A Study of Copper Recovery by Liquid Membrane Containing a Chelating Agent

by

Ahmed Mohammed Edress

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
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This thesis, written by MR. AHMAD MOHAMMAD EDREES under the direction of his Thesis Committee, and approved by all its members, has been presented to and accepted by the Dean, College of Graduate Studies, in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

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وقل رب زدني علماً

إهـــداء

الخلاصـــة

ان عملية استخلاص الفلزات الثقيلة باستخدام الاغشية السائلة هي طريقة حديثة نسبيا وتستعمل على نطاق محدود صناعيا . وتتركز استخداماتها في معالجة فضـــلات المياه المتبقية من عملية غسل خامات المعادن المستخرجة من المناجم وذلك نظـــرا لكلفة معالجتها بالطرق الاعتيادية .

ويمكن تلخيص العملية بانها تزاوج بين خاصيه الفصل بطريق الانتشار وبيـــن التفاعلات الكيميائية المساعدة . وبصورة عامة يلزم لاتمام هذه العملية وجـــود عاملين كيميائيين احدهما هو عامل الحمل الكيميائي المذاب في مادة الغشاء السائـــل والاخر هو عامل الفصل الكيميائي المذاب في سائل مائي بدرجة تركيز معينة ، حيـــث يقوم الاول بالتفاعل كيميائيا فقط مع الايون الخاص المراد فصله ليكون مركبا كيميائيـــا قادرا على الانتشار في الغشاء السائل بينما يقوم العامل الثاني بتحرير الايون مـــن المركب عن طريق تفاعل كيميائي معاكس .

لذا فان اهم الاغراض الرئيسية لهذا البحث هي : اولا التركيز على دراسة فصـــل ايونات النحاس كمثال للفلزات الثقيلة باستخدام الاغشية السائلة المحتوية على عامـــل حمل الايونات الكيميائي ، بالاضافة الى دراسة بعض اهم العوامل المؤثرة على عمليـــة الفصل المذكورة . وهذه العوامل هي : التركيز الاولي لايونات النحاس ، وايضا عمليـــة تركيز عامل الحمل الكيميائي بالاضافة الى دراسة تاثير زيادة فعالية سرعة المزج فـــي السوائل على عملية الفصل . وقد تم تصميم جهاز خاص لاجراء التجارب المعمليـــة اللازمة لتحقيق الاغراض السابقة .

ويمكن تلخيص اهم النتائج المستقاة من هذه التجارب كالتالي :

(١) بالنسبة لعملية الفصل الاولية فيمكن تمثيلها على مرحلتين : الاولى هي عمليـــة انتشار ايونات النحاس خلال السائل الابتدائي (مائي التكوين) حتى قرب السطح الفاصل بينه وبين الغشاء السائل (عضوى التكوين) وعندها تبدأ المرحلـــة الثانية الخاصة بالتفاعل الكيميائي المشابه لتفاعلات الدرجة الاولى وذلك بيـــن ايونات النحاس وبين عامل الحمل الكيميائي حيث ينتج المركب الكيميائي الـــلازم لانتقال الايونات الى داخل الغشاء السائل .

(٢) بالنسبة لعملية الفصل المعاكسة (النهائية) فيمكن تفسيرها على انها تتأثر ايجابيا بوجود بعض الاسطح النشطة والمنتشرة بتوزيع متعادل على السطح الفاصل بين الغشاء السائل وبين السائل المائي المحتوى على عامل الفصل ، حيث يحدث على هذه الاسطح التفاعل الكيميائي المعاكس والمشابه لتفاعلات الدرجة صفر واللازم لتحرير الايونات من الغشاء السائل . وبناء على النتائج المعملية يمكن افتراض ان هذه الاسطح تتزايد طرديا مع ازدياد التركيز الاولى لايونات النحاس .

(٣) اما بالنسبة لتركيز النحاس في الغشاء السائل فيمكن تمثيله بالمرحلة الانتقالية في اى تفاعل كيميائي متسلسل بسيط .

كما امكن بواسطة النتائج المعملية تصنيف عوامل الحمل الكيميائية المستعملة في هذا البحث بالنسبة لتاثيرها على عملية الفصل الاولية وكذلك بالنسبة لقدرتها على استرجاع الايونات بعد عملية الفصل النهائية .

واخيرا امكن من خلال هذا البحث رسم خطوط التعادل التي توضح توزيع تركيز ايونات النحاس بين الغشاء السائل وكل من السائل المائي الابتدائي والسائل المائي المحتوى على عامل الفصل الكيميائي . كما تم ايضا اجراء تجربة بسيطة لقياس معامل انتشار ايونات النحاس في السائل المائي الابتدائي .

DEDICATION

This thesis is dedicated to:

My beloved parents:

My father: Mr. M. Edrees

My mother: Mrs. S. Zu'aiter

and

To the peopel I care about ....

ABSTRACT

The liquid membrane process is being used in a small commercial scale for the recovery of copper and other heavy metals from mine waste waters, specially from leach solutions. The process used to give pure concentrated solutions which are suitable as a feed to a convetional tankhouse to recover equivalent grade of metals to those produced by solvent extraction.

This study is concerned with the copper recovery by unsupported liquid membrane containing a chelating agent. The objectives of this research study are:

1) To study the transfer process of copper ion across a liquid membrane containing a chelating agent.

2) To investigate the parameters that affect this transfer process. The investigated parameters are; copper concentration in feed solution, mixing speed, and the chelate concentration in the liquid membrane phase. The data obtained were then interpreted in terms of above variables.

In this study an experimental setup was designed specially for copper recovery by LIX reagent-containing membranes. Most of the work was devoted on utilization of LIX64N reagent as a cation carrier, dissolved in kerosene at different concentrations. Different quantities of $CuSO_4$ were dissolved in deionized water to form variety of feeds.

The copper concentrations in the aqueous phases were analysed by

an Atomic Adsorption Spectrophotometer. The amount of copper complex in the organic phase can be calculated from mass balance of copper.

Results show briefly that, the extraction process of copper can be modeled in terms of series resistances; first mass transfer resistance due to diffusion of copper ions in bulk of aqueous phase and then, kinetic resistance due to pseudo first order reaction (extraction reaction) at the interface. Based on results also, the stripping process is modeled in terms of active sites distributed evenly at tthe other interface. The number of active sites is assumed to be related to the feed concentration while the stripping reaction is consedered under pseudo zero order reactin rate. In addition, the copper concentration appeared in the organic phase is modeled as the intermediate product of a series reactin.

Furthermore, the chelates studied were classified in terms of their performance with copper extraction rate alone, and with respect to their effectiveness on the overall process of copper recovery based on the maximum copper yeild obtained from experimental results. Explanations due to changes in copper feed concentration and changes in mixing speed were also given.

Finally the equilibrium data of copper distribution betweem the aqueous phases and the organic phase, for the chelates used, were obtained. In addition a simple diffusion experiment to obtained the diffusion coefficient of copper in aqueous feed was performed in a Diffusion Cell unit.

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The author is indebted to all department lab technicians for their helps and to the Instrument Workshop people, specially Mr. Mehdi A. Safar, Mr. Ibrahim A. Salem and Mr. John Chapman for their helps in apparatus construction. He is also indebted to the Chemistry Department , specially Mr.Martin Dawson the Atomic Adsorption Spectrophotometer expert for his valuable helps in sample analysis.

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THE CONTENTS

I. INTRODUCTION

A substantial number of the unit operations of chemical engineering are concerned with the problem of changing the compositions of solutions and mixtures through methods not necessary involving chemical reactions. Usually these operations are directed toward separating a substance into its component parts. For mixtures, such separations may be entirely mechanical, e.g., the filteration of a solid from a suspention in a liquid. On the other hand, if the operations involve changes in composition of solutions, they are known as the mass-transfer operations.

The chemical engineer faced with the problem of separating the components of a solution must ordinarly choose from several possible methods. While the choice is usually limited by the peculiar physical characteristics of the materials to be handled, the necessity of making a decision nevertheless almost always exist.

The principal basis for choice in any case is cost: a method which costs the least is usually the one to be used. Occasionally, other factors also influence the decision, however. The simplest operation, while it may not be the least costly, is sometimes desired because it will be trouble-free. Sometimes a method will be discarded because of imperfect knowledge of design.

In that respect, technical interest in the processes of mass transfer through membranes has increased greatly in the last years. This is particularly true for separating or enriching materials from

gaseous or liquid mixtures by means of solid or liquid membranes. Compared with conventional separation processes, the membrane processes are characterized by the following properties:

1) They are technically simple;
2) They are characterized by high efficiency in small equipment;
3) In the case of solid membranes, the components to be separated are neither chemically altered nor subjected to thermal effects.

The broadest definition of a membrane is: a region of discontinuity interposed between two phases.

This statement implies that membranes can be gaseous, liquid or solid or combinations of these phases. The term "region" in the definition is used to eliminate ordinary interfaces. Thus, the interface of two immiscible liquids for example, would not ordinarily considered as membrane structure.

An example of gaseous membrane would be a front of a shock wave. So far, at least, no one is aware of any instance where this gaseous membrane has been used successfully for separation. Other known examples of membranes are porous solids and the recently developed liquid membranes, which will be discussed in details in the forthcoming chapters.

Separation in membrane processes is the result of different transport rates of various chemical species, under one or more driving forces, through the membrane phase. Driving forces in membrane separation processes result from differences in (a) hydrostatic

pressure, (b) chemical or electrochemical potential, or (c) tempereture between two subsystems separated by the membrane.

In membrane separation the driving force of a concentration gradient not only may result in a flow of matter but also can cause the buildup of a hydrostatic pressure gradient, a phenomenon refered to as "OSMOSIS".

Analogously a hydrostatic pressure gradient not only may result in a volume flow but also can lead to the buildup a concentration gradient, refered to as "REVERSE OSMOSIS".

A gradient in the electrical potential across a membrane may lead not only to an electrical current but also to a transport of matter, as in "ELECTRODIALYSIS," or to the buildup of a hydrostatic pressure gradient, refered to as "ELECTRO-OSMOSIS".

A temperature gradient across the membrane not only creates a flow of heat but also can result in a flow of matter. This process is called "THERMO-DIFFUSION". In contrast a mass flow due to concentration gradient may cause a temperature gradient. This phenomenon is referred to as the "DUFOUR EFFECT".

Furthermore, the transport of certain components can also be as a result of a kinetic interaction with the flow of other components, referred to as "CROSS or COUPLING EFFECTS," which are mainly encountered in liquid membrane processes. In the membrane separation processes driving forces such as gradients in the hydrostatic pressure, in the concentration, and in the electrical

potential, are of practical importance.

The membrane separation technology is found of promising feature in industry. The incorporation of chemical reaction and diffusion process in the liquid membrane system, has attracted attention of scientists in recent years.

The use of liquid membranes for hydrometallurigical recovery of metal ions has recently aroused considerable interst. For example, copper ion can be extracted from leach liquors of various feed using liquid membrane. In this case solvent extraction of copper ion is achieved by an organic phase. Copper can be transfered into an aqueous phase which may be used as the electrolyte for electrowining the metal. This method can also be used for recovery of other heavy metal ions.

In order to apply this method of separation in hydrometallurgy and other industrial purposes, more research work is needed to ease possible engineering difficulties, and with this noble aim the topic of this experimental project was chosen.

II. LITERATURE SURVEY

The review of the literature in the area of copper extraction by liquid membrane with chelating agent presented in this chapter, is divided into two sections. Section II.1 is confined to liquid membranes in general and those containing chelating agent in particular. Major commercial chelating agents being utilized in the area of heavy metals recovery are also discussed, whereas, section II.2 deals with the contributions in the specific area of copper recovery by liquid membrane enclosing a chelating agent.

II.1 LIQUID MEMBRANE

The proper definition of liquid membrane is " a liquid phase separating two other phases in which the membrane phase is immiscible ".

In general, it can be said that liquid membranes are pore-free membranes. A meterial which is to pass through a pore-free membrane must dissolve in this membrane on one side,diffuse across it and then to reverse the dissolution process to appear in the third phase. Such a mass-transport process is independent of the geometry of a membrane. The geometry governs only the rate with which the final state is reached. The thinner the membrane the more rapid the mass transport will be.

The idea of separation by liquid membrane dates back to late 1963, when Martin (1) discovered the first successful liquid membrane during his study of desalination by revers osmosis. In that study, a

few ppm of PVME added to the saline feed was capable of forming a membrane at the interface between a cellulose acetate membrane and a saline solution. A tremendous increase was noted in permselectivity accompanied by a small decrease in flux. The explanation of the increased permselectivity was given by Kesting (2) based on the hypothesis of the existence of liquid membrane. Liquid membranes can be fashioned in two physical forms; immobilized on a solid support (supported liquid membrane) and an emulsion liquid membranes (ELM) (Fig.1).

The liquid membrane discovered by Martin is a good example of liquid membrane on solid support. The membrane phase can be supported by various forms of porous solids. In this regard the liquid layers are stabilized by capillary and surface forces. Thus for instance the membrane phase can be absorbed on a diaphragm of glass,clay or paper (3,4) In this case the mass-trnsport process depends both on the pore size of the solid support, and the solubility of the desired solute in the liquid membrane phase.

The unsupported liquid membrane (ELM) could be used in three different modes. The modes will be discussed in detail in the forthcoming paragraph. However, the formation of the ELM needs to be described first to clear the picture of separation by this method.

As mentioned before, thinner membranes are required for rapid mass-transport process. Therefore the ideal arrangement of a membrane would be a thin skin stretched at its boundaries. However for the liquid, this state is quite unstable. Spherical surfaces which

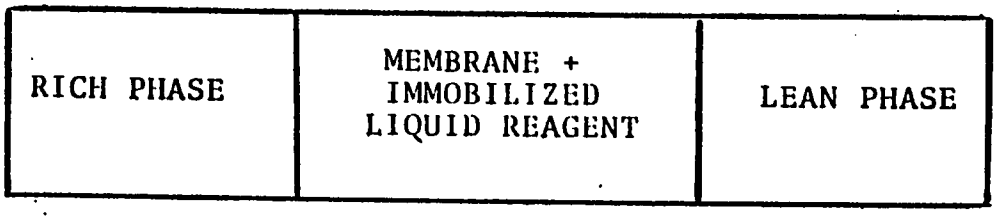


Fig.1.a Immobilized Liquid Membrane Type

Fig.1.b Emulsion Liquid Membrane Type

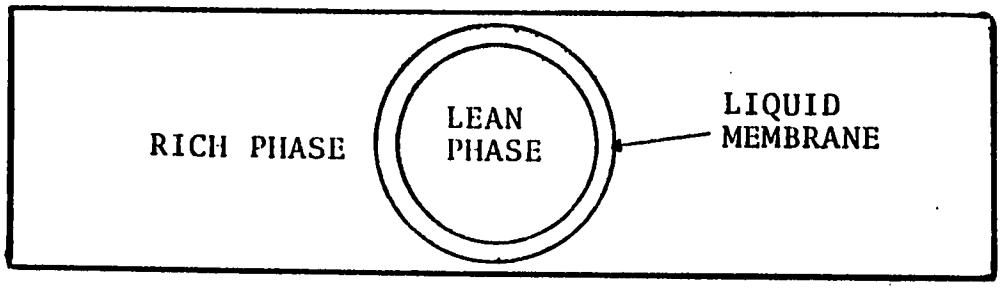


Fig.1 THE TWO FORMS OF LIQUID MEMBRANES

are encountered in ELM are particularly important, from stability point of view.

The ELM is created by first emulsifying two immiscible phases, and then dispersing the emulsion into a third phase (the rich phase, see Fig.1-b). Usually, the feed phase, and the encapsulated (lean) phase are miscible. The feed phase and the membrane phase must not be miscible if the emulsion is to remain stable. The liquids, immiscible with each other that one comes across in membrane technology are usually water and oil; stabilization in this case is frequentely effected by means of a surface-active material or emulsifier.

The formation of an emulsion is due to reduction of the interfacial tension between the two immiscible liquids. The addition of emulsifier causes this desired reduction. The requirement for such a material is that an interaction must occur both with water and with oil. In other words it must have an amphiphilic molecular structure. One part of the molecule must be of nonpolar structure (lipophilic part). The hydrophilic part of the emulsifier molecule then resides in water, while the lipophilic part in the oil. In general the emulsifier dissolves better in one of the two liquids whose surface tension is strongly reduced. On the other hand, the possibility of droplet formation exists in other liquid phase. The consequence of this physical effect is a curvature of the interfacial film formed by the emulsifier. In the mechanical treatement of such system,e.g., by stirring, the phase with the higher surface tension will appear in the form of core of droplet, while the phase in which the emulsifier dissolves better will form the outer

layer of the droplet (Bancroft's Rule) (5).

The emulsion can be of the oil-in-water form or the water-in-oil. If water forms the inner (dispersed) phase, we speak of a " water-in-oil" emulsion and if oil forms the inner phase, we speak of an "oil-in-water" emulsion. Therefore if a water-in-oil emulsion is introduced into an aqueous medium a multiple emulsion of water/oil/water is obtained and visa versa.

When the multiple emulsion is established, globules of emulsion are formed which are stable and do not disintegrate. Their sizes depend on the nature and concentration of the surfactant (emulsifier) in the emulsion, the emulsion viscosity and the mode and intensity of mixing. Normally, the size is controlled in the range of (0.1—5.0) mm diameter. Each emulsion globule contains many tiny encapsulated droplets with a typical size range of (1—10) μm in diameter (Fig.2). A large number of gloubles of emulsion can be formed to produce a correspondingly large membrane surface area; increasing the rate of mass transfer from either the feed phase to the encapsulated phase through the liquid membrane or visa versa.

Figure 3 shows the three major transport mechanisms occuring in the liquid membrane. The description of these principal mechanisms follows:

1) The selective permeation (Fig.3.a) is the simplest separation mechanism, which depends solely on the differential permeation rate through the membrane. This mechanism has been utilized successfully

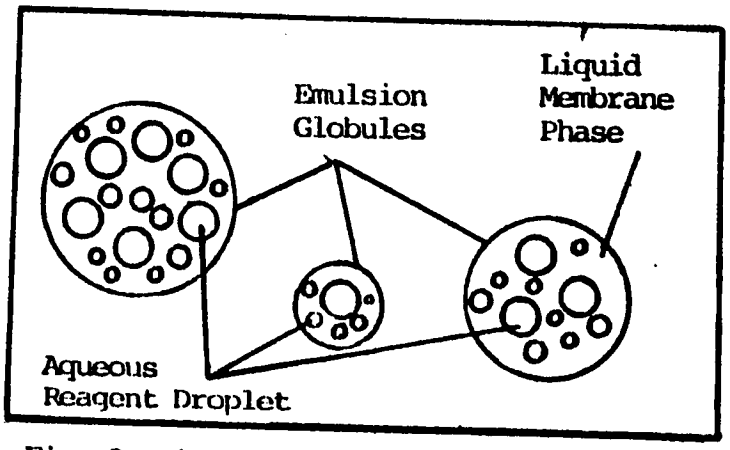
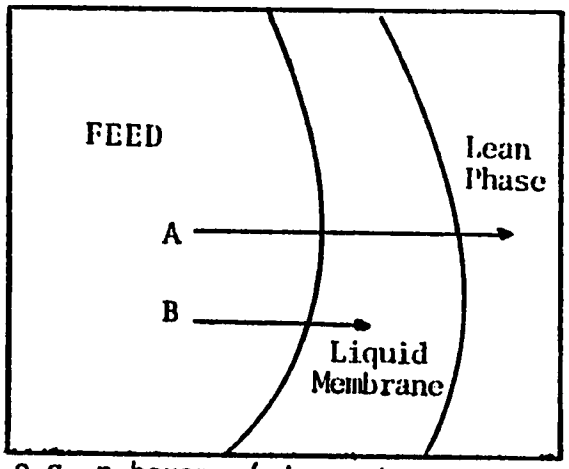


Fig. 2. Dispersion of Liquid Membrane Emulsion

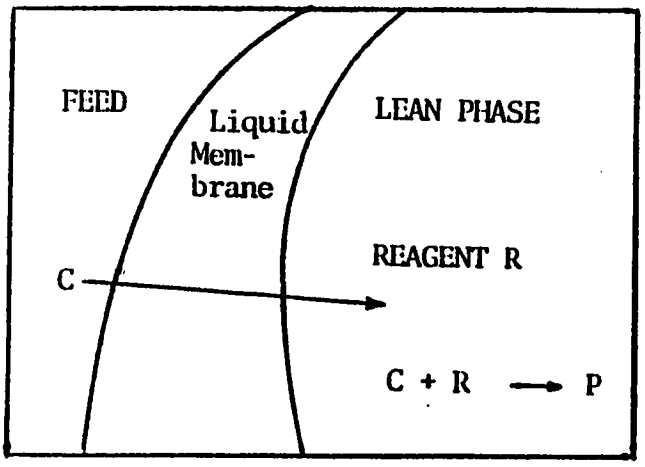
MECHANISMS OF SEPARATION BY ELM

Fig.3.a 1. Selective Permeation



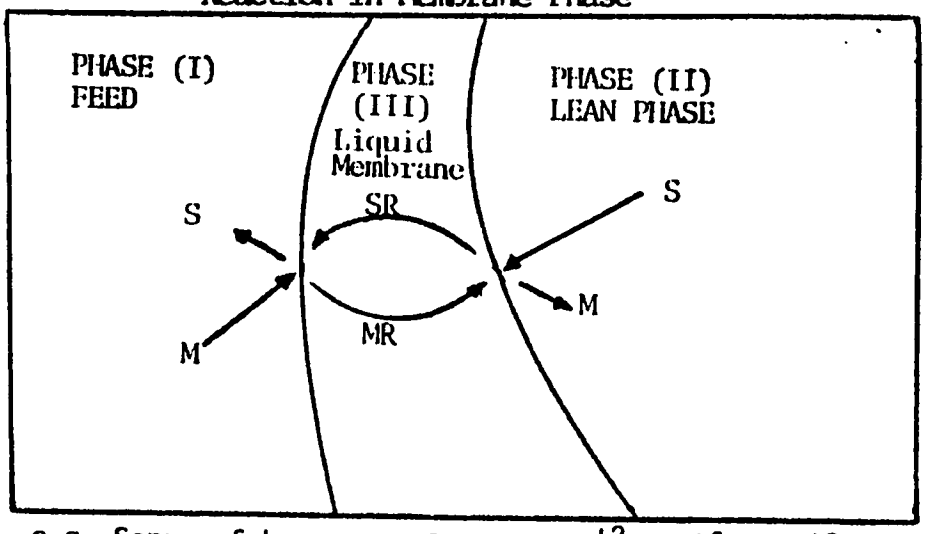
e.g. n-hexane (mix. n-hexane/benzane)

Fig.3.b 2. Chemical Reaction Inside Droplet



e.g. Phenol removal (NaOH Phenolate)

Fig.3.c 3. Chemical Reaction in Membrane Phase



e.g. Sepr. of heavy metal ions: Hg^{+2}, C_i^{+6} & Cu^{+2}
(Carrier)

Fig. 3 VARIOUS LIQUID MEMBRANE MECHANISMS.

in the separation of hydrocarbon. Halwachs et.al. (6) applied it in the separation of n-hexane from a mixture of n-hexane/benzene using a Single-Drop Extraction Column.

