61	6.13
460	7.62	6.40
793	9.31	6.67

Table G2 Comparison between experimental and predicted values of molar flux of Zn, using S6/2 type of fibre, 0.1M DEHPA and Re=17.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	3.96E-06	
K_H (m/s)	3.96E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	9.35E-07	
K_{zo} (m/s)	6.65E-07	
α_o (kmol/m^3)	0.061	
α_{zo} (kmol/m^3)	0.014-0.027	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
67	3.53	3.20
132	6.32	5.87
199	8.59	8.40
327	11.71	11.50
455	13.92	13.90
795	16.53	16.50

Table G3 Comparison between experimental and predicted values of molar flux of Zn, using S6/2 type of fibre, 0.15M DEHPA and Re=17.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	3.96E-06	
K_H (m/s)	3.96E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	9.35E-07	
K_{zo} (m/s)	6.65E-07	
α_o (kmol/m^3)	0.089	
α_{zo} (kmol/m^3)	0.0001-0.1	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
68	3.91	3.47
138	7.51	7.73
195	10.05	11.6
341	14.55	14.4
456	16.62	16.4
840	18.01	18.0

Table G4 Comparison betweenexperimental and predicted values of molar flux of Zn, using S6/2 type of fibre and 0.2M DEHPA and Re=17.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	3.96E-06	
K_H (m/s)	3.96E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	9.35E-07	
K_{zo} (m/s)	6.65E-07	
α_o (kmol/m^3)	0.118	
α_{zo} (kmol/m^3)	0.00001-0.11	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
67	3.91	3.73
133	7.49	7.73
197	10.68	12.0
348	16.8	19.2
465	20.4	20.3
803	21.03	21.1

Table G5 Comparison between experimental and predicted values of molar flux of Zn, using S6/2 type of fibre, 0.2M DEHPA and Re=5.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	2.64E-06	
K_H (m/s)	2.64E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	9.35E-07	
K_{zo} (m/s)	6.65E-07	
α_o (kmol/m^3)	0.118	
α_{zo} (kmol/m^3)	0.0001-0.195	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
134	5.15	5.6
201	7.51	8.72
331	11.58	11.9
465	13.11	13.1
815	13.65	13.6

Table G6 Comparison between experimental and predicted values of molar flux of Zn, using S6/2 type of fibre, 0.2M DEHPA and Re=45.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	5.51E-06	
K_H (m/s)	5.51E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	9.35E-07	
K_{zo} (m/s)	6.65E-07	
α_o (kmol/m^3)	0.118	
α_{zo} (kmol/m^3)	0.0001-0.07	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
131	9.96	8.54
202	14.41	14.7
332	20.85	22.9
465	25.53	25.6
780	27.82	27.7

Table G7 Comparison between experimental and predicted values of molar flux of Zn, using S6/2 type of fibre, 0.2M DEHPA and Re=71.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	6.43E-06	
K_H (m/s)	6.43E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	9.35E-07	
K_{zo} (m/s)	6.65E-07	
α_o (kmol/m^3)	0.118	
α_{zo} (kmol/m^3)	0.05-0.195	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
133	10.59	7.61
200	14.55	12.9
333	20.58	20.4
464	21.93	22.0
810	25.89	23.7

Table G8 Comparison between experimental and predicted values of molar flux of Zn, using Q3/2 type of fibre, 0.05M DEHPA and Re=50.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	11.9E-06	
K_H (m/s)	11.9E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	18.7E-07	
K_{zo} (m/s)	13.3E-07	
α_o (kmol/m^3)	3.20E-02	
α_{zo} (kmol/m^3)	0.01-0.048	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
67	7.84	4.93
134	12.48	12.3
192	15.18	15.2
328	17.21	15.5
469	18.19	15.6
810	21.48	16.5

Table G9 Comparison between experimental and predicted values of molar flux of Zn, using Q3/2 type of fibre, 0.1M DEHPA and Re=50.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	11.9E-06	
K_H (m/s)	11.9E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	18.7E-07	
K_{zo} (m/s)	13.3E-07	
α_o (kmol/m^3)	0.061	
α_{zo} (kmol/m^3)	0.045-0.085	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
68	7.83	7.73
137	15	15.2
195	18.82	18.5
337	25.71	25.2
458	29.71	29.9
800	36.55	41.5

Table G10 Comparison between experimental and predicted values of molar flux of Zn, using Q3/2 type of fibre, 0.15M DEHPA and Re=50.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	11.9E-06	
K_H (m/s)	11.9E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	18.7E-07	
K_{zo} (m/s)	13.3E-07	
α_o (kmol/m^3)	0.089	
α_{zo} (kmol/m^3)	0.05-0.1	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
67	9.73	9.46
138	17.65	17.9
196	22.92	22.5
334	29.49	29.2
463	34.44	34.0
798	43.89	46.5

Table G11 Comparison between experimental and predicted values of molar flux of Zn, using Q3/2 type of fibre, 0.2M DEHPA and Re=50.

$^{K}I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	11.9E-06	
K_H (m/s)	11.9E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	18.7E-07	
K_{zo} (m/s)	13.3E-07	
α_o (kmol/m^3)	0.118	
α_{zo} (kmol/m^3)	0.0001-0.165	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
66	10.95	14.0
132	20.49	21.7
196	27.19	26.5
329	34.08	33.6
460	38.22	38.4
813	49.74	49.5

Table G12 Comparison between experimental and predicted values of molar flux of Zn, using Q3/2 type of fibre,0.2M DEHPA and Re=15.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	7.93E-06	
K_H (m/s)	7.93E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	18.7E-07	
K_{zo} (m/s)	13.3E-07	
α_o (kmol/m^3)	0.118	
α_{zo} (kmol/m^3)	0.00001-0.065	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
132	14.41	17.5
201	18.19	18.1
332	26.29	18.7
460	32.55	19.7
825	45.01	21.2

Table G13 Comparison between experimental and predicted values of molar flux of Zn, using Q3/2 type of fibre, 0.2M DEHPA and Re=128.

$\kappa I\alpha$ (m/s)	3.95E-06	
$\kappa' I\alpha$ (m/s)	2.96E-05	
$K_{z\alpha}$ (m/s)	16.3E-06	
K_H (m/s)	16.3E-06	
C_H (kmol/m^3)	1.00E-03	
K_o (m/s)	18.7E-07	
K_{zo} (m/s)	13.3E-07	
α_o (kmol/m^3)	0.118	
α_{zo} (kmol/m^3)	0.06-0.17	

$C_{z\alpha}$ [ppm]	**R_z (x10^9) (kmol m^{-2} s^{-1})**	**$R_{z(exp.)}$ (x10^9) (kmol m^{-2} s^{-1})**
132	24.09	23.7
204	28.68	28.3
334	38.94	33.9
462	46.23	38.3
780	58.51	42.8

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