2) The second mechanism (Fig.3-b) improves significantly the separation rates and selectivities by encapsulating reactive species inside the membrane microdroplet (lean solution) which converts the extracted species into nonpermeable derivatives. For example, encapsulated aqueous bases have been used to trap acidic compounds (7) and vica versa (8). Li et.al (7) utilized this mechanism in phenol separation by encapsulating NaOH species into the lean solution which converted the transferred phenol into the nonpermeable phenolate compound.

3) The third mechanism (Fig.3-c) provides further improvements in transport rates by the incorporation of a transport facilitator or "cation carrier" in the membrane phase itself.

Cation carriers are ligands which serve to solubilize cations in non-polar solvents allowing the diffusion of a cation-carrier complex across the membrane phase. From the process engineering point of view, the carrier can be regarded as a "TRANSPORT CATALYST". The carriers are named chemically as "CHELATING AGENT". As shown in figure(3-c) the two solutes M and S in this process are transported in opposite directions with the following steps occuring:

a) Solute M diffuses to the membrane phase and reacts at the first boundary with the complex SR. As a rersult the solute S is liberated

in phase(I) and the coplex MR is formed.

b) Complex MR then diffuses to the other side of the membrane phase.

c) At the second boundary MR reacts with solute S to form complex SR , as a result of which solute M is liberated in phase(II).

d) Complex SR then diffuses back through the membrane phase, and so the carrier cycle is closed.

If we consider solute M as the metal ion in the feed (phase I), solute S as the stripping agent in the lean phase (phase II), and R as the cation carrier in the membrane phase (phase III),
hence we can say that the carrier binds the metal ions at the "feed-membrane" interface under the extraction reaction, and releases them at the "membrane-lean phase" interface under the stripping reaction.

The main requirement for this type of transport mechanism is the carrier to react competitively with two simultaneously diffusing solutes. An excess amount of solute S in the system leads to a complete separation of solute M to the lean phase. This means that due to transport of solute S from phase II to phase I by its concentration gradient, solute M can still be transported in the opposite direction even against its concentration gradient. This process of transporting mass against its concentration gradient is termed "PUMPING". Therefore solute M is cosidered here as the pumped solute, while solute S as the energy supplier for the pumping process. In this respect Cussler (9) defined the metal ions separation process by ELM

to be unlimitted by equilibrium .

In practice this technique has been used successfully for the separation of oil-insoluble materials, such as heavy metal ions like, Hg^{+2}, Cr^{+6}, Cd^{+2} (8) and of special interest to this research the Cu^{+2} ion (10). The copper extraction by ELM enclosing a chelating agent (carrier) is shown in figure 4. Some typical results of metal ion extractions, which serve to illustrate the versatility of this method are shown in figure 5 (8).

The extraction mechanism of heavy metal ions by ELM have been studied by Cussler et.al(9). In the copper extraction (Fig.4), two possible reactions may occur at the membrane boundaries (i.e.,liquid membrane--aqueous interfaces). The two chemical reactions can be expressed as follows :

1) The extractoin reactoin (i.e., feed—LM interface):

$$2\ RH + Cu^{+2} \rightleftharpoons R_2Cu + 2\ H^+$$

2) The stripping reaction (i.e., LM—lean phase interface):

$$2\ H^+ + R_2Cu \rightleftharpoons Cu^{+2} + 2\ RH$$

where:

RH: represents the chelating agent or the stripping agent-carrier complex, and

R_2Cu: represents the cation-carrier complex.

The utility of this separation mechanism, in fact, is limited by the ability to find suitable cation carriers. In this respect the following

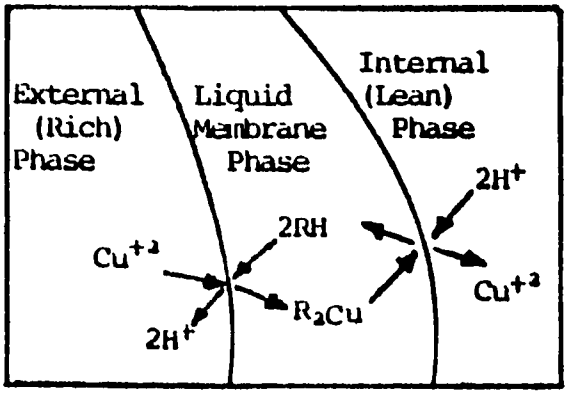


Fig. 4. The Mechanism of Copper Transport in Emulsion Liquid Membrane.

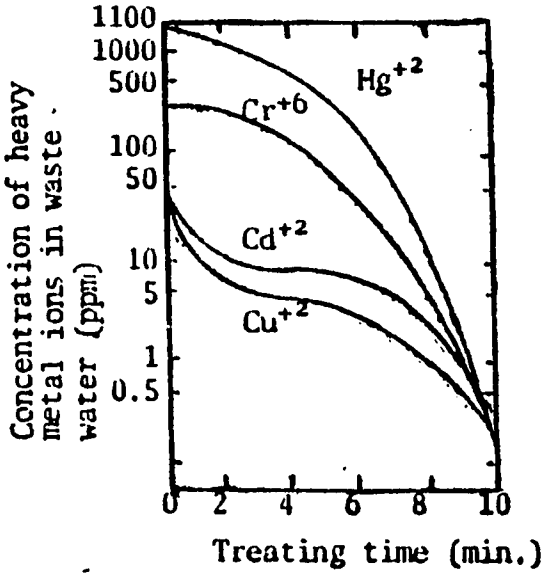


Fig. 5. Metal removed by Liquid Membrane

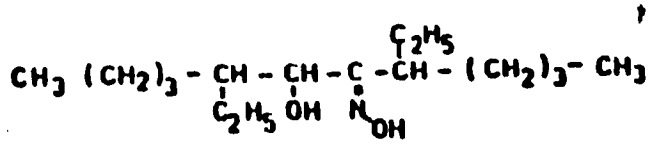
characteristics are necessary for ligand to qualify being a membrane carrier.

1) It must be soluble in the membrane phase, and insoluble in extraction or stripping phase.

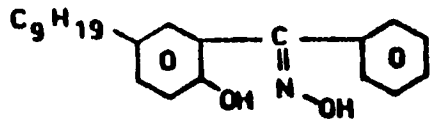
2) It must complex the cation strongly enough to overcome the cation's energy of hydration (chance of hydroxide formation) at the feed-membrane interface, and yet not so strongly that it will not release the cation into the stripping phase.

3) It must diffuse rapidly through the membrane phase.

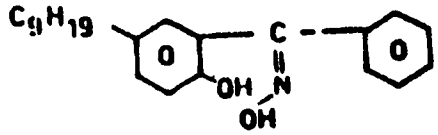
In the case of carriers for copper ion, both aliphatic and aromatic oximes have been used and the patent literature is indeed extensive and receiving tremendous attention (Fig.6). The most well known aliphatic and aromatic oximes have the trade name of LIX-reagents created by General Mills such as LIX63N, LIX65N and LIX64N and the latest is a mixture of LIX63N and LIX65N. In the case of LIX65N, both anti-and-syn isomers exist, but only the former is active (11) (Fig.6-b & c). The Shell company has been developing a class of selective copper extractants with the general formula of (Fig.6-d). The o-hydroxyaryl oxime with the general formula of (Fig.6-e), has been suggested by Price and Tumilty (11). Modifications, such as variation of R, R', X, etc., for the substituent in the aromatic ring of LIX65N for example, have been suggested for improved selective performance (11,12). Derivatives of quinoline have been used as



(a) 5,8-diethyl-7-hydroxy-dodecan-6-one-oxime
(Trade name LIX 63N)

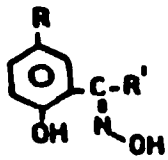


(b) 2-hydroxy-5- nonylbenzophene oxime
(Trade name LIX 65N) (anti-form)

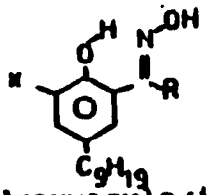


(c) LIX 65N (syn-form)

Fig.6-a, b & c. The Lix-reagents (General Mills)



(d) 5-alkyl-2-hydroxyphenyl alkyl ketone oxime
(Shell)



(e) o-hydroxyaryloximes
(X may be C_5H_{11},H,Br etc.)

(Trade name SME 529, R = C_9H_{19} & R' = CH_3)

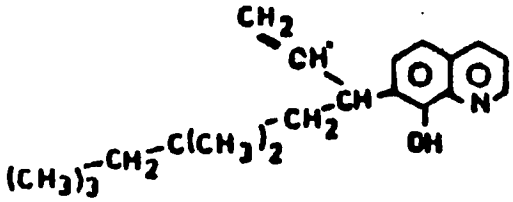
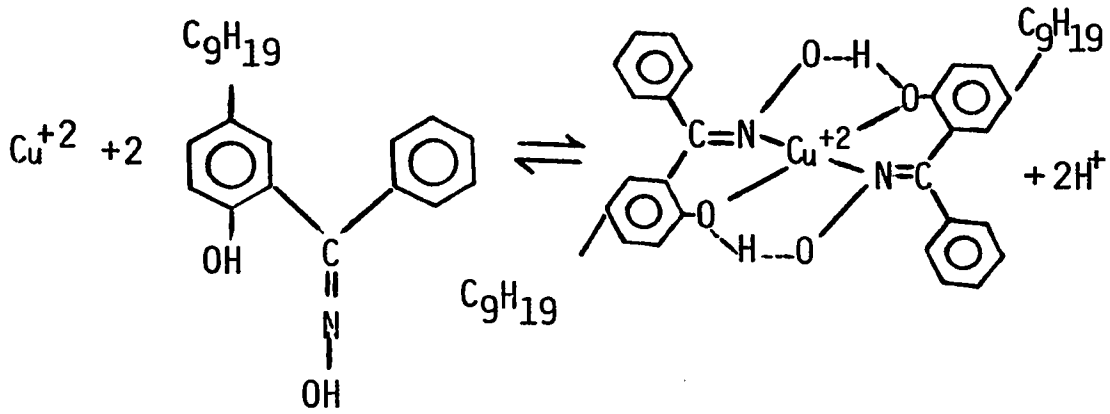


Figure 6-f.7-alkenyl-8-hydroquinoline
(Trade name KELEX 100) (Ashland)

Figure 6. Miscellaneous oxime-type extractants for the solvent extraction of metals

chelating agents for copper extraction. The most well known is 7-alkeyl-8-hydroquinoline by Ashland Company, with the trade name KELEX 100 (Fig.6-f) (13).

In all the chelating agent utilized in heavy metals extraction the presence of "N" and "O" atoms plays a dominant role in the separation mechanisms (see Fig.6, for formulas). This is due to their ability to provide unshared pair of electrons for metal ion binding as shown in the following reaction for Cu^{+2} extraction with LIX65N.



Furthermore the presence of cation-carriers in the liquid membrane phase affect its physical characteristics. Some investigations in this regard have been described earlier in literature (8), and in the proceeding sections further information about properties of liquid membranes containing a chelating agent is given.

II.1.1 The Nature of The Organic Phase

It is well known that the commercial extractants (carriers) of the hydroxyoxime type are relatively impure materials. Major impurities are chemicals such as nonyl phenol employed during the synthesis

(14). In addition to possible minor impurities which could be surface active, there may exist the syn-and-anti oxime isomers, but these have been differentiated only for the LIX65N and LIX63N chemicals.

The presence of impurities make the interpretation of the kinetics of chemicals (as received) difficult. Table-1 gives the oxime content in (wt%) as delivered (commercially) and after purification (15).

II.1.2 Viscosity of Organic Phase

The viscosities do not change dramatically as the various extractants are loaded into diluents (liquid membrane-solvents) up to 30 % V/V (16). Hanson et. al. (15) did not record any substantial increase in viscosity of the bulk organic phase as copper is loaded into the phase. Unfortunately, the organic phase bulk viscosities do not necessarily represent the viscosity of the interface.

II.1.3 Interfacial Tention

Hanson et.al. have also measured the interfacial tension of some oxime systems at 28 ^{o}C (17). The results showed that for certain oximes, organic phase interfacial tension depends on pH value, and this is ascribed to salt formation at high pH values and to oxime protonation at low pH values, both processes leading to ionized species at the interface. The affinity of the oximes for acids can be ordered as follows (18),

$$LIX63N > SME529 > P17 \backsim LIX65N\ anti \backsim LIX65N\ syn.$$

Hanson et.al. have confirmed that LIX65N is more interfacially active if

TABLE - 1

OXIME ANALYSES BY ULTIMATE LOADING OR BY NON-AQUEOUS TITRATION, BASED ON NOMINAL MOLECULAR WEIGHTS

Reagent as delivered	Oxime content (wt %)
LIX 64N (ID 1502)	34.1 (syn) 4.8 (LIX 63) 1.75
LIX 65N (4B19214)	36.4 (syn) 4.8
LIX 63 (3D 10025)	24.9
SME 529	47.4
P 17	57.0
P 50	92.1

Reagent as Purified	Oxime content (wt %)
LIX 65N anti	99.0 (total) (syn) 3.4 to 10.9
LIX 65N syn	100.3
LIX 63	97.5
SME 529	97.1
P 17	101.0
P 50	100.9

dissolved in hexane than in toluene, and that LIX63N is less interficially active than LIX65N.

II.1.4 The Solubility in Aqueous Phase

The solubility of the purified oximes in an aqueous phase can be measured readily by turbidometric titration technique (19). Solubilities at 25° C of the oximes in an aqueous phase of 1.78 pH are presented in table 2 (15).

TABLE - 2

SOLUBILITIES OF PURIFIED EXTRACTANTS AT 25°C IN AN AQUEOUS PHASE OF pH 1.78

Reagent	Solubility		Reagent	Solubility	
	ppm	(mol dm^{-3})		ppm	(mol dm^{-3})
LIX 65N anti	0.33	1.0	SME 529	0.84	3.0
LIX 65N syn	1.03	3.0	LIX 63	4.2	15.5
P 17	0.36	1.0	Nonyl-phenol	7.8	35
P 50	1.78	6.8	Cu (LIX 65N)$_2$	0.10	0.13

As shown in the table the LIX63N oxime is noticeably more soluble than the β-hydroxyoximes among which there is a trend of decreasing solubility with increasing molecular weight.

The partition coefficients of the oximes between organic solvent and aqueous phases are more difficult to measure. Only the P50 oxime, has been successfully studied so far (19). Its partition coefficient is given by,

$$P_{HR} = \frac{[P50\ monomer]_{org}}{[P50]_{aq}}$$

and was determined as 1.08 $\times 10^4$ for n-heptane/water. It was shown by Hanson et.al. (15), that the species present in the aqueous phase is monomeric. The organic monomer concentration is all-important in the rate model.

II.1.5 Mechanism of Copper Extraction

One initial problem in deciding on a mechanism for copper extraction is to ascertain the relative importance of the chemical against the diffusional resistances. It is possible that a knowledge of the activation energy will indicate the relative importance of the two resistances. Unfortunately, several workers (20-24) reported different values for the activation energy depending on the techniques chosen for kinetic study, the organic solvent and the concentration range of the reactants. The results are summarized in table 3 (15).

TABLE - 3

DEPENDENCE OF RATE ON TOTAL OXIME CONCENTRATION AND ON TEMPERATURE: APPARENT ACTIVATION ENERGIES (kJ mol^{-1})

Diluent	Oxime concentration	Apparent order (LIX 65N)	Activation energy (LIX 64N)
Chloroform	Low and commercial	1.0-1.3	19
Toluene	Low	1.0-1.3	15
Xylene	Intermediate	0.5	25
Escaid 100	Commercial	0.5	45

Hanson et.al. (15) have obtained that the low diffusional activation energy characterise the extraction of copper by the monomeric oxime. Even with high concentrations of organic copper, a low activation energy (15 Kj mol^{-1}) (15) is observed indicating a diffusion control. It might be noted here that in a study where the LIX-reagent was supported on a solid substrate a diffusion control was observed (25).

The diffusion process involves both the aqueous species and the organic species. The diffusivity of copper in aqueous phases have been reported as 0.5×10^{-5} cm^2/sec (26), and since $D_{Cu(org)} < D_{Cu(aq)}$. Therefore, it may be concluded that there is a chemical reaction accompanied by diffusion phenomena (15). The precise location of this reaction can not be stated exactly, but it could be estimated in a zone on the aqueous side of the interface. It has also been shown by Hanson that oximes do exist in aqueous phases at finite concentrations.

For the overall copper extraction reaction of the form,

$$2\ RH + Cu^{+2} \rightleftharpoons R_2Cu + 2\ H^+$$

The overall equilibrium constant is given by,

$$K = \frac{[R_2Cu]\ [H^+]^2}{[RH]^2\ [Cu^{+2}]}$$

Possible reaction mechanisms were proposed by different workers (15,21). However, in all the studies, the rate determining step has not been determined for definite. This may be due to the presence of

impurities in chelates and the lack of proper methods of measurements..etc.

II.2 EXPERIMENTAL AND MODELING STUDIES OF COPPER RECOVERY

Many recent experimental studies have described the transport of Cu^{+2} ions through both supported and emulsion liquid membrane. The mixer settler system and the single drop technique in extraction column, are the two main units utilized in the field of copper recovery by ELM. However, the experimental data and hence the results being reported in literature vary tremendously among researchers. This is propably due to the following reasons:

1) Insufficient homogeneity of emulsion droplets dispersion in the continous phase.

2) Lack of uniformity of droplet sizes

3) Chances of droplet break ups during separation

4) The effect of surfactant (emulsifier) concentrations on the rate of copper extraction.

Amongs the important studies, Martin and Davies (27), performed an experimental work on copper separation by ELM from dilute aqueous solutions. The process was shown to work effectively with solutions ranging in concentrations from 2000 ppm down to 100 ppm of Cu^{+2} as copper sulphate. In the case of the least dilute solutions, the copper

concentration in the final rafinate could be taken down to < 1 ppm. The chelating agent utilized in this study was SME 529(Shell product). Factors influencing the mass transfer, such as membrane composition, the organic/aqueous ratio, the pH values of the feed and stripping solutions, and contacting conditions have been studied. Provided that membrane droplet breakups were low, the extraction process has been represented by "pseudo first order rate".

Compared with conventional liquid-liquid extraction, the amount of solvent (chelate diluent) required is very much reduced. It has been shown in this study that successful extraction of copper can be achieved using over two order of magnitude less solvent than with solvent extraction.

Hughes and Middlebrook (28), conducted an experiment to study the importance of organic phase diffusion in the solvent extraction of copper by ELM containing LIX64N. To remove the hydrodynamic effect, a static diffusion cell was used in the study. An aqueous copper solution of 4.94 g/lit $CuSO_4$ (1300 ppm Cu^{+2}) and 5.26 g/lit acid content is contacted with 5 % V/V of LIX64N solution diluted in Escaid 100. The concentration-distance distribution of the diffusional band of copper complex in the organic phase was measured at various times, and the results were modeled by equations based on diffusion about an interface with and without interficial resistance. The diffusion constant of copper in the aqueous phase was estimated to be 5.2×10^{-6} cm^2/sec and in the organic phase as 2.0×10^{-6} cm^2/sec. Finally, the workers proposed that as the organic product film

developed, the diffusivity of the copper complex is reduced.

Volkel et.al. (29) studied the copper extraction from dilute solutions by ELM using a mixer settler system. The LIX64N was used as chelating agent and H_2SO_4 as stripping agent. Feed solutions of 1000 ppm down to 100 ppm copper concentrations as $CuSO_4$ were processed. A removal up to 98% of Cu^{+2} was achieved in 30 minutes in batch operations. In the stripping phase, the Cu^{+2} ions could be enriched up to 500:1 ratio.

A theoretical model was presented which adequately described the kinetics of carrier-mediated copper removal by means of ELM based on diffusion control and instantaneous sorption (adsorption/desorption) process. Mass transfer coefficients ($k_l a$) were determined and found to range from 10^{-4} to 10^{-3} sec^{-1} within experimental conditions.

Frankenfeld et.al. (30), studied the important variables governing the permeation of Cu^{+2} ion through liquid membrane and their effects on the separation process. The liquid membrane phase consisted of 2.5 wt% of nonionic polyamine (surfactant), 2.5 wt% LIX64N and 95 wt% S100N the isoparaffine solvent. The stripping solution was H_2SO_4 solution of 20 % V/V ratio in deionized water. The variables studied were membrane viscosity, treatment ratio (emulsion/ feed volume ratio) and chelating agent concentration in the membrane phase. The information obtained was used for scaling up equipment and further process development. The economic evaluation based on bench-scale pilot plant runs showed that the process is 40% cheaper than solvent extraction.

A more recent experimental study by Hatton et.al. (31) was confined to mass transfer characterization with ELM using an Internal Recycle Mixer (Fig.7).

With this device, the solvent-to-feed ratio was proposed to be enhanced without the introduction of an external recycle stream. In the study the device was tested on, and found to be effective for the extraction of ammonia from water using ELM system.

A detailed model of the mass transfer processes occurring within the system was presented and used to develop an equation suitable for the sizing of liquid membrane contactor. The equation accounted for the effect of the internal reagent on the overall mass transfer rate.

The simplest type of model which can be used for charactrization of the mass transfer processing occurring in a mixer is the "D' Model" of Cahn and Li (1974). The model implicitly assumes that the emulsion globules are internally well mixed and that the mass transfer rate is directly proportional to the difference between the solute concentrations in the feed solution and the globule.

Based on the "D' Model", Hatton et.al. in the subsequent study developed the "Advancing Front Model" (Fig.8) (31) to explain the effects of different operating variables encountered on the experimental data obtained which could not be interpreted by the previous simple model.

The basic assumptions underlying the development of the model were (Ho et.al., 31):

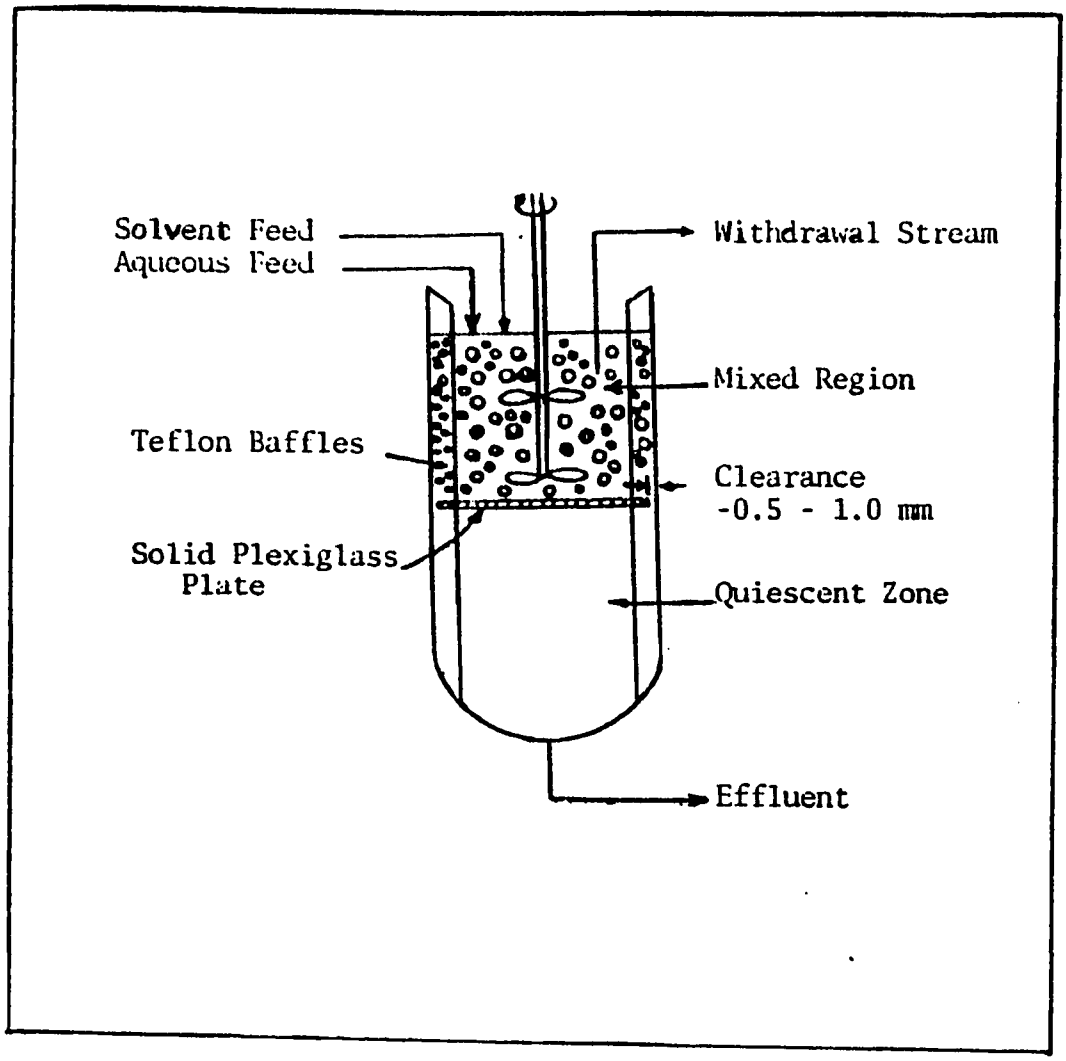


Fig. 7. The internal recycle mixer.

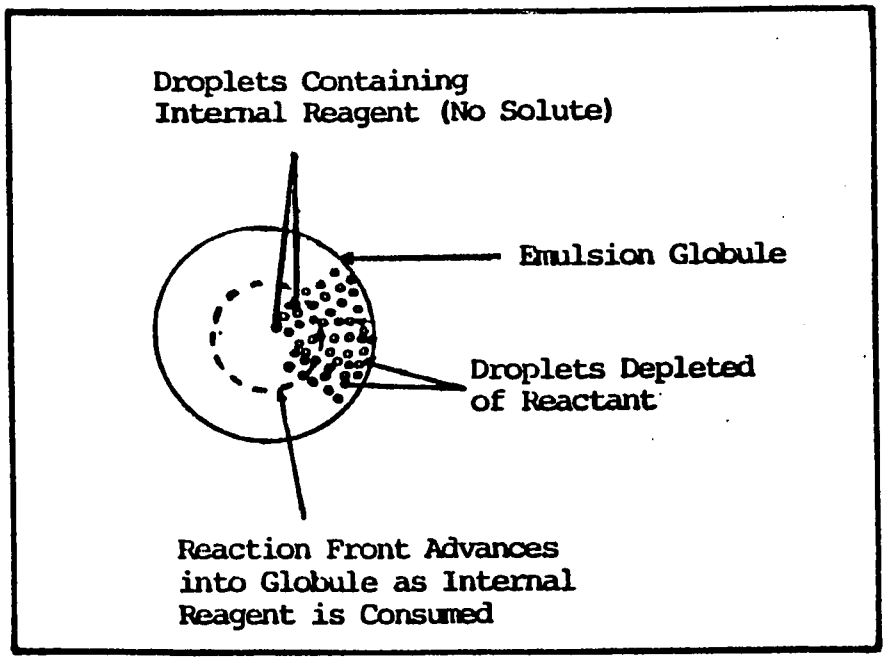


Figure 8. Spherical globule with advancing reaction front.

(i) uniform globle size

(ii) no internal circulation in the glouble;

(iii) no coalescence and redispersion of globules,(i.e., once formed, they retained their identities);

(iv) mass transfer is by diffusion only;

(v) negligible external mass transfer resistance;

(vi) instantaneous reaction between the solute and the internal reagent at a reaction front inside the globule;

(vii) well mixed tank such that the globule residence time distribution is exponential.

The experimental data obtained was in favourable agreement with the model predictions.

On the other hand Caracciolo et.al. (1975) extended Cussler's work (1971) which was the first mathematical treatment of the coupled transport of two different ions, by considering the effect of the association of the transported solutes to form ion pairs. Baker et.al. (1977) also developed a simplified mathematical treatment of coupled transport which relates the flux of the coupled ion. More recently, Danesi et.al. (1981), have also presented mathematical models of the coupled transport of metal ions. However, these studies were confined to the immobilized or supported liquid membrane configuration.

In general, it can be observed that the rate controlling step in the transfer of copper from aqueous phase to liquid membrane phase containing a chelating agent is diffusion through aqueous phase. The kinetic study of the chelating reaction has shown the activation

energies of the order 50 KJ/mole, which implies a fast reaction. The effect of temperature on Cu^{+2} ion transfer from aqueous to organic phase was studied too (32). It was reported that the activation energy found was 10 KJ/mole. This implies strongly that diffusion is the rate controlling mechanism.

As stated earlier, the work involving emulsion is not uniformly reproducible due to problems of unknown interficial areas (though extremely large), the break up of emulsion, nonuniformity of droplets,.. etc. No work has been reported which includes pure chelating agents. The quality of commercially available chelating agent can not be guaranteed, hence the results obtained from such agents are not uniform.

One important problem with emulsion membrane is that after separation, the emulsion droplets need to be broken and then the two phases separated. Due to this reason, the results of copper concentration change with time in the encapsulated aqueous phase (stripping) have never been reported yet.

This thesis work intends to fulfill that gap and postulates a hypothesis on the mechanism of transfer of Cu^{+2} ion from aqueous to organic to aqueous phase (stripping side).

III. EXPERIMENTAL SETUP

Earlier in this project, an attempt was made to reproduce some of the experimental data reported in literature for the extrtaction of copper by ELM. The "JKA Ultra Turrax" high speed homogenizer was recommended in literature (30), to form a water-in-oil emulsion type(i.e., stripping acid-in-membrane phase) at 10,000 to 20,000 rpm speed, and also for the dispersion of this emulsion in the feed phase at 250 to 500 rpm speed. Neither this kind of agitator nor any other ultra high speed agitators of similar behavior were available in our labs, hence a home juice blender with variable high speed cotrol was used for the emulsion formation. Unfortunately, the emulsion which obtained by the blender was so thick, that it did not disperse at all in the third phase (feed) when agitated at the lower agitation speed range. Instead, it collided in a large random shape, which floated in the feed phase. In this case, no multiple emulsion in which the memprane phase is encapsulating the stripping phase was formed in order to accomplish the copper recovery mechanisms. Even the variation in the blender speed and in the impeller shape and orientation were not enough to improve the situation any better.

Furthermore a small single drop formulation test was also performed as another alternative, and again we faced difficulties, but this time in maintaining the stability of the dispersed droplet long enough in the organic phase. Hence, to overcome this difficulties we decided to increase the surfactant concentration in the liquid membrane phase ,which implies an additional resistance for the diffusion.

From the discussion above it is obvious that niether of the two previous techniques is enough to fulfill the whole objective requirements of this research work. Besides the study of the stripping phase behaviour in copper recovery system is as one of the major parts of the objectives. This type of data has not been reported in any of the reviewed literature, (see Sec.II.2).

Therefore, a new modified unit for copper recovery by liquid membrane based on stirred cell idea (5), was designed here for this purpose. In this system, the characteristics of both supported liquid membrane and ELM were combined .Thus all the three phases (feed, LM and stripping) were separately available for continuous analysis as in supported liquid membrane, and at the same time, no solid support for the liquid membrane phase was needed. Moreover the uses of surfactance had been eliminated too. Due to the simultaneous contact for the two aqueous phases (feed and lean solutions) with the liquid membrane phase, the extraction and stripping mechanisms, together with the diffusion of complexes in the organic phase will be occured at the same time in this new copper recovery unit. This in fact provided a novel opportunity to study the complete picture of the copper recovery mechanisms by chelated liquid membrane using this system.

At the begining, the first preliminary tests applied on the apparatus showed almost a negligible copper separation behavior, based on sampling analysis for copper concentrations in both aqueous solutions. Hence further modifications on the original apparatus were introduced before the final utilization in the experimental studies of

the research objectives. The final preliminary experimental tests on the apparatus performance indicated an immense improvement in the copper recovery in both aqueous phases. The final modified design for the Copper Recovery Unit will be described in detail in the coming section.

In addition a small diffusion cell was also designed in order to evaluate experimentally the copper diffusion coefficient "D" in the feed phase when contacted whith the liquid membrane phase. The description of this cell will be discussed too.

III.1 THE COPPER RECOVERY UNIT

The apparatus which has been utilized in the copper recovery experiments (Fig.9) consists of the following parts: a box shaped reactor of perspex material with an inside base area of 3.5 x 7 in^2, and a wall height of 9 ins. The reactor inside volume is divided into two equal compartments by means of a central perspex wall of 6 ins height. This arrangement allows the immediate interaction between both aqueous phases (feed and stripping) in the two compartments with the liquid membrane phase, hence the copper ions will be transferred from the feed (extraction) phase to the stripping phase through the liquid membrane phase, without any direct contact between the two miscible aqueous phases.

Two glass stirrers of special design (see Fig.9) are used to ensure the uniform mixing of the phases available in the reactor. The stirrers are driven by a single motor of variable speed and are

THE EXPERIMENTS

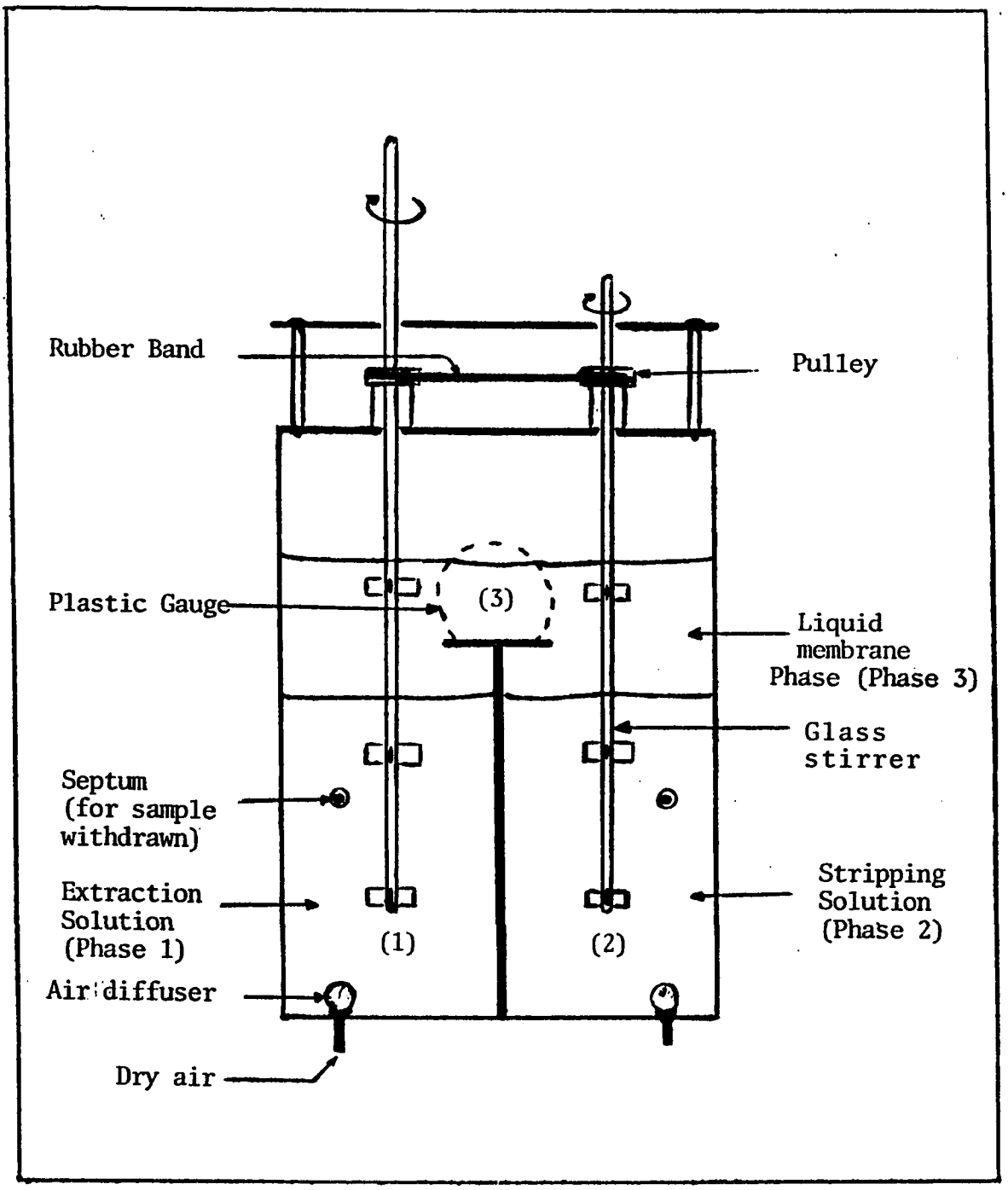


Fig. 9. The Copper Recovery Unit

connected together through a pulley so that both the stirrers will rotate with the same rpm.

Two air diffusors, made of inert material, are placed at the bottom of both compartment with an off-center position of the compartment base area.

Regulated air bubbles at specific flow rate are diffused through aqueous phases to back up the mixing process and to increase the interficial area between the liquid membrane phase and both aqueous solutions.

Besides other auxillaries are also required in the system. A plastic tubular gauze (inert) is placed on top of the reactor dividing barrier, hence to prevent any aqueous overflow. Air regulator, pair of rotameter and needle valves are used to maintain the regulated air flow at the desired level. The rpm value is indicated by a "Tackometer" connected to the driving motor. Samples are withdrawn by syringes through a pair of rubber septums attached to the compartment walls.

III.2 THE DIFFUSION CELL

To obtain the diffusion coefficient "D" of copper ion in an aqueous phase when contacted with liquid membrane phase, the following Diffusion Cell (Fig.10) is used. The cell simply consists of a cylindrical column of perspex material, with 3.5 ins inside diameter and 9 ins long. Four sampling positions are located at the lower part at 1/4, 1, 2 and 3 ins. heights above the column base, where the

rubber septums are attached.

The aqueous phase in the cell occupies the lower part of the column, with a suitable height (1.5 ins) above the highest septupm from the base. The liquid membrane phase, which is of lower density value occupies the remaining upper level. Samples are withdrawn through the four septums by the syringes.

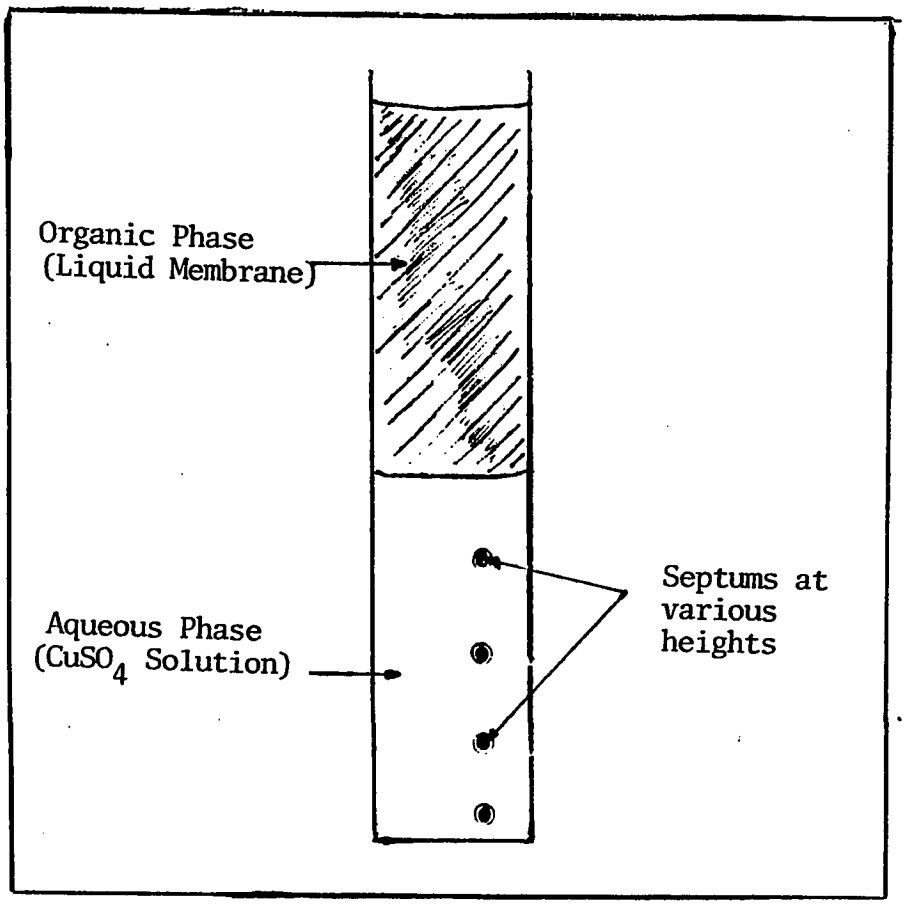


Fig.10 The Diffusion Cell.

IV. THE EXPERIMENTS

The experemental part of this research is devoted to fulfill the proposed objectives. In this regard, the following prameters were studied to analyse their effect on the process of copper extraction by liquid membrane: (a) the mixing speed, (b) the chelating agent concentrations in the liquid membrane phase, and types of the chelate to be utilized, (c) the copper feed concentrations, and (d) the pH values of feed and stripping solutions.

Due to the geometrical restrictions, three mixing speeds have been tested. The speed values are 160, 200 and 250 rpm. Speeds higher than 250 rpm caused an aqueous overflow between the two compartments, while speeds less than 160 rpm did not provide good mixing. To increase the rate of transfer of copper during the actual experimental runs, air bubbles were introduced into the two compartments. This increases the mixing and the interficial area between the immiscible phases.

Furthermore three types of chelates were used in this study. The three chelates are members of the LIX-reagent family manufactured by General Mills. They are LIX64N, LIX65N and LIX51. Since most of the reviewed literature recommended the LIX64N as the most suitable chelate for copper recovery, it was the first candidate for testing. The LIX65N was chosen because it is one of the constituent of the LIX64N (see Fig.6), while the LIX51 was chosen as a third alternative for copper separation study. These chelates have been utilized as delivered with no further purification treatment. With regard to

chelate concentrations in the liquid membrane phase, the LIX64N has been dissolved in kerosene at two different concentrations of 2.5 and 5 wt%. The other two chelates (LIX65N and LIX51) have only the concentration of 2.5 wt% in kerosene.

Copper sulphate diluted in deionized water was used to form the copper feed at four prescribed concentrations: 2000, 1000, 500 and 200 ppm approximately.

In the experiments the H_2SO_4 acid was utilized as a stripping agent in the copper recovery process by ELM.

The strength values of 7 and 1 pH were chosen for the feed and stripping solutions respectively. These pH values were arrived at by doing certain preliminary experiments, which will be discussed later in the chapter.

IV.1 THE MIXING SPEED EXPERIMENTS

In this part, the effect of mixing speed on the transport of copper between aqueous phases through the organic phase was investigated. The investigation was performed at three mixing speeds. The speeds were 160, 200, and 250 rpm. The upper limit on speed of mixing was dictated by overflow in the unit. The number of experiments were three (i.e.,one expirement/speed). In the three expirements, all the conditions except the speed were maintained constant (i.e., feed concentration, pH strengths, chelate type and its cocentration). The expirements were performed in the Copper Recovery Unit at room temperature with no air bubbles introduced into the unit.

A feed of about 1000 ppm of copper concentration and 7 pH strength was tested in every speed experiment. This feed is prepared by dissolving about 3.93 gr of $CuSO_4$ in 1 lit volume of dionized water using a 1000 cc Volumetric Flask.

The stripping solution was maintained in all three experiments at 1 pH strength. The solution is prepared by dissolving a 99% concentrated H_2SO_4 acid in deionized water untill it reached the desired strength. The pH value was measured using a pH-Meter during preparation procedure.

Finally the liquid membrane phase was also maintained in every experiment at a 2.5 wt% concentration of LIX64N chelating agent. This chelate concentration is prepared by dissolving about 20 gr of the LIX64N agent in 1 lit of commercial kerosene using a 1000 cc Volumetric Flask.

During the experiments an 850 ml of feed solution occupied one of the two compartments in the reactor (Fig.9), while an identical volume of stripping solution occupied the other one. A volume of 680 ml of the liquid membrane phase was then poured into the reactor. Due to the geometry of the reactor, the liquid membrane phase was in a direct interfacial contact with both the feed and the stripping solutions simultaneously.

Each speed experiment was run for 6 hours duration, and samples of feed and stripping solutions were withdrawn after every one hour. This sampling rate was decided upon after a few initial runs.

The volume of every sample was about 4 ml. Thus at the end the total reduction in the volumes of each aqueous phase would be less than 2.5 % .

The samples so obtained were analyzed by using the Atomic Absorption Spectroscope.

IV.2 EXPERIMENTS TO STUDY THE EFFECT OF CHELATING AGENTS

From the literature review , the LIX64N chelate was considered the most popular copper carrier among researchers. Therefore it was decided to devote most of the experimental work to study the effect of this chelate on copper recovery at various concentrations. The LIX64N was dissolved in kerosene to form the liquid membrane phase of four different concentrations. They were 2.5 wt%, 5 wt%, 10 wt% and 15 wt%.

However the preliminary runs indicated that, though the 10 wt% and 15 wt% of LIX64N in kerosene did extract large amount of copper from the feed solution, it was very difficult to strip a significant amount of that copper from the organic phase. Hence, the experiments were only restricted to study the effect of the 2.5 wt% and 5 wt% LIX64N concentrations.

In addition feed solutions with four different copper concentrations were used for experimental testing. The copper cocentrations were 2000, 1000, 500 and 200 ppm. Following the same preparation procedure discribed earlier (Sec IV.1.1), the amount of the $CuSO_4$ to be dissolved in the 1 liter volume of deionized water (7 pH) was about

7.89 gr, 3.93 gr, 1.97 gr and 0.98 gr respectively. The stripping solution was maintained in all cases at 1 pH strength.

The two desired chelates concentrations (2.5 & 5 wt%) were prepared by diluting about 20 gr and 40 gr of chelate respectively in 1 liter of kerosene.

Therefore the number of experiments performed in this case were eight (i.e., one expr./chelate conc.). The volumes of the three phases (feed,organic and stripping) in the unit were kept at 850 ml for aqueous phase and 680 ml for organic phase.

The mixing speed in all the experiments conducted from now on was maintained at 220 rpm (based on result from the previous mixing speed study). The mixing process is enhanced by introducing bubbles of dry air at 45 cc/min @ S.T.P. The air was injected into both compartments through a diffusor placed off-center at the bottom of the compartments.

The duration of each experiment was increased to 7 hours, while the same sampling and analytical procedure

Similar experiments were conducted using LIX65N and LIX51. However their concentration in the solvent kerosene were kept at 2.5 wt%. The feeds treated with the LIX65N reagent were 200, 500 and 2000 ppm. For the LIX51 experiments, the feeds were 500, 1000 and 2000 ppm.

IV.3 OTHER SUPPORTING EXPERIMENTS

IV.3.1 The pH Strength Tests

As discussed earlier, a large hydrogen ion concentration gradient should be maintained between the two aqueous phases (extraction and stripping) in order to encourage the copper transport. The literature survey indicated that the pH of feed solution was 2, while that of stripping solution was 1. To decide on the proper pH strength values the following equilibrium tests were conducted.

To decide on the pH strength of the feed phase, two feed solutions of the same copper concentration (1000 ppm) but of different pH values (one at 7 pH and the other at 2 pH) were contacted with a 2.5 wt% LIX64N liquid membrane phase. The volume ratio of the two immiscible phases (organic/aqueous) was kept at unity for both feed solutions. Under equilibrium conditions, the amount of copper transferred from both the aqueous solutions was similar within the experimental accuracy (Table-4).

Also to determine the suitable pH for the stripping phase, similar experimental tests were conducted. In this case stripping solution with three differing pH (1, 2 and 3 pH) were tested with an identical pre-equilibrated organic phase.

The pre-equilibrated organic phases were prepared as follows. At first equilibrium conditions were established between the 2.5 wt% LIX64N organic phase and a $CuSO_4$ solution about 1000 ppm copper concentration and 7 pH strength in three identical separatory funnels

TABLE - 4 PH TEST FOR EXTRACTION SOLUTION

SAMPLE CODE	p.p.m. COPPER
A	526.3
B	526.8
FEED : B (7 PH)	1157.9
FEED : A (2 PH)	1126

of equal volumes. The "organic/aqueous" volume ratios were kept at unity, and the funnels were immersed in a constant temperature bath at 25°C for two days untill equilibrium was reached. Then the three equilibrated organic layers, of known copper concentrations, were treated with the three stripping solutions of 1, 2 and 3 pH strength at the same "organic/aqueous" volume ratio. The separatory funnels were again immersed in a constant temperature bath at 25°C for two days. Under equilibrium conditions, the 1 pH stripping solution was found to be extremely effective in stripping most of the copper in the organic phase than the other two pH solutions (Table-5).

Therefore the 7 pH and the 1 pH strengthes were chosen for the feed phase and stripping phase respectively.

IV.3.2 The Equilibrium Data Experiments

The experiments were performed to determine the equilibrium distribution of copper ions between the feed and the liquid membrane phase and also between the liquid membrane phase and the stripping solution.

Four LIX64N concentrations (15, 10, 5 & 2.5 wt%) dissolved in kerosene were tested, while for the LIX65N and LIX51 only 2.5 wt% concentration was studied. These solutions were prepared by dissolving about 120, 80, 40 and 20 grams of the chelates in 1 lit of commercial grade kerosene respectively.

The feed concentrations were about 2000, 1000, 500 and 200 ppm of copper in deionized water (7 pH). The strength of stripping solution

TABLE - 5.a PH TEST FOR STRIPPING SOLUTION PART (1)

SAMPLE CODE	p.p.m. COPPER
A	570
B	590
C	590
FEED	1090

TABLE - 5.b PH TEST FOR STRIPPING SOLUTION PART (2)

SAMPLE CODE	p.p.m. COPPER
A pH 1	398.5
B pH 2	94.62
C pH 3	2.92

was 1 pH. The preparation of the the stripping and the feed solutions is previously discribed.

Two sets of equilibrium data were obtained from the experiments. The first data set was for the equilibrium distribution of copper between the feed solutions and each of the liquid membrane phases (Feed —> LIX data). The second data was for the equilibrium distribution of copper between the liquid membrane phase and the stripping solution (LIX —> H^+ data).

The "Feed —> LIX" data was obtained as follows. Each liquid membrane phase was treated separately with the four feed concentrations at an "organic/aqueous" volume ratio equal to unity in four different separating flasks of equal volumes. The flasks were kept in a constant temperature bath at 25 ^{o}C, with regular shaking for a considerable time, long enough to approach equilibrium conditions.

The copper concentrations were intermittently checked for the equilibrium approach. The equilibrium was approached after a day. Every time an aqueous phase sample was removed, equal amount, equal of the liquid membrane phase was withdrawn to maintain the same volume ratio. Aqueous phase samples were analysed for copper using an Atomic Absorption Spectrometer. The equilibrium concenterations of copper in the liquid membrane phase were determined by material balance.

To obtain the seconed equilibrium data set (i.e.,LIX—>H^+ data), the same procedure previously described was followed here. However

in this case, the equilibrated liquid membrane phases were contacted with the 1 pH stripping solution till the equilibrium conditions were achieved.

IV.3.3 The Diffusion Experiment

In this experiment, the diffusion coefficient (D) of copper in the aqueous feed was determined based on the intermolecular diffusion forces. The Diffusion Cell unit, described before (Fig.10) was used for this purpose. A 680 ml of feed solution of about 1000 ppm copper and 7 pH strength occupied the lower volume of the cell. An identical volume of the liquid membrane phase containing a 2.5 wt% LIX64N agent concentration was slowly poured on top. This was to ensure that copper transport was only due to intermolecular diffusion in the feed phase plus the extraction reaction at the feed-liquid membrane interface, and not due to any disturbance in the system.

The experimental setup containing the two immiscible contacted solutions, was left for 28 hours. Samples were withdrawn after 4, 8, 12, 24 and 28 hours starting from the time when the two solutions were brought into contact in the cell. Four samples (4 ml each) were withdrawn at every specified time from different locations in the cell (see Fig.10). The collected samples were then analysed, as before, in order to determine the corresponding changes in copper concentration with respect to time and elevations.

V. RESULTS AND DATA ANALYSIS

In this chapter the data obtained from the Copper Recovery Unit will be analysed. The results of analyses may indicate the behavior of the copper transport process in the two aqueous phases (i.e., extraction process in phase 1 and stripping process in phase 2). The theoretical explanation of the observed results will be given in the following chapter.

The results obtained from the Atomic Absorption Spectroscopy indicate the actual changes in concentration of copper (ppm) in the extraction phase and stripping phase with time under the experimental conditions. Although no samples were obtained from the organic phase (phase 3) while the experiments were running, the concentration of copper in this phase can still be determined by material balance. In addition, the equilibrium data results and data from the Diffiusion Cell will also be presented.

V.1 MIXING SPEED EXPERIMENTS

As mentioned in chapter(IV), the experiments were performed to test for the mixing speed influence on copper recovery by means of chelated liquid membrane. Experiments conducted at three different mixing speeds (160, 200 & 250 rpm) under otherwise identical experimental conditions(i.e., concentration of copper in feed= 1000 ppm with 7 pH, membrane phase comprising of kerosene with LIX64N 2.5 wt% and aqueous stripping phase with 1 pH). Methods used to analyse the data are indicated below.

V.1.1 Analysis of The Extraction Phase Results

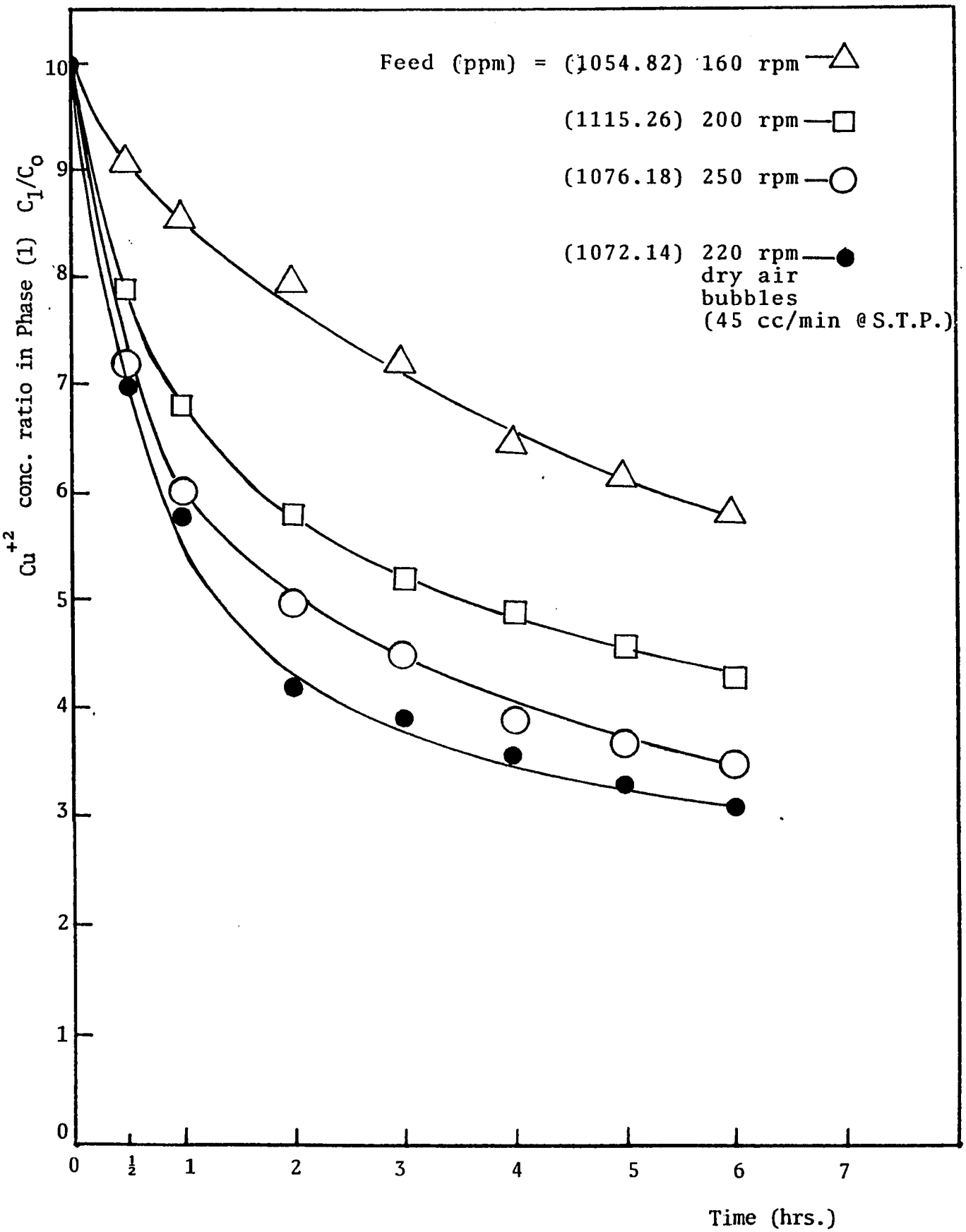
For the analysis of phase 1 (i.e., aqueous phase from which copper is being extracted) the ratio of instantaneous copper concentration to initial copper concentration (C_1/C_0) was plotted against time on a linear scale for various mixing speeds (Fig.11). For comparisson the figure also includes a typical experimental result in which air was introduced to enhance mixing.

From the experimental results (see APX.1), it is clear that amount of copper transfered from aqueous feed phase to organic liquid membrane phase increases with higher speeds (i.e., more mixing). During the initial period,the rate of transfer of copper(as indicated by the slope of a typical dimensionless concentration versus time curve) increased with increased intensity of mixing. This may imply that the transfer process may be mass transfer controlled in the initial period. It was ensured during the experiments that the interface was maintained as flat as possible.

In comparission, the typical experimental data with air bubbles shows a further increase in the amount of copper transfered and also the extraction rate of copper (see Fig.11). This is due to introduction of dry air bubbles into the system which provided more surface area for the copper transfer.

Fig. 11 Extraction Rate Behaviour

Mixing Speed Experiments



V.1.2 Analysis of The Stripping Phase Results

Following the procedure for analysis of phase 1, the copper concentrations (C_2) in the aqueous stripping phase (phase 2) are plotted against time on a linear scale for the three mixing speeds. A typical experimental run is also plotted on the same curve for comparission purposes (Fig.12).

The experimental results of this phase (see APX.1) indicated an increase in the amount of copper transfered from the membrane phase to the stripping phase with the increase in mixing speed. Furthermore, the figure shows that the copper concentration in phase 2 increases linearly with time. In terms of rates, it is obvious that the stripping rate increases with mixing speed. Again as in extraction, higher stripping rate is obtained in the typical run due to the increased surface area.

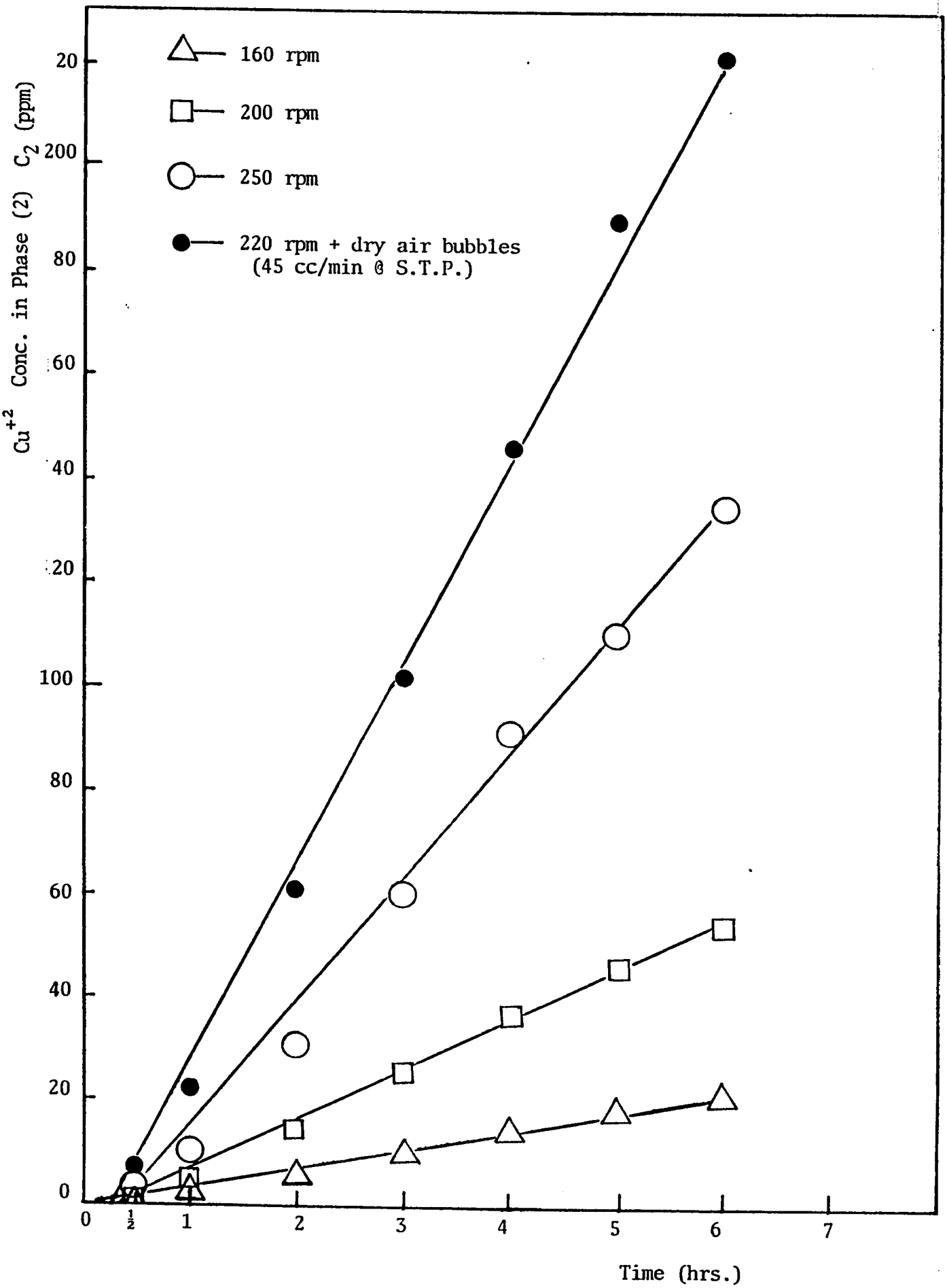
V.2 EXPERIMENTS TO STUDY THE EFFECT OF CHELATING AGENTS

The purpose of these experiments was to study the effect of feed and type of chelating agent on the transport process of copper by means of chelated liquid membrane. In the experiments the mixing speed was maintained constant at 220 rpm while dry air bubbles at 45 cc/min @ S.T.P were introduced into the

system. A variety of diluted feeds (phase 1) and differing chelating agents dissolved in kerosene (phase 3) were studied, while the strength of stripping phase (phase 2) was fixed at 1 pH and no copper initially.

Fig. 12 Stripping Rate Behaviour

Mixing Speed Experiments



V.2.1 Analysis of The Extraction and Stripping Phase Results

Under fixed membrane phase conditions, the experimental results of phase 1 (see APX.1) show larger amounts of copper transfered from this phase at high feed concentration than at low feed concentration of copper. At very low feed concentration of copper (200 ppm), it is observed that the entire amount of copper is extracted into the organic phase during initial period (less than 2 hrs).

Figure 13 shows a plot of dimensionless concentrations (C_1/C_0) in phase 1 against time for various feeds using a fixed chelate condition (LIX64N 2.5 wt%).

From the figure it can be seen that the initial rate of change in copper concentration is less at higher feeds than at lower feeds. As a conclusion one can say that the increase in feed concentration (C_0) decreases the extraction rate of copper under the given experimetal conditions.

The experimental results for phase 2 under fixed chelate conditions (LIX64N 2.5 wt%) (APX.1) are plotted in figure 14.

The figure shows that copper concentration in phase 2 increases linearly with time, and also rises with in feed concentration of copper.

Fig. 13 Extraction Rate Behaviour

(LIX64N 2.5 wt %)

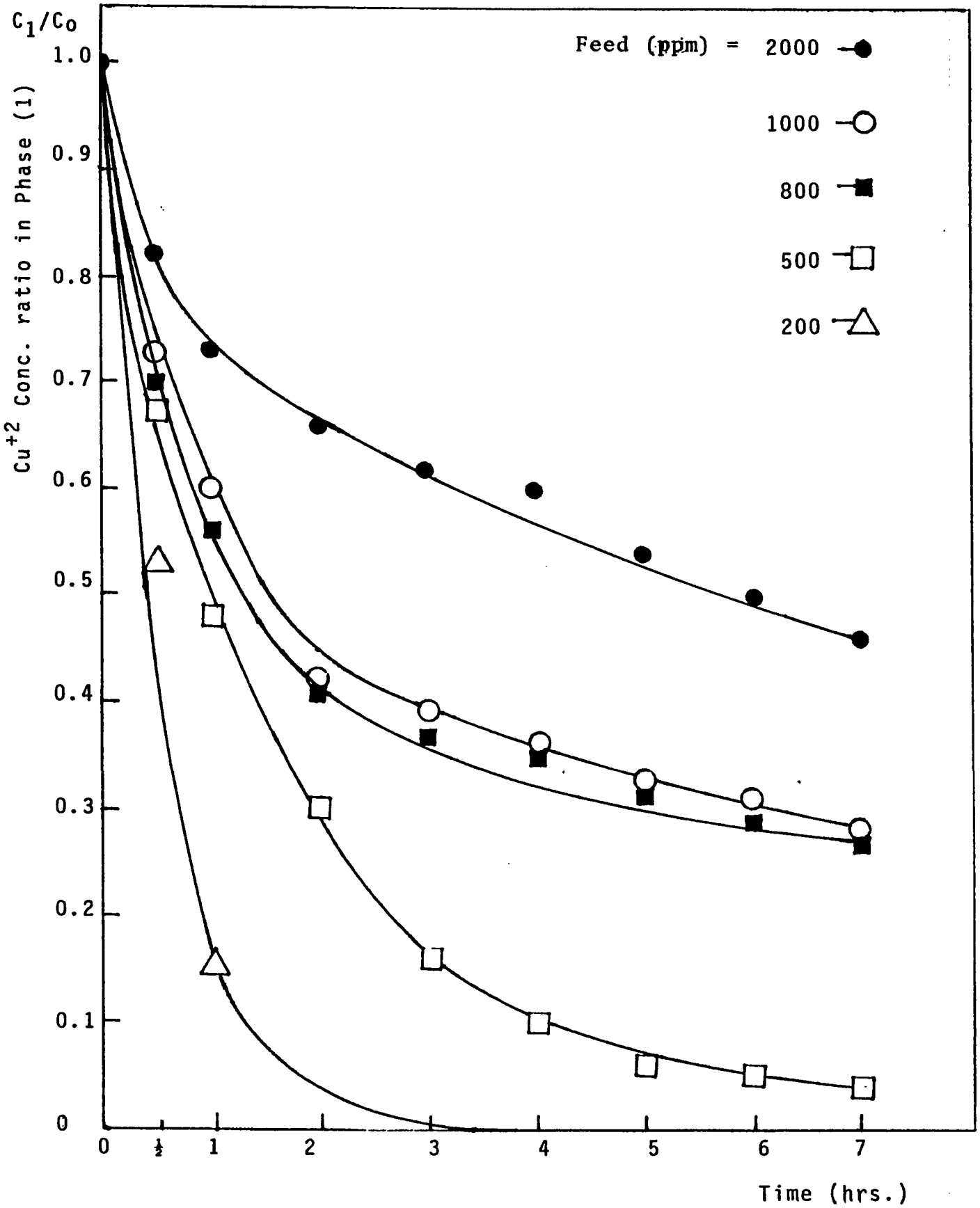
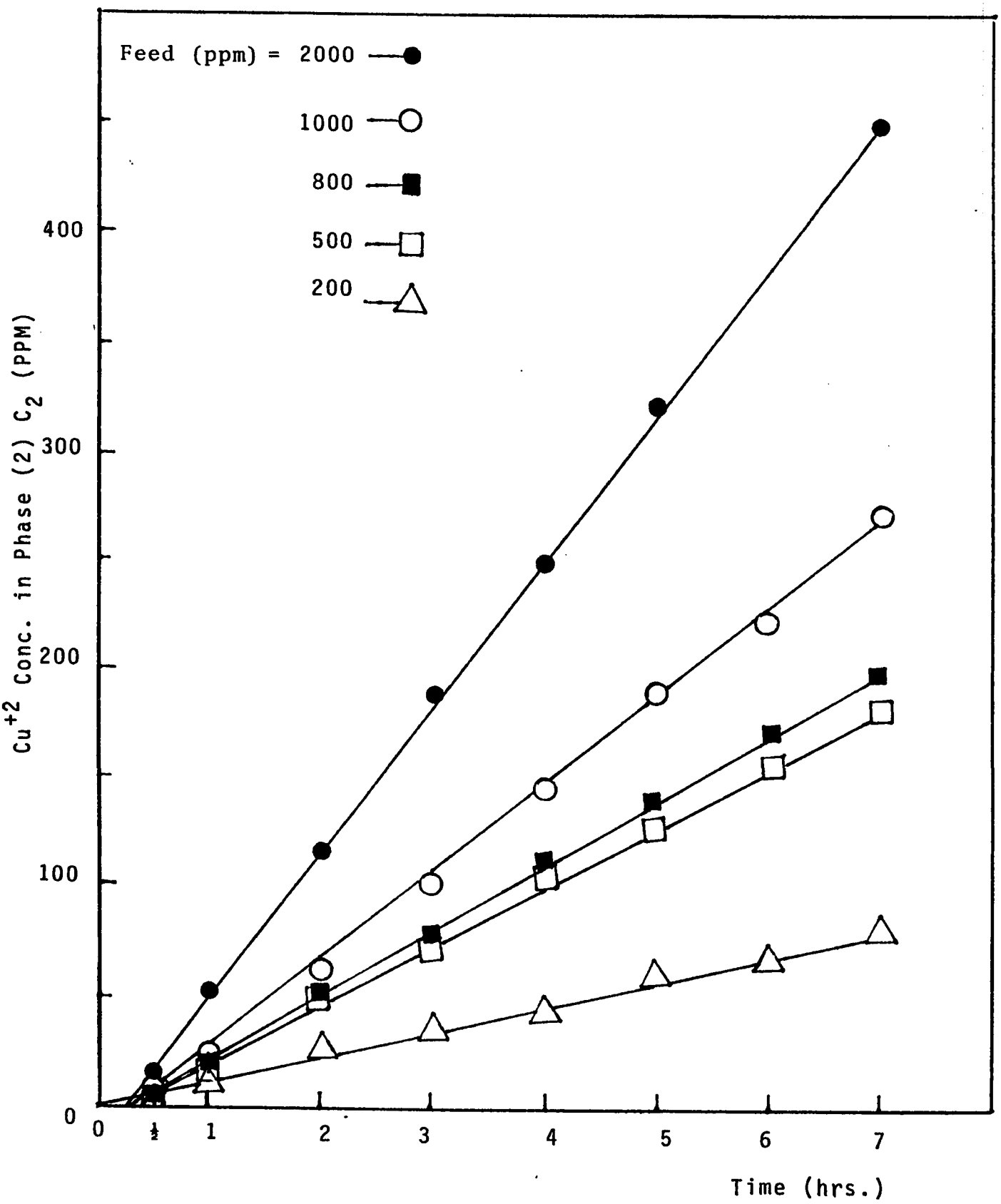


Fig. 14 Stripping Rate Behaviour
(LIX64N 2.5 Wt %)



V.3 ANALYSIS OF THE EQUILIBRIUM DATA RESULTS

In these experiments the liquid membrane phase is first equilibrated with various copper feeds, and then stripped till a new equilibrium is established with the stripping solution.

It has been pointed out for the data of the LIX64N chelate that, under equilibrium conditions higher chelate concentrations in the organic phase extracted larger amount of copper from aqueous phase. Under equilibrium conditions, at the high chelate concentrations (10 & 15 wt%), most of the copper ions were transfered from aqueous phase into organic phase (liquid membrane). At the lower chelate concentrations (5 & 2.5 wt%), similar behaviour was observed but not as severely as in the previous case, and again the 5 wt% organic layer was relatively more efficient in removing copper (Fig.15).

On the other hand, the previously equilibrated membrane phases containing lower chelate concentrations (5 & 2.5 wt%), were found extremely favourable to be stripped (to release copper) by the 1 pH stripping solution. In fact under equilibrium conditions, the higher the chelate concentration the more difficult it was to strip copper (very small amount of copper were transfered from the equilibrated 10 & 15 wt% LIX64N membranes) (Fig.16).

The two other chelates (LIX65N and LIX51) at 2.5 wt% concentration in liquid membrane phase, were found less efficient than the lower LIX64N concentrations (5 & 2.5 wt%) in terms of copper extraction, and moderate in their stripping equilibrium behavior. In

Fig. 15 The Equilibrium Curves:

Feed ⟶ LIX64N

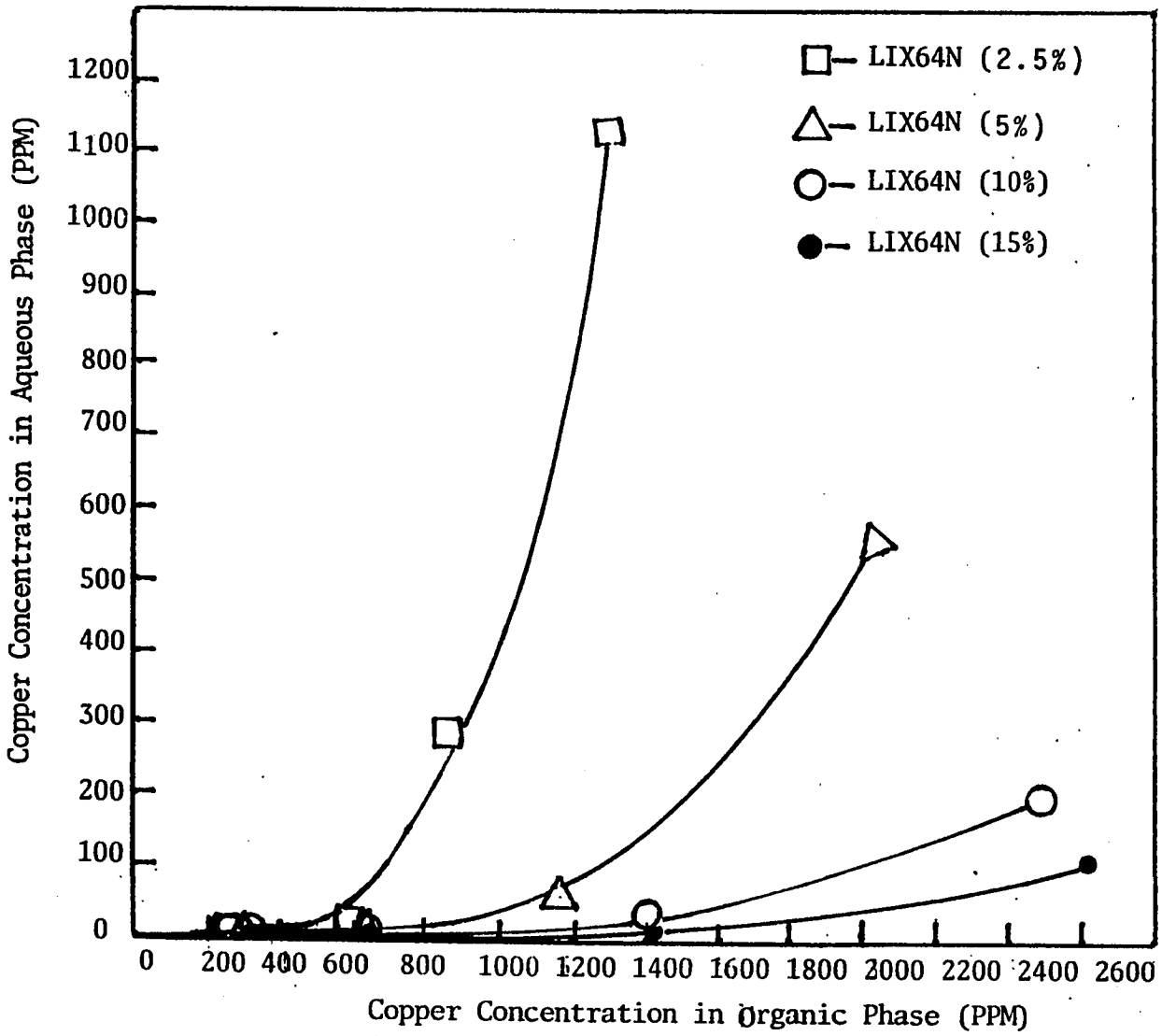
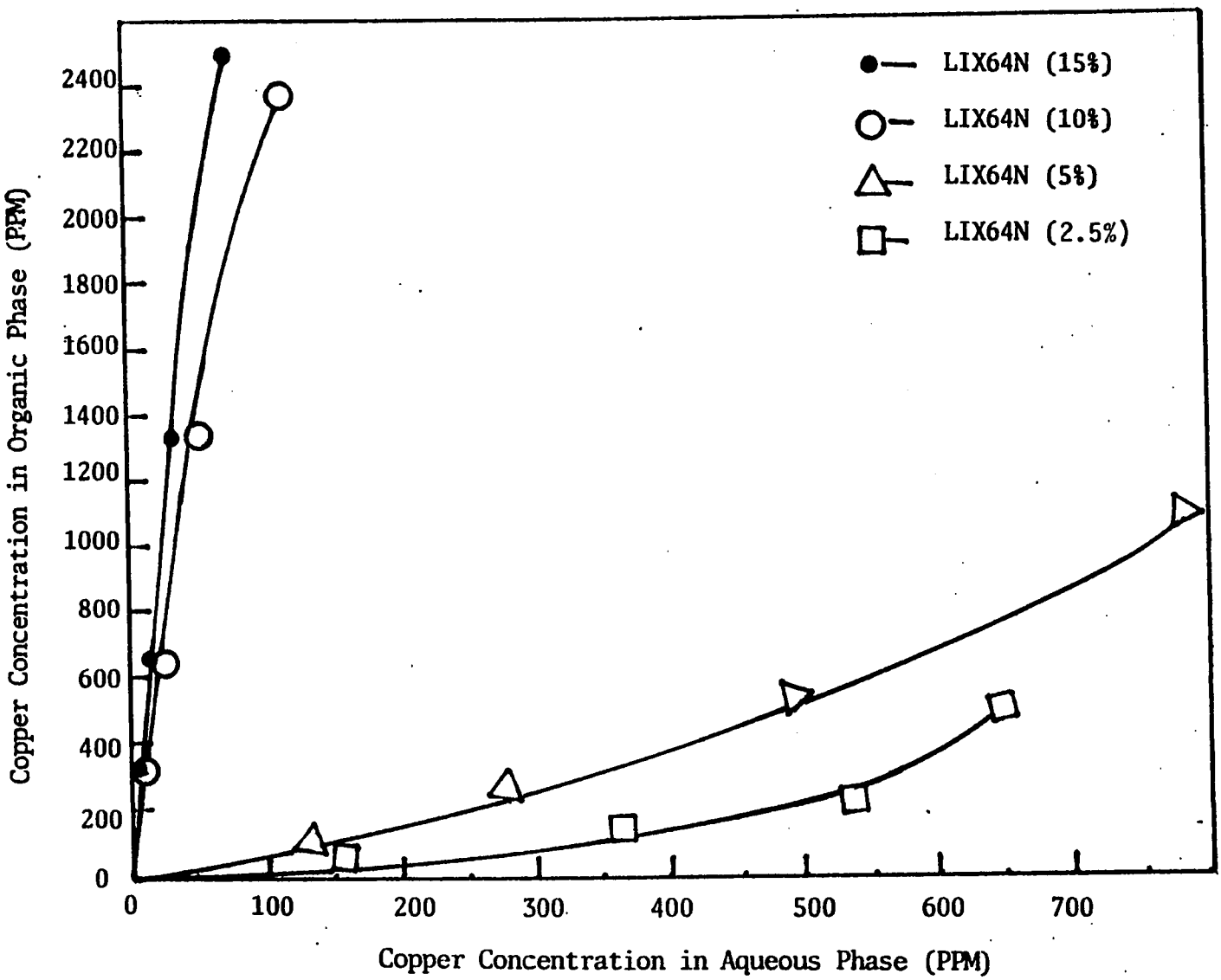


Fig. 16 The Equilibrium Curves:

$LIX64N \longrightarrow H^+$



other words, they lay in between the lower and higher LIX64N concentration ranges. However, the LIX65N is relatively more efficient in terms of copper extraction than the LIX51 and less efficient with regard to copper stripping under equilibrium conditions (see APX.1&2, for the equilibrium results).

V.4 ANALYSIS OF THE DIFFUSSION EXPERIMENT RESULTS

The system is expressed by Fick's second law of diffusion,

$$\partial C_A/\partial t = D_{AB} * \partial^2 C_A/\partial Z^2 \qquad (V.2)$$

This partial differential equation describes a physical situation in which there is no bulk motion contribution that is,

$V = 0$ and also no chemical reaction in bulk, that is $R_A = 0$. This situation is encountered when diffusion takes place in solids, in stationary liquids or in system having equimolar diffusion. Knowing from literature that the copper extraction mechanism by ELM is controlled by diffusion, and that the extraction reaction at the interface is very fast (i.e., negligible surface resistance), we can consider the system to be similar to diffusion in stationary liquids.

The following are the initial and boundary conditions,

I.C.	*at* $t = 0$,	$C_A = C_{A_0}$	*for* $0<Z<L$
B.C(1)	*at* $Z = 0$,	$C_A = C_{A_0}$	*for* $t>0$
B.C(2)	*at* $Z = L$,	$C_A = C_{A,S}$	*for* $t>0$

Hence, the general solution of Eq.V.1 is,

$$\left(\frac{C_A - C_{A,S}}{C_{A,0} - C_{A,S}}\right) = 1 - \frac{Z}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \sin\left(\frac{n\pi z}{L}\right) * e^{-(n\pi)^2 \cdot X_D} \qquad (V.3)$$

where:

n = 1,2,3,....., and

X_D: is the relative time ratio of the form "$D_{AB}.t/L^2$".

Therefore in the treatment of the experimental data, first the values of $[C_A-C_{A,S}/C_{A_0}-C_{A,S}]$ are determined (Table-6), using the data obtained. A trial and error solution for Eq.V.2 is then applied in order to determine the corresponding values of the relative time ratio (X_D). From the given definition of X_D, an average value of the diffusion coefficient (D_{AB}) of copper ion in aqueous phase which is in contact with an organic liquid membrane phase could be determined. The average "D" value determined is approximately equal to 3.59×10^{-6} in^2/sec., which is in reasonable agreement (about 31% error) with the "D" values reported in literature (29). The data obtained from this experiment is given in run #19 (APX.1), and also a plot of this data is given in figure 35(APX.2).

TABLE - 6

DIFFUSION EXPERIMENT

CHANGE IN CONCENTRATION RATIO WITH TIME AT DIFFERENT HEIGHTS

Z (ins)	[Ca-Ca,s/ Ca-Ca,s] t=4 hr.	[Ca-Ca,s/ C_a-$C_{a,s}$] t = 8 hr.	[Ca-$C_{a,s}$/ C_a-$C_{a,s}$] t=12 hr.	[C_a-$C_{a,s}$/ C_a-$C_{a,s}$] t=24 hr.	[C_a-$C_{a,s}$/ C_a-$C_{a,s}$] t=28 hr.
1/4	0.99	0.95	0.92	0.90	0.88
1	0.97	0.93	0.92	0.89	0.87
2	0.96	0.93	0.91	0.88	0.85
3	0.95	0.90	0.91	0.88	0.85

VI. DISCUSSION OF RESULTS

In this chapter, the experimentaly observed results will be discussed and analysed. It is attempted to propose a model for the extraction and the sritpping processes of copper. The model should reflect the physical situation. The validity of the model can be then tested by comparing the experimental resuls obtained from the Copper Recovery Unit.

This justification of the results is based on two important factors; first, on the models proposed by other workers in literature for the separation of copper or any other heavy metal ions by emulsion liquid membrane (specially in modeling the extraction process in phase 1), and second, by analysing the effects of varying some important experimental parameters (i.e.,mixing speed and feed concentration).

VI.1 MODELING OF EXTRACTION PHASE PROCESS

The extraction of copper from the aqueous phase (phase 1) to the organic phase (phase 3) can be assumed to occur in series of steps. The first step is transfer of copper from the bulk to close to the interface and, the second step is the reaction with chelate to form a complex. Thus there is mass transfer resistance followed by a resistance provided by the kinetics of the reaction, represented by the overall extraction rection at the "feed-organic" interface (see Sec. II.1 for rxn.).

One initial problem in deciding the dominant mechanism for copper extraction is to ascertain the relative importance of chemical and

diffusional resistances. In most reviewed works it was assumed that, the reaction is very fast and that diffusion through aqueous phase is the rate controlling step. Thus a semilogarithmic plot of dimensionless concentration with time should be a straight line with constant slope. However in the present analysis the experimental results could not be represented by a single unique straight line on a semilogarithmic graph. The experimental data was represented by two straight lines.

The only reasonable explanation for this behavior can be obtained if we consider the process of copper transfer as comprising of the two steps indicated earlier. The relative magnitudes of each of the resistances to the transfer process is likely to be affected during the experiment. As an exmple varying mixing speed will change the diffusional resistance while amount of complex formed (C_{R_2Cu}) will affect the resistance due to kinetics of reaction. Schematics of the extraction process is shown in the following (Fig.17),

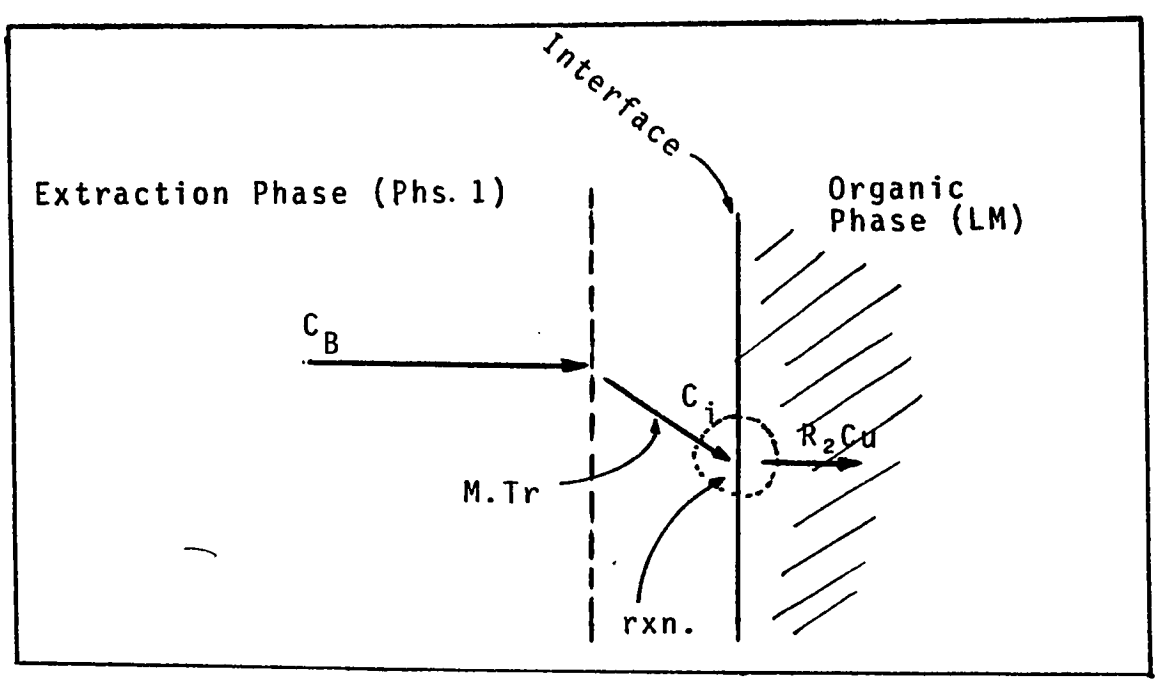


Fig. 17 Extraction Process Scheme

Thus first there is the diffusion resistance in the aqueous film between phase 1 and the interface with the organic. Then the extraction reaction resistance near the interface which is considered in literature as a pesudo first order rate (27). Therefore the rate of copper transfer in phase 1 (R_1) can be represented in terms of mass transfer resistance as,

$$R_1 = k_l a \, (C_B - C_i) \qquad (VI.1)$$

and in terms of pseudo first order rate as,

$$R_1 = k_1 \, C_i \qquad (VI.2)$$

In terms of an overall resistance which combines the two previous resistances, the rate of transfer can be expressed as,

$$R_1 = K_o \, C_B \qquad (VI.3)$$

where:

R_1: is the extraction rate of copper [ppm/hr],

C_i:is the copper concentration at the interface [ppm],

C_B:is the copper concentration in bulk of phase(1) [ppm],

$k_l a$:is the local mass transfer coefficient [1/hr],

k_1:is the pseudo first order rate constant [1/hr] and,

K_o:is the overall capacity coefficient [1/hr],

Notice that k_1 includes the chelate concentration (C_{RH}) at the interface. It is recognised that during the course of transfer amount of C_{RH} available decreases.

After rearranging the previous three equations, one can obtain the following relation,.

$$1/K_o = 1/k_l a + 1/k_1 \qquad (VI.4)$$

Equation(VI.4) represents the assumed influence of both resistances on the overall resistance.

To test for the validity the proposed model, the experimental results of phase 1 are plotted against time on "semi-log" graphs.

VI.1.1 The Mixing Speed Results

Similar to data analysis procedure, the results of phase 1 for the three specified mixing speed are plotted against time on the same "semi-log" graph (Fig.18). In the figure, one can observe the following important points;

1) At the lowest speed (160 rpm), the experimental results can be represented by a single straight line.

2) As speed increased (200 & 250 rpm), two zones represented by two straight lines, appear very clearly.

3) When estimating values of the slopes, it is found that, in the first zone the slope increases with the increase in speed, while in the second zone the straight lines have almost the same slope (i.e., parallel lines) (Table-7).

Based on these points, the following conclusions can be drawn;

Fig. 18 MODELING OF EXTRACTION PROCESS

SPEED RESULTS

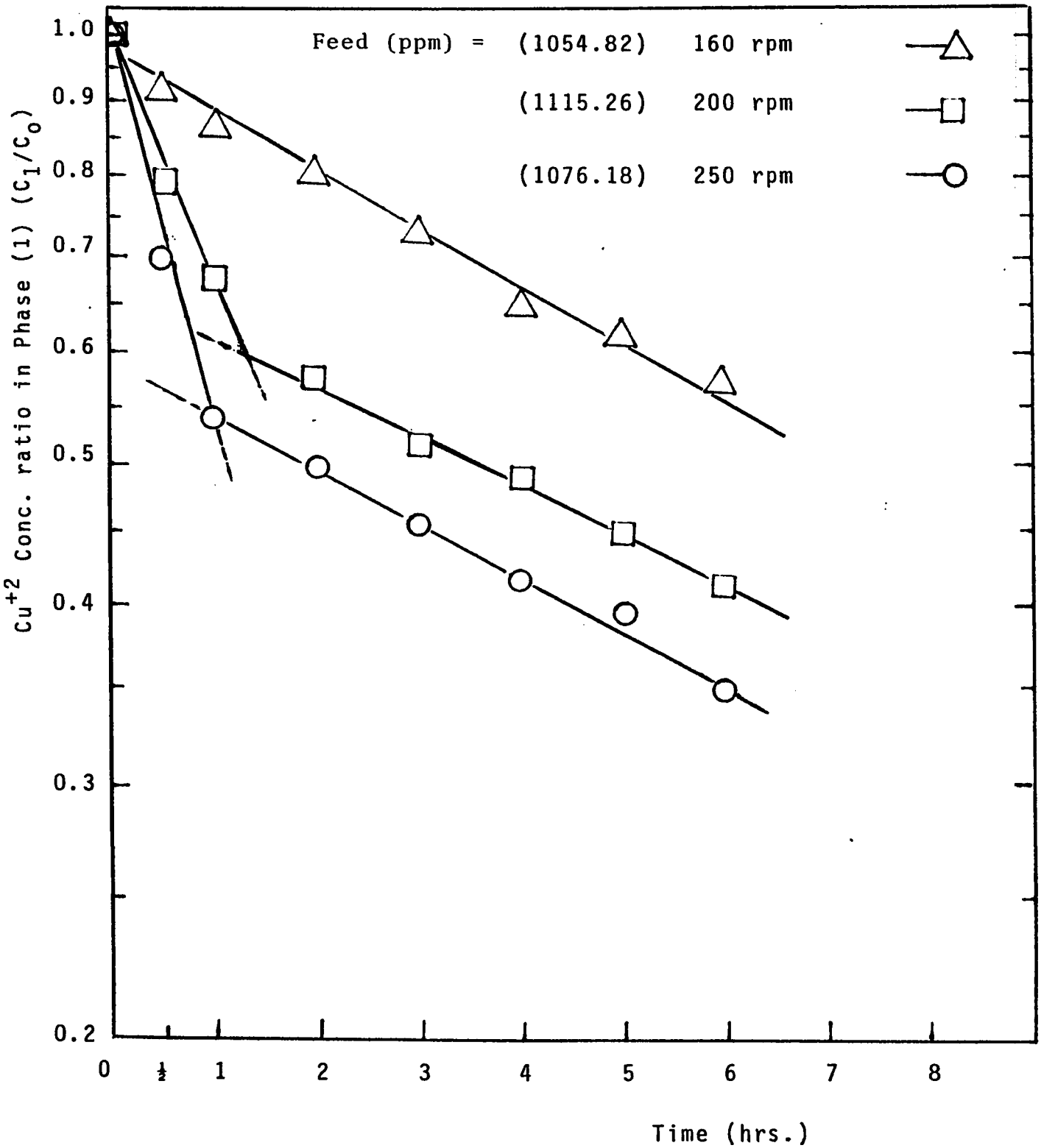


Table- 7 Modelling of Extraction Phase

(Speed Experiment)

Speed (rpm)	Slope of First Zone $m' \equiv k_1 a$ (M.Tr)	Slope of Second Zone $m'' \equiv k_1$ (Kinetics)
160	0.038	-
200	0.167	0.033
250	0.268	0.035

1) The mixing speed affects the diffusional resistance. Increased intensity of mixing as indicated by increased mixing speed should increase the rate. It can be clearly seen from the figure that the increased mixing speed results in an increased rate of transfer as indicated by the slopes of the lines in the first zone (m'). Thus this region must be under mass transfer control.

2) With time, amount of copper transfered increases resulting in a decrease of chelate concentration (C_{RH}) and, consequent decrease in apparent rate of reaction constant (k_1). If $k_1 << k_l a$ then the overall extraction process will be kinetically controlled and no effect of speed will be observed on the slope of the second zone (m"). Thus the second zone represents kinetic regime.

3) At the lowest speed (160 rpm), the mass transfer regime is the only zone as the amount of copper transfered is too low to affect the chelate concentration and hence the apparent rate of reaction.

The observed shift from one zone into the other is reasoned due to chelate concentration, which is combined in the apparent reaction rate constant (k_1) as stated earlier. This change of zones can be reasonably explained by Eq.VI.4 which combines the influence of the two series resistances on the overall resistance. In that relation, one can assume that in the begining the value of k_1 is large compared to the value of $k_l a$ and hence, mass transfer can be considered as the controlling regime. On the other hand, as the value of k_1 decreases due to consumption of chelating agent the kinetic regime is established.

The location at which this shift occurs can be astimated from the reduction in copper concentration of phase 1 by stoichiometry. From the results, it was seen that the regime shift was expected at arround 500 ppm reduction in C_1 value, for the LIX64N (2.5 wt%) which was used in the mixing speed experiments. As a result one might expect the second zone, for the 160 rpm speed experiment, to appear after 7 hrs from the experiment startup.

VI.1.2 The Chelate Effect Results

The results from the second experimental part are also plotted on a "semi-log" graphs, against time for each chelate case as shown in figure 19 for the LIX64N 2.5 wt% case.

In the figure, the two distinct zones appeared very clearly except for the 200 ppm feed since all copper was transfered from phase(1) within the first regime period. The slope values for the two zones are estimated and tabulated (Table-8) (see APX.1 for other cases).

Notice that, due to fixed mixing speed condition in this experimental part (220 rpm+45 cc/min dry air), one must expect a constant slope for the stright lines in the first zone (since the slope is directely related to the rate). However, the results presented in (Fig.19) and the tabulated values of m' (Table-8) show decrease in slope values with the increase in feed concentration. To explain the situation, one must refer to both Eq.VI.4 and the idea of reduction in C_{RH} value and hence the k_1 value.

Fig. 19 MODELLING OF EXTRACTION PHASE
(LIX64N 2.5 Wt %)

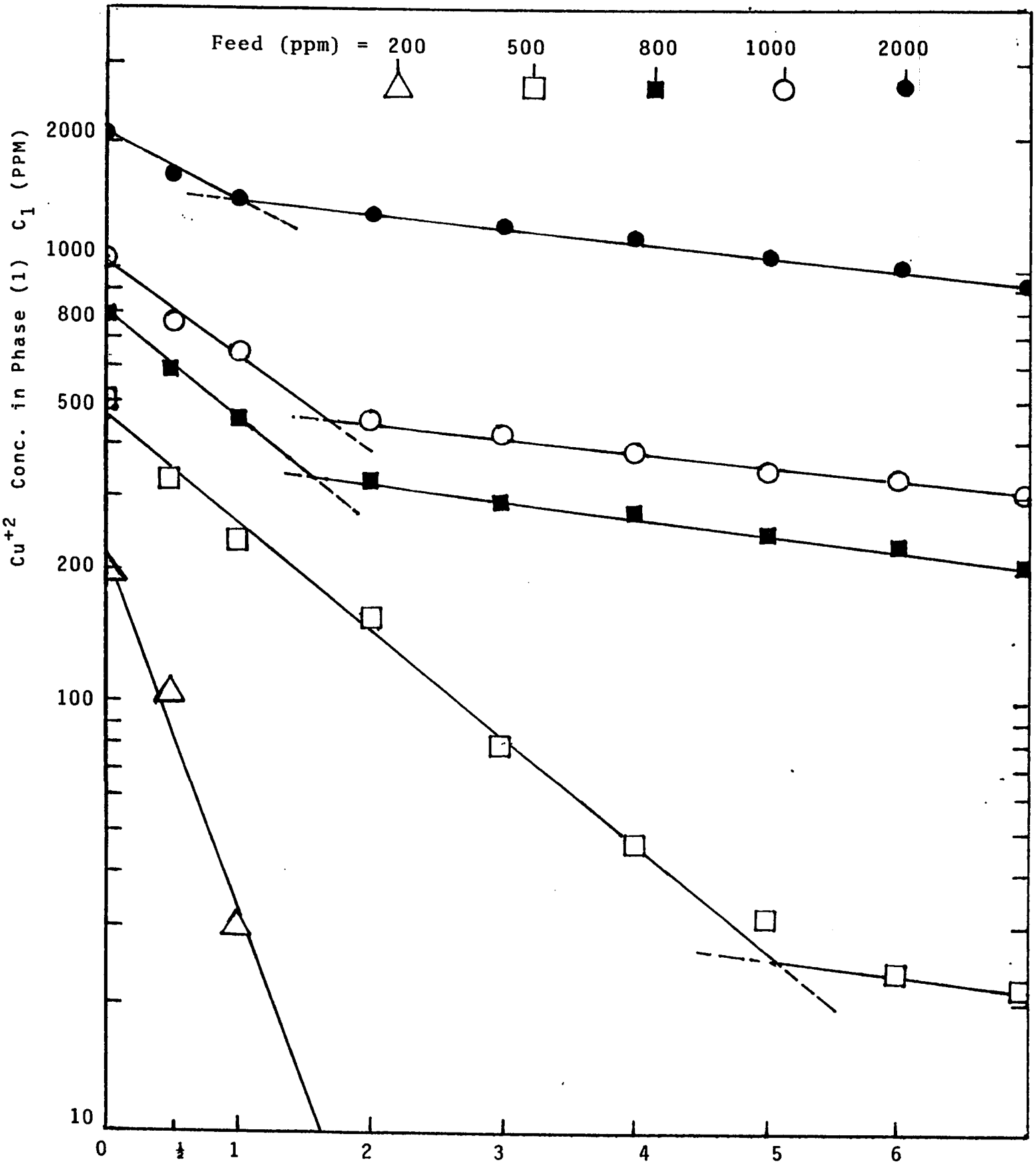


Table- 8 Modelling of Extraction Phase

(LIX64N 2.5 wt%)

Feed (ppm)	Slope of First Zone $m' \equiv k_1 a$ (M.Tr)	Slope of Second Zone $m'' \equiv k_1$ (Kinetics)
194.98	0.813	-
493.28	0.248	0.037
797.92	0.255	0.037
1072.14	0.223	0.035
2010.86	0.138	0.032

The possible explanation here may be that the transfer process in the first zone, is a mixed influence of diffusional and kinetic resistances especially at the highest concentration of feed (2000 ppm). As the feed concentration decreases, the influence of mass transfer regime starts to increase till it governs the entire process, especially at 200 ppm. In fact the slope of the line in this feed case (i.e., 200 ppm) may indicate the intrinsic mass transfer coefficient alone.

VI.2 MODELING OF STRIPPING PHASE PROCESS

One important problem with emulsion membrane is that after enrichment of the desired species has been attained, the emulsion droplets need to be broken and then the two phases separated. Due to this reason, the change in copper concentration with time in the encapsulated aqueous phase (stripping phase) has never been reported in literature yet.

In the earlier data analysis of phase 2, it was indicated that the copper concentration (C_2) increases linearly with time (see Fig. 12). This implies the rate of copper stripping (R_2) from organic phase to stripping phase is constant and independent of copper concentration in phase 2. The results also showed an increase in R_2 value with the increased feed concentration under fixed chelate condition. The values of the rate, R_2, also showed an increase with mixing speed (the value of R_2 is estimated as the slope of the C_2 Vs time line).

Based on these observations the linear increase in C_2 (concentration of copper in the stripping phase) with time implies a

possibility of a pseudo zero order reaction rate of stripping. The zero order rate constant must not vary due to any change in the reactant concentration which however, is not case as indicated earlier (i.e., R_2 increases with the increase in feed concentration).

As an explanation, the stripping process is modeled in terms of active sites distributed evenly at the "organic-stripping" interface, as shown in the following schematics (Fig.20). The number of active sites are assumed to be affected by the feed concentration. The stripping of copper from the copper complex (R_2Cu) by hydrogen is assumed to occur according to a pseudo zero order reaction rate.

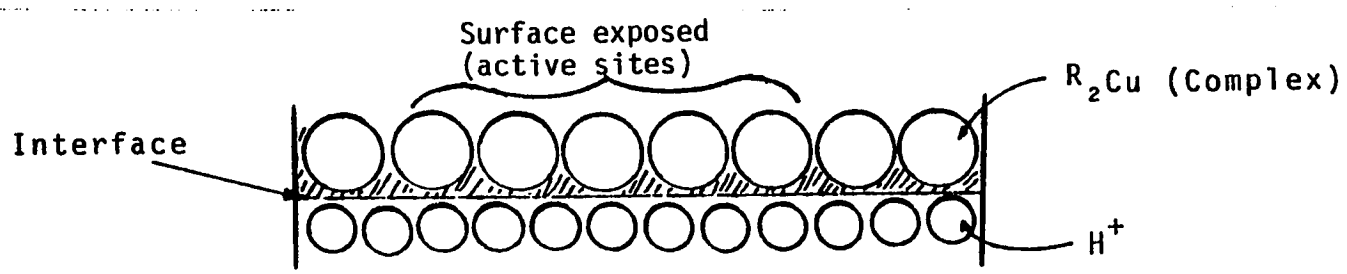


Fig. 20 Stripping Process Scheme

Reaction rate can be defined as,

$$r_i = (1/S) * (dN_i/dt) = \frac{\text{moles i formed}}{\text{(Surface) (time)}} \qquad (VI.4)$$

and in terms of zero order rate,

$$r_2 = (1/S) * (dm_2/dt) = k_2 \qquad (VI.5)$$

Therefore, the total stripping rate (R_2) can be expressed as,

$$R_2 = S.r_2 = dm_2/dt = S.k_2 \qquad (VI.6)$$

where:

R_2:is the total stripping rate of copper in mass per unit time,

r_2:is the stripping rate based on unit interfacial surface,

S:is the active sites (surface) exposed at the interface,

dm_2/dt: is the change of mass of copper in phase 2 with time,

k_2:is the pseudo zero order rate constant.,

In the model the active sites are assumed to depend upon feed concentration. The experimental results indicate the relationship between number of active sites and the feed concentration of the following form,

$$S = (m_0)^n \qquad (VI.7)$$

where:

m_0: is the mass of copper in feed and,

n: is the exponential correlation factor.

From Eq's.VI.6 and 7 one obtains,

$$R_2 = S.k_2 = m_0^n.k_2 \qquad (VI.8)$$

hence,

$$Ln(R_2) = n.Ln(m_0) + Ln(k_2) \qquad (VI.9)$$

According to Eq.VI.9, the plot of $\ln(R_2)$ versus $\ln(m_0)$ should be a straight line, for each chelate condition, which is reasonably the case as shown in figure 21 (see APX.1 for the required data of the plot).

In the figure, the slope of each straight line indicates the value of the factor (n) of the assumed site-feed relation, while the intersection with the "y-axis" (i.e., ln R_2-line) represents the pseudo zero order rate constant (k_2). As mentioned earlier the results of phase 2 agree reasonably with the proposed stripping model, specially since a very close value of k_2 was obtained for the two specified chelate concentration of LIX64N (2.5 & 5 wt%), where the same reaction mechanism is expected (see table-9 for n & k_2 values). Also the same explanation can be applied for the mixing speed results by assuming an increase in sites due to increased mixing speed.

VI.3 DISCUSSION OF THE ORGANIC PHASE PROCESS (THE SYSTEM OVERALL VIEW)

From literature it is well known that in the organic phase, the diffusion of copper-carrier complex (produced by extraction reaction at "extraction-organic" interface) and diffusion of the free chelate (produced due to stripping reaction at "organic-stripping" interface) occured in a counter current manner.

Although no samples of this phase were analysed during the

Fig. 21 Modeling of Stripping Phase

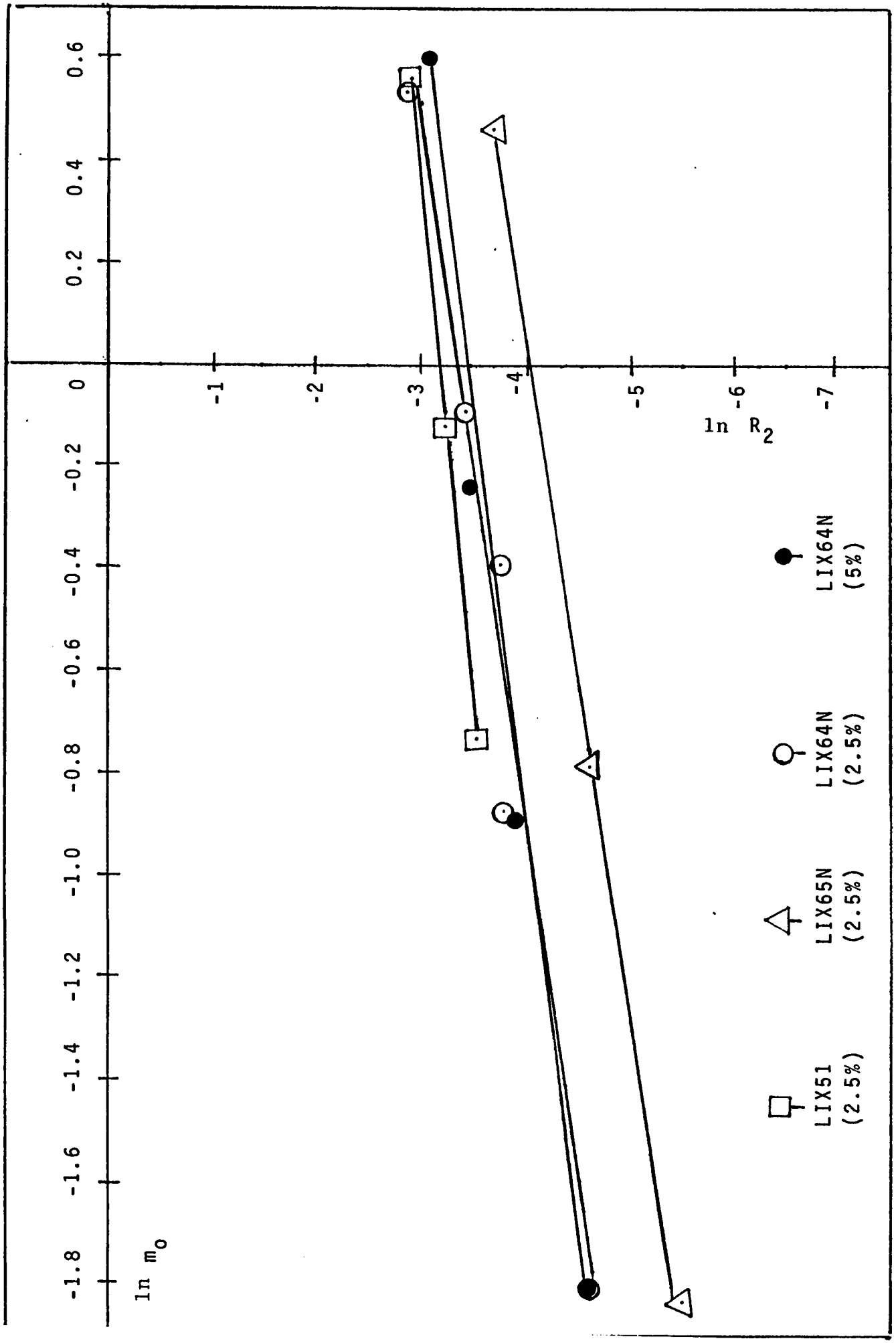


TABLE - 9

THE STRIPPING PHASE MODELING RESULTS

LIX	k_2	n
64N 2.5%	0.036	0.71
64N 5%	0.034	0.64
65N 2.5%	0.019	0.79
51 2.5%	0.041	0.48

experiments, mass of copper (m_3), in the organic phase, was obtained by material balance. Assuming a homogeneous organic phase due to stirring, the mass of copper (m_3) at any time is determined using the following equation,

$$m_3 = \rho_{aq} * V_{aq} * [C_0 - C_1 - C_2] * 10^{-6} \qquad (VI.10)$$

where:

ρ_{aq}: is the density of the aqueous phases in [gr/ml], which is considered approximately equal to density of water,

V_{aq}: is the volume of the aqueous phase in [ml], ($V_{extr.} = V_{strip.}$),

C_0, C_1 and C_2: are the feed, extraction, and stripping concentrations of copper (ppm) respictevely.

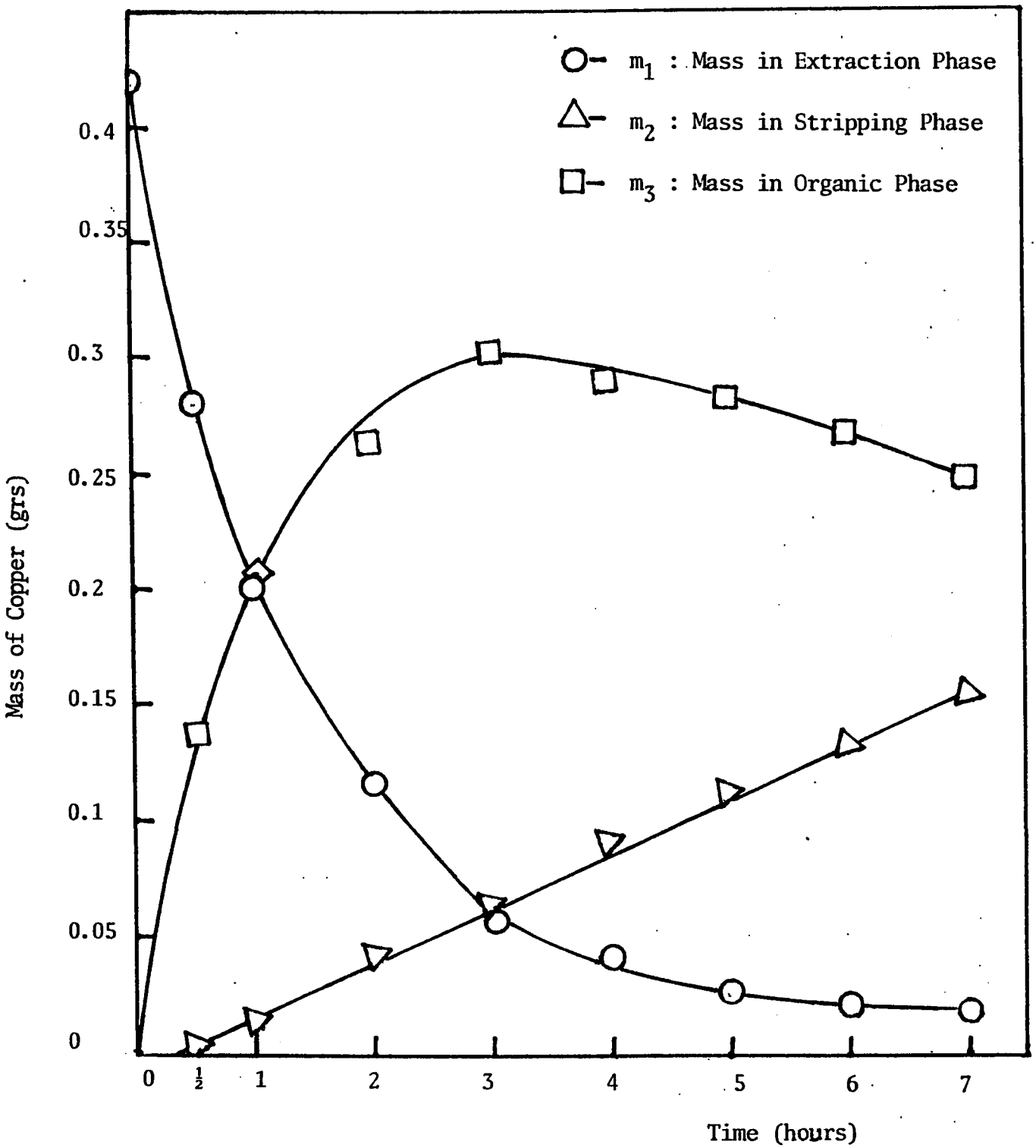
The concentration of copper in the two aqueous phases and the organic phase are plotted as shown (Fig.22) for a typical run#(5) [i.e., feed=493.29 ppm and chelate=LIX64N (2.5 wt%)], (see results in APX.1 for all runs).

In the figure it can be observed that, the amount of copper in phase 1 decreases, the amount of copper in phase 2 increases, while the amount of copper in phase(3) increases with time, reaches a maximum and then decreases. As a result the concentration of copper in the organic phase can be modeled as the intermediate product of a series reaction of the form,

$$A \longrightarrow P \longrightarrow S \qquad (VI.11)$$

Unfortunately the concentration "P" can not be predicted a priori

Fig. 22 The Change in Mass of Copper in the Three Phases of the Unit, Using Run # (5) Data



because the reaction "A —> P" can not be modeled by using a unique rate constant.

VI.4 CLASSIFICATION OF CHELATES

Finally, based on experimental results of similar feed (== 2000 ppm), shown in tables 10 and 11, the utilized chelates may be classified with regard to copper extraction and maximum copper yeild as follows:

For copper extraction,

LIX64N (5 wt%) ∽ LIX64N (2.5 wt%) ∽ LIX65N (2.5 wt%) > LIX51 (2.5 wt%)

and for copper stripping,

LIX64N (2.5 wt%) ∽ LIX51 (2.5 wt%) ∽ LIX64N (5 wt%) > LIX65N (2.5 wt%)

These classifications are chosen based on experimental results as previously mentioned. For accurate reasoning, it requires a full knowledge of the nature and chemistry of each chelate separately, which is not reported yet.

TABLE-10 PERCENTAGE OF INITIAL EXTRACTED COPPER

LIX Wt %	Feed C_0 (PPM)	Initial Copper Conc. in Phase (1) C_1 (PPM)	Initial Extrc. Copper Conc. in Phase (3) C_3 (PPM)	% Extrc. $(C_3/C_0)10^2$
64N 5%	2141.82	1399.08	742.74	34.7
64N 2.5%	2010.86	1573.80	437.06	21.7
65N 2.5%	1866.48	1613.28	253.20	13.6
51 2.5%	2054.84	1777.86	276.98	13.5

TABLE-11 MAXIMUM YIELD OF COPPER

LIX Wt %	Feed C_0 (PPM)	Maximum Stripp. Copper Conc. in Phase (2) C_2 (PPM)	% Yield $(C_2/C_0)10^2$
64N 2.5%	2010.86	448.62	22.3
51 2.5%	2141.82	424.20	20.6
64N 5%	2054.84	363.82	17.0
65N 2.5%	1866.48	197.86	10.6

VII. CONCLUSIONS AND RECOMMENDATIONS

VII.1 THE CONCLUSIONS

Based on experimental results, the following conclusion may be drawn.

1) From the "Feed —> LIX" equilibrium data, the utilized chelates can be arranged in a descending order in terms of their ability to extract copper as,

LIX64N (15 wt%) ∽ LIX64N (10 wt%) >> LIX64N (5 wt%) ∽ LIX64N (2.5 wt%) > LIX65N (2.5 wt%) ∽ LIX51 (2.5 wt%).

2) From the other "LIX —> H^+" equilibrium data, the chelates which are in favor of stripping copper, can be arranged in the following descending order,

LIX64N (2.5 wt%) ∽ LIX64N (5 wt%) > LIX51 (2.5 wt%) ∽ LIX65N (2.5 wt%) >> LIX64(10 wt%) ∽ LIX64N (15 wt%).

3) At equilibrium condition, the variation in pH value of feed between 2 pH and 7 pH does not affect the extraction ability for copper in the liquid membrane phase .

Contrarily, the stripped amount of copper at equilibrium seems to decrease rapidly with the increase in pH of the stripping solution.

Based on experimental results, the 7 and 1 pH values for the extraction and stripping solution respectively were found suitable for creating enough hydrogen gradient for copper transfer.

4) The increase in mixing speed is found to enhance both extraction and stripping rates of copper in the two aqeous phases (extraction and stripping phases respectively).

5) The increase in feed concentration decreases the extraction rate in the extraction phase due to chelate consumption and increases the stripping rate in the stripping phase due to increase in active sites at the interface.

6) In the system, the extraction process can be modeled in terms of series resistances (i.e., first diffusion resistance in the bulk, followed by a pseudo first order reaction kinetic resistance at the interface.

7) The stripping process is modeled in terms of active sites distributed evenly at the "organic-stripping" interface. The number of the active sites are assumed to be affected by feed concentration. The stripping reaction of copper from copper complex by hydrogen is assumed to occur according to pseudo zero order reaction rate.

8) The copper concentration in the organic phase may be modeled as the intermediate product of a series reaction.

9) The chelates can be classified in the following descending order as:

i) with regard to maximum copper extraction:

LIX64N (5 wt%) ∽ LIX64N (2.5 wt%) ∽ LIX65N (2.5 wt%)
> LIX51 (2.5 wt%)

ii) with regard to maximum copper yeild:

LIX64N (2.5 wt%) ∽ LIX51 (2.5 wt%) ∽ LIX64N (5 wt%)
> LIX65N (2.5 wt%)

VII.2 RECOMMENDATIONS

Based on the difficulties encountered and the results obtained in this study, the following recommendations need to be taken into account:

1) The presence of a proper analytical device (specially one giving cotinuous measurments) for copper and other heavy metal ion concentrations, is required for continuous sample analysis.

2) Due to limited mixing speed range, with respect to reactor dimensions, further modifications in the Copper Recovery unit are Recommended. Hence, to apply higher speeds, which are enough to eliminate the mass transfer effect in the extraction phase, and yet not creating any turbulance and aqueous overflow in the system. This will enable us to concentrate more on the kinetic study of the copper recovery system by liquid membrane containing a chelating agent.

3) The incorporation of the study on the effect of temperatures, and also of pH changes with time, in the extraction and the stripping phases of the Copper Recovery Unit system, is also important.

4) The Purification of the commercial chelates from impurities is required too, for better understanding of experimental results.

5). Also studies of the chelate effect on a mixed feed of heavy metal ions and on the recovery of some rare heavy metals such as Uranium, Silver and Gold are needed using the designed apparatus.

6) Finally, the study of the designed apparatus performance under steady state conditions is also recommended.

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IX. APPENDICES

IX.1 APPENDIX 1

(TABLES)

CONTENTS PAGE #

Run Number :- (1)

Speed = 160 rpm

LIX 64N (2.5%)

Analytical Services Laboratory

Laboratory Test Report Number : 1395-1409/239/84

Sample Identification : Aqueous extracts for Copper assay

Reference : Mr.A.Edrees (Chem.Eng.)

Date Received : 8.1.84

Date Reported : 10.1.84

Sample Code	p.p.m. Copper Solution #1	Solution #2
1	958.10	1.07
2	903.88	2.21
3	847.12	5.94
4	767.66	10.84
5	686.96	14.88
6	651.86	18.41
7	615.58	21.52
Feed	1054.82	

Analytical Services Supervisor

M Dawson
Analyst

NOTE:

SOLUTION # 1 : Extraction Solution

SOLUTION # 2 : Stripping Solution

Run Number : - (2)

Speed = 200 rpm

LIX 64N (2.5%)

Analytical Services Laboratory

Laboratory Test Report Number : 1410-1424/239/84

Sample Identification : Aqueous extracts for Copper assay

Reference : Mr. A.Edrees (Chem.Eng.)

Date Received : 9 .1.84

Date Reported : 10.1.84

Sample Code	p.p.m. Copper Solution #1	Solution #2
1	882.18	1.49
2	757.56	4.79
3	642.44	14.86
4	579.64	25.56
5	550.60	37.18
6	517.54	46.11
7	477.04	54.28
Feed	1115.26	

Analytical Services Supervisor

M Dawson
Analyst

Note

Solution # 1 : Extraction Solution
Solution # 2 : Stripping Solution

Run # (3)

Speed : 250 rpm
LIX 64N (2.5%)

Analytical Services Laboratory

Laboratory Test Report Number : 1437-1451/239/84

Sample Identification : Aqueous extracts for Copper assay

Reference : Mr. A.Edrees (Chem.Eng.)

Date Received : 10.1.84

Date Reported : 10.1.84

Sample Code	p.p.m. Copper Solution #1	Solution #2
1	775.96	3.05
2	628.22	10.42
3	536.98	31.22
4	482.08	61.07
5	423.92	91.81
6	400.48	110.80
7	381.86	135.44
Feed	1076.18	

Analytical Services Supervisor

M Dawson
Analyst

Note:
Solution # 1 : Extraction Solution
Solution # 2 : Stripping Solution

Speed: 220 rpm + 45 cc/min (DA @ STP)
LIX 64N (2.5%)

RUN # (4)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER 1626-1642/239/84

SAMPLE IDENTIFICATION : Aqueous extracts for Copper Assay

REFERENCE : Mr. A. Edrees (CHEM ENG)

DATE RECEIVED : 8.4.84

DATE REPORTED : 26.2.84

Sample Code	ppm Copper	
	Sample #1(solution)	Sample # 2 (Solution)
1	103.48	2.60
2	29.97	8.39
3	NIL	25.60
4	NIL	35.34
5	NIL	44.80
6	NIL	61.75
7	NIL	68.93
8	NIL	78.02
Feed	194.98	-

A. Abdennabi
Analytical Services Supervisor

M Dawson
Analyst

Note:

Solution # 1 : Extraction Solution

Solution # 2 : Stripping Solution

RUN # (5)

Speed: 220 rpm + 45 cc/min
LIX 64N (2.5%)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER : 1972-1988/239/84

RECEIVED FROM : Mr. A. Edrees (Chemical Engineering Dept.)

DATE REPORTED : 15.4.1984

Sample Code	ppm Copper	
	Sample # 1 (Solution)	Sample # 2 (Solution)
1	329.22	2.43
2	236.03	15.52
3	146.29	49.28
4	79.30	72.42
5	47.48	106.60
6	31.37	130.38
7	23.42	155.35
8	21.51	180.44
Feed	493.28	0.0

A. Abdennadi
Analytical Services Supervisor

M Dawson
Analyst

Note:
Solution # 1 : Extraction Solution
Solution # 2 : Stripping Solution

RUN# (6)

Speed: 220 rpm + 45 cc/min
LIX 64 N (2.5%)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER : 1955-1971/239/84

RECEIVED FROM : Mr. A. Edrees (Chemical Engineering Dept.)

DATE REPORTED : 15.3.84

Sample Code	ppm Copper	
	Sample # 1 (Solution)	Sample # 2 (Solution)
1	582.94	5.16
2	443.86	19.91
3	331.16	54.06
4	292.18	75.63
5	278.32	109.98
6	249.10	131.88
7	232.42	165.27
8	214.54	192.67
Feed	797.92	0.0

A Abdennil
Analytical Services Supervisor

M Dawson
Analyst

Note:
Solution # 1 : Extraction Solution
Solution # 2 : Stripping Solution

Run # (7)

Speed : 220 rpm + 45 cc/min
LIX 64 N (2.5%)

Analytical Services Laboratory

Laboratory Test Report Number : 1544-1562/239/84

Sample Identification : Aqueous extract for Copper assay

Reference : Mr. A.Edrees (Chem.Eng.)

Date Received : 17.1.84

Date Reported : 21.1.84

Sample Code	Solution #1	p.p.m. Copper Solution #2
1	752.70	6.76
2	641.32	22.58
3	448.04	61.28
4	420.86	101.84
5	382.04	145.89
6	349.38	190.02
7	330.22	221.20
8	300.82	253.02
9	263.78	287.22
Feed	1072.14	

A. Abdennabi
Analytical Services Supervisor

M Dawson
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

Run # . (8)

Speed = 220 rpm + 45 cc/min
LIX 64 N (2.5%)

Analytical Services Laboratory

Laboratory Test Report Number : 1509-1525/239/84

Sample Identification : Aqueous extracts for Copper assay

Reference : Mr. A.Edrees (Chem.Eng.)

Date Received : 14.1.84

Date Reported : 14.1.84

Sample Code	p.p.m. Copper Solution #1	Solution #2
1	1643.80	13.73
2	1462.72	52.35
3	1335.08	117.49
4	1252.60	189.96
5	1198.80	249.72
6	1087.40	321.12
7	1011.04	381.12
8	928.57	448.62
Feed	2010.86	

Analytical Services Supervisor

M Dawson
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

Speed : 220 rpm + 45 cc/min
LIX 64 N (5%)

RUN # (9).

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER : 1781-1797/239/84

SAMPLE IDENTIFICATION : Aqueous extracts for copper assay

REFERENCE : Mr. A. Edrees (Chem.Engg.)

DATE RECEIVED : 7.3.84

DATE REPORTED : 18.3.84

Sample Code	p.p.m. Copper	
	Sample #1 (Sol.)	Sample # 2 (Sol.)
1	49.29	1.44
2	11.75	5.19
3	NIL	15.21
4	NIL	25.33
5	NIL	45.48
6	NIL	56.46
7	NIL	66.84
8	NIL	76.43
Feed	195.34	-

A. A Gahennaty
Analytical Services Supervisor

M Dawson
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Sampling Solution

Speed : 220 rpm + 45 cc/min
LIX 64 N (5%)

RUN # (10)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER 1702-1718/239/84

SAMPLE IDENTIFICATION : AQUEOUS EXTRACTS FOR COPPER ASSAY

REFERENCE : MR. A. EDREES (CHEM ENG.)

DATE RECEIVED : 26.2.84

DATE REPORTED : 27.2.84

Sample Code	ppm Copper	
	Sample #1 (Solution)	Sample # 2 (Solution)
1	186.07	10.03
2	67.49	19.46
3	17.90	49.13
4	8.02	75.31
5	7.16	95.01
6	6.59	122.16
7	6.07	141.28
8	5.40	176.97
Feed	482.30	-

A. Abdennadi
Analytical Services Supervisor

M Daoud
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

Speed : 220 rpm + 45 cc/min

LIX 64 N (5%)

RUN #(11)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER 1798-1814/239/84

SAMPLE IDENTIFICATION : Aqueous extracts for Copper Assay

REFERENCE : Mr. A. Edrees

DATE RECEIVED : 7.3.84

DATE REPORTED : 18.3.84

Sample Code	ppm Copper	
	Sample #1(Solution)	Sample # 2 (Sol)
1	534.80	5.76
2	350.64	21.96
3	149.50	60.33
4	84.10	100.35
5	75.66	134.72
6	67.81	171.95
7	61.93	207.69
8	54.67	253.40
Feed	928.90	-

A Abdennabi
Analytical Services Supervisor

M Dawson
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

Speed : 220 rpm + 45 cc/min
LIX 64 N (5%)

RUN # (12)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER : 1660-1676/239/84

SAMPLE IDENTIFICATION : Aqueous extracts for Copper Assy

REFERENCE : Mr. A. Edrees (Chem. Eng.)

DATE RECEIVED : 8.2.84

DATE REPORTED : 26.2.84

Sample Code	ppm Copper	
	Sample #1 (Sol.)	Sample # 2 (Sol)
1	1399.08	10.22
2	1233.36	39.86
3	945.28	93.49
4	823.42	153.22
5	766.74	215.36
6	735.40	260.60
7	679.90	316.14
8	603.32	363.82
Feed	2141.82	-

A. Nadennaly
Analytical Services Supervisor

M Dawson
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

RUN # (13)

Speed: 220 rpm + 45 cc/min

LIX 65 N (2.5%)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER : 1887-1903/239/84

RECEIVED FROM : Mr. A. Edrees (Chemical Engineering Dept.)

DATE REPORTED : 15.3.84

Sample Code	ppm Copper	
	Sample # 1 (Solution)	Sample # 2 (Solution)
1	111.91	2.08
2	60.65	5.46
3	23.32	9.91
4	8.17	16.92
5	2.81	19.21
6	1.10	22.61
7	-	29.57
8	-	33.52
Feed	188.39	0.0

Analytical Services Supervisor

Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

Speed: 220 rpm + 45 cc/min

RUN # (14)

ANALYTICAL SERVICES LABORATORY

LIX 65 N (2.5%)

LABORATORY TEST REPORT NUMBER 1832-1848/239/84

SAMPLE IDENTIFICATION : Aqueous extracts for Copper Assay

REFERENCE : Mr. A. Edrees (Chem.Engg.)

DATE RECEIVED : 7.3.84

DATE REPORTED : 18.3.84

Sample Code	ppm Copper	
	Sample #1 (Sol.)	Sample # 2 (Sol.)
1	422.84	4.15
2	332.68	9.35
3	203.99	21.20
4	137.69	41.07
5	102.15	56.48
6	98.13	60.12
7	88.79	78.90
8	83.22	92.16
Feed	533.56	-

A. Abdemalk
Analytical Services Supervisor

M Dawson
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

Speed: 220 rpm + 45 cc/min

LIX 65 N (2.5%)

RUN # (15)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER 1815-1831

SAMPLE IDENTIFICATION : Aqueous extract for copper Assay

REFERENCE : Mr. A. Edrees (Chem.Engg.)

DATE RECEIVED : 7.3.84

DATE REPORTED : 18.3.84

Sample Code	ppm Copper	
	Sample #1 (Solution	Sample # 2 (Sol.)
1	1613.28	5.63
2	1413.27	16.02
3	1348.51	53.97
4	1289.38	79.86
5	1234.14	113.53
6	1159.10	147.78
7	1102.02	170.77
8	1024.24	197.86
Feed	1866.48	-

A. Abdennadi
Analytical Services Supervisor

M Dawson
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

Speed : 220 rpm + 45 cc/min

LIX 51 (2.5%)

RUN # (16)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER : 1921-1937/239/84

RECEIVED FROM : Mr. A. Edrees (Chemical Engineering Dept.)

DATE REPORTED : 15.4.84

Sample Code	ppm Copper	
	Sample # 1 (Solution)	Sample # 2 (Solution)
1	409.62	13.55
2	372.84	40.65
3	293.18	82.29
4	208.42	114.45
5	199.92	146.29
6	191.44	182.90
7	186.51	213.18
8	171.93	243.18
Feed	568.28	0.0

Analytical Services Supervisor

Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER : 1938-1954/239/84

RECEIVED FROM : Mr. A. Edrees (Chemical Engineering Dept.)

DATE REPORTED : 15.4.1984

Sample Code	ppm Copper	
	Sample # 1 (Solution)	Sample # 2 (Solution)
1	839.84	12.74
2	738.86	33.86
3	664.20	85.70
4	640.40	134.92
5	617.38	186.23
6	582.26	234.60
7	571.18	264.00
8	540.70	299.04
Feed	1039.48	0.0

A. Abdennadi
Analytical Services Supervisor

M Davison
Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

RUN # (18)

Speed: 220 rpm + 45 cc/min
LIX 51 (2.5%)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER : 1904-1920/239/84

RECEIVED FROM : Mr. A. Edrees (Chemical Engineering Dept.)

DATE REPORTED : 15.4.84

Sample Code	ppm Copper	
	Sample # 1 (Solution)	Sample # 2 (Solution)
1	1777.86	17.74
2	1693.28	58.65
3	1614.08	136.93
4	1582.58	203.68
5	1510.20	269.70
6	1468.50	324.68
7	1393.74	384.40
8	1335.20	445.20
Feed	2054.84	0.0

Analytical Services Supervisor

Analyst

Note:

1. Solution # 1 : Extraction Solution
2. Solution # 2 : Stripping Solution

RUN # (19)

ANALYTICAL SERVICES LABORATORY

LABORATORY TEST REPORT NUMBER: 2005-2029/239/84
RECEIVED FROM : Mr. A. Edrees (Chem Eng)
DATE REPORTED : 21.4.84
SAMPLE TYPE : Diffusion Experiment

Sample Code		PPM Copper
Period #1	1	1249.38
	2	1253.62
	3	1273.88
	4	1300.18
Period #2	1	1179.18
	2	1217.40
	3	1220.76
	4	1239.84
Period #3	1	1186.16
	2	1192.90
	3	1202.22
	4	1209.70
Period#4	1	1151.64
	2	1148.12
	3	1163.74
	4	1175.20
Period#5	1	1107.26
	2	1116.56
	3	1142.84
	4	1146.04
Feed		1309.18

A. Abdennabi
Analytical Services Supervisor

M Dawson
Analyst

*Note: Period #1 was not diluted to the mark properly.

RUN # (1)

TABLE 1 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.8966	0	0
½	0.8144	0.0009	0.0813
1	0.7683	0.0019	0.1264
2	0.7201	0.0050	0.1715
3	0.6525	0.0092	0.2349
4	0.5839	0.0126	0.3001
5	0.5541	0.0156	0.3269
6	0.5232	0.0183	0.3551
7			

RUN # (2)

TABLE 2 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.9480	0	0
½	0.7499	0.0013	0.1968
1	0.6439	0.0041	0.3000
2	0.5461	0.0109	0.3910
3	0.4927	0.0226	0.4327
4	0.4680	0.0311	0.4489
5	0.4399	0.0396	0.4685
6	0.4055	0.0481	0.4944
7			

RUN # (3)

TABLE 3 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.9148	0	0
½	0.6596	0.0026	0.2526
1	0.5340	0.0089	0.3719
2	0.4564	0.0265	0.4319
3	0.4098	0.0519	0.4531
4	0.3603	0.0733	0.4812
5	0.3404	0.0942	0.4802
6	0.3246	0.1151	0.4751
7			

RUN # (4)

TABLE 4 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.1657	0	0
½	0.0880	0.0022	0.0755
1	0.0255	0.0071	0.1331
2	-	0.0243	0.1414
3	-	0.0345	0.1312
4	-	0.0423	0.1234
5	-	0.0525	0.1132
6	-	0.0586	0.1071
7	-	0.0638	0.1019

RUN # (5)

TABLE 5 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.4193	0	0
½	0.2798	0.0021	0.1374
1	0.2006	0.0132	0.2055
2	0.1244	0.0419	0.2530
3	0.0674	0.0616	0.2903
4	0.0404	0.0906	0.2883
5	0.0267	0.1108	0.2818
6	0.0199	0.1320	0.2674
7	0.0183	0.1534	0.2476

RUN # (6)

TABLE 6 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.6782	0	0
½	0.4955	0.0044	0.1783
1	0.3773	0.0169	0.2840
2	0.2815	0.0457	0.3510
3	0.2483	0.0643	0.3656
4	0.2366	0.0930	0.3486
5	0.2117	0.1121	0.3544
6	0.1975	0.1403	0.3404
7	0.1824	0.1634	0.3324

RUN # (7)

TABLE 7 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.9113	0	0
½	0.6398	0.0057	0.2658
1	0.5451	0.0192	0.3470
2	0.3808	0.0521	0.4784
3	0.3577	0.0866	0.4670
4	0.3247	0.1213	0.4653
5	0.2970	0.1643	0.4501
6	0.2807	0.1880	0.4426
7	0.2557	0.2151	0.4405

RUN # (8)

TABLE 8 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	1.7092	0	0
½	1.3972	0.0117	0.3003
1	1.2433	0.0445	0.4214
2	1.1348	0.0967	0.4777
3	1.0692	0.1655	0.4745
4	1.0190	0.2175	0.4727
5	0.9243	0.2730	0.5119
6	0.8594	0.3240	0.5285
7	0.7893	0.3813	0.5386

RUN # (9)

TABLE 9 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.1660	0	0
½	0.0419	0.0012	0.1229
1	0.0100	0.0044	0.1516
2	-	0.0129	0.1531
3	-	0.0215	0.1445
4	-	0.0387	0.1273
5	-	0.0480	0.1180
6	-	0.0568	0.1092
7	-	0.0650	0.1010

RUN # (10)

TABLE 10 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.4100	0	0
½	0.1582	0.0085	0.2433
1	0.0574	0.0165	0.3361
2	0.0152	0.0418	0.3530
3	0.0068	0.0640	0.3392
4	0.0061	0.0806	0.3233
5	0.0056	0.1012	0.3032
6	0.0052	0.1218	0.2830
7	0.0046	0.1424	0.2630

RUN # (11)

TABLE 11 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.7896	0	0
½	0.4546	0.0049	0.3301
1	0.2980	0.0187	0.4729
2	0.1271	0.0513	0.6112
3	0.0715	0.0853	0.6328
4	0.0643	0.1145	0.6108
5	0.0576	0.1462	0.5857
6	0.0526	0.1765	0.5604
7	0.0465	0.2154	0.5277

RUN # (12)

TABLE 12 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	1.8205	0	0
½	1.1892	0.0087	0.6226
1	1.0484	0.0339	0.7382
2	0.8035	0.0795	0.8375
3	0.7998	0.1302	0.8905
4	0.6517	0.1731	0.9657
5	0.6251	0.2215	0.9739
6	0.5779	0.2670	0.9756
7	0.5128	0.3125	0.9652

RUN # (13)

TABLE 13 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.1601	0	0
½	0.0951	0.0018	0.0632
1	0.0516	0.0046	0.1039
2	0.0198	0.0098	0.1305
3	0.0069	0.0125	0.1407
4	0.0024	0.0160	0.1417
5	0.0009	0.0192	0.1400
6	-	0.0251	0.1350
7	-	0.0294	0.1307

RUN # (14)

TABLE 14 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.4535	0	0
½	0.3594	0.0038	0.0903
1	0.2828	0.0076	0.1631
2	0.1734	0.0180	0.2621
3	0.1170	0.0349	0.3016
4	0.0868	0.0421	0.3246
5	0.0834	0.0545	0.3156
6	0.0834	0.0670	0.3110
7	0.0708	0.0775	0.3052

RUN # (15)

TABLE 15 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	1.5865	0	0
½	1.4138	0.0048	0.1679
1	1.2013	0.0136	0.3716
2	1.1462	0.0459	0.3944
3	1.0960	0.0625	0.4280
4	1.0490	0.0962	0.4413
5	0.9852	0.1251	0.4762
6	0.9359	0.1457	0.5049
7	0.8706	0.1683	0.5476

RUN # (16)

TABLE 16 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.4830	0	0
½	0.3482	0.0195	0.1153
1	0.3169	0.0346	0.1315
2	0.2492	0.0639	0.1698
3	0.1771	0.0941	0.2118
4	0.1699	0.1213	0.1918
5	0.1627	0.1509	0.1694
6	0.1585	0.1812	0.1433
7	0.1461	0.2077	0.1292

RUN # (17)

TABLE 17 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	0.8836	0	0
½	0.7139	0.0108	0.1589
1	0.6281	0.0288	0.2267
2	0.5646	0.0728	0.2462
3	0.5443	0.1147	0.2246
4	0.5248	0.1503	0.2085
5	0.4949	0.1995	0.1892
6	0.4855	0.2298	0.1683
7	0.4596	0.2587	0.1653

RUN # (18)

TABLE 18 THE CHANGE IN Cu^{+2} MASS WITH TIME IN THE SYSTEM

Time (hr)	m_1 (gram) Extraction	m_2 (gram) Stripping	m_3 (gram) Organic
0	1.7466	0	0
½	1.5112	0.0251	0.2103
1	1.4393	0.0499	0.2574
2	1.3720	0.1064	0.2682
3	1.3452	0.1607	0.2407
4	1.2837	0.2182	0.2447
5	1.2482	0.2623	0.2361
6	1.1847	0.3214	0.2405
7	1.1349	0.3750	0.2367

EQUILIBRIUM DATA

FEED ⟶ LIX 64N (15 %)

TABLE I - 1

X	ORGANIC [I] COPPER (PPM)	AQUEOUS [I X) COPPER (PPM)
A	2613.93	115.09
B	1434.15	14.25
C	657.47	1.59
D	332.29	0.14

LIX 64N (15 %) ⟶ H^+

TABLE I - 2

X	ORGANIC [I] COPPER (PPM)	AQUEOUS [1- I X] COPPER (PPM)
A	2504.98	77.10
B	1363.65	42.81
C	635.89	15.27
D	322.09	7.22

EQUILIBRIUM DATA

FEED ⟶ LIX 64N (10 %)

TABLE II- 1

X	ORGANIC [II] COPPER (PPM)	AQUEOUS [II X) COPPER (PPM)
A	2509.11	199.15
B	1422.93	23.25
C	656.83	2.10
D	332.17	0.24

LIX 64N (10 %) ⟶ H^+

TABLE II - 2

X	ORGANIC [II] COPPER (PPM)	AQUEOUS [1-II X] COPPER (PPM)
A	2381.25	90.48
B	1352.66	56.36
C	628.68	22.58
D	320.94	9.01

EQUILIBRIUM DATA

FEED ⟶ LIX 64N (5 %)

TABLE III- 1

X	ORGANIC [III] COPPER (PPM)	AQUEOUS [III X) COPPER (PPM)
A	2022.29	545.26
B	1168.97	60.21
C	610.47	5.24
D	274.75	0.33

LIX 64N (5 %) ⟶ H^+

TABLE III- 2

X	ORGANIC [III] COPPER (PPM)	AQUEOUS [1-IIIX] COPPER (PPM)
A	1047.30	781.94
B	557.52	490.38
C	271.92	271.52
D	111.56	130.88

EQUILIBRIUM DATA

FEED ⟶ LIX 64N (2.5 %)

TABLE IV - 1

X	ORGANIC [IV] COPPER (PPM)	AQUEOUS [IV X) COPPER (PPM)
A	1293.54	1129.72
B	878.85	292.88
C	590.15	21.54
D	274.115	0.84

LIX 64N (2.5 %) ⟶ H^+

TABLE IV - 2

X	ORGANIC [IV] COPPER (PPM)	AQUEOUS [1- IV X] COPPER (PPM)
A	489.25	645.04
B	203.94	541.28
C	134.46	365.46
D	78.80	156.64

EQUILIBRIUM DATA

FEED ⟶ LIX 65N (2.5 %)

TABLE V- 1

X	ORGANIC [V] COPPER (PPM)	AQUEOUS [V X) COPPER (PPM)
A	1198.53	1210.76
B	837.73	445.42
C	662.86	35.35
D	263.50	1.55

LIX 65N (2.5 %) ⟶ H^+

TABLE V - 2

X	ORGANIC [V] COPPER (PPM)	AQUEOUS [1- V X] COPPER (PPM)
A	684.13	412.55
B	454.54	360.53
C	321.95	295.35
D	113.44	152.35

EQUILIBRIUM DATA

FEED ⟶ LIX51 (2.5 %)

TABLE VI - 1

X	ORGANIC [VI] COPPER (PPM)	AQUEOUS [VI, X) COPPER (PPM)
A	954.84	1406.20
B	612.87	625.76
C	473.79	186.98
D	194.21	57.12

LIX51 (2.5 %) ⟶ H^+

TABLE VI - 2

X	ORGANIC [VI] COPPER (PPM)	AQUEOUS [1-VI X] COPPER (PPM)
A	500.14	364.67
B	295.74	254.34
C	224.10	199.25
D	124.32	136.25

Table - 1 Modelling of Extraction Phase

(LIX64N 5 wt%)

Feed (ppm)	Slope of First Zone $m' \equiv k_1 a$ (M.Tr)	Slope of Second Zone $m'' \equiv k_1$ (Kinetics)
195.34	1.221	-
482.30	0.713	0.042
928.90	0.391	0.0461
2141.82	0.240	0.040

Table-2 Modelling of Extraction Phase

(LIX65N 2.5 wt%)

Feed (ppm)	Slope of First Zone $m' \equiv k_1 a$ (M.Tr)	Slope of Second Zone $m'' \equiv k_1$ (Kinetics)
188.39	0.448	-
533.56	0.198	0.028
1866.48	0.121	0.024

Table-3 Modelling of Extraction Phase

(LIX51 2.5 wt%)

Feed (ppm)	Slope of First Zone $m' \equiv k_1 a$ (M.Tr)	Slope of Second Zone $m'' \equiv k_1$ (Kinetics)
568.28	0.133	0.021
1039.48	0.148	0.018
2054.84	0.084	0.017

Table-1 Effect of Speed on Stripping Rate

Speed (rpm)	Stripping rate constant k_2 (ppm/m)	Stripping rate constant k_2 (g/m)
160	3.88	0.0033
200	10.12	0.0086
250	23.65	0.0201

Table-2 Effect of Feed on Stripping Rate

(LIX64N 2.5 wt%)

Feed C_o (ppm)	Feed m_o (gr.)	Stripping rate constant k_2 (ppm/hr)	Stripping rate constant k_2 (g/hr)
194.98	0.1657	11.41	0.0097
493.28	0.4193	26.94	0.0229
797.92	0.6782	27.65	0.0235
1072.14	0.9113	38.24	0.0325
2010.86	1.7092	65.53	0.0557

Table -3 Effect of Feed on Stripping Rate

(LIX64N 5 wt %)

Feed C_o (ppm)	Feed m_o (gr.)	Stripping rate constant k_2 (ppm/hr)	Stripping rate constant k_2 (g/hr)
195.34	0.1660	11.77	0.0100
482.30	0.4100	24.23	0.0206
928.90	0.7896	36.70	0.0312
2141.82	1.8205	54.00	0.0459

Table-4 Effect of Feed on Stripping Rate

(LIX65N 2.5 wt%)

Feed C_o (ppm)	Feed m_o (gr.)	Stripping rate constant k_2 (ppm/hr)	Stripping rate constant k_2 (g/hr)
188.39	0.1601	4.71	0.0040
533.56	0.4535	13.53	0.0115
1866.48	1.5865	29.65	0.0252

Table-5 Effect of Feed on Stripping Rate

(LIX51 2.5 wt%)

Feed C_o (ppm)	Feed m_o (gr.)	Stripping rate constant k_2 (ppm/hr)	Stripping rate constant k_2 (g/hr)
568.28	0.4830	34.12	0.0290
1039.48	0.8836	45.64	0.0388
2054.84	1.7466	63.18	0.0537

DATA OF FIGURE 21 (MODELLING OF STRIPPING PHASE)

Table -1 The LIX64N (2.5%) Experiments

Feed m_o (gr.)	Stripping rate R_2 (gr/hr)	$\ln m_o$	$\ln R_2$
1.7092	0.0557	0.54	- 2.89
0.9113	0.0325	- 0.09	- 3.43
0.6782	0.0235	- 0.39	- 3.75
0.4193	0.0229	- 0.87	- 3.78
0.1657	0.0097	- 1.80	- 4.63

Table -2 The LIX64N (5%) Experiments

Feed m_o (gr.)	Stripping rate R_2 (gr/hr)	$\ln m_o$	$\ln R_2$
1.8205	0.0459	0.60	- 3.08
0.7896	0.0312	- 0.24	- 3.47
0.4100	0.0206	- 0.89	- 3.89
0.1660	0.0100	- 1.80	- 4.61

Table-3 The LIX65N (2.5%) Experiments

Feed m_0 (gr.)	Stripping rate R_2 (gr/hr)	ln m_0	ln R_2
1.5865	0.02519	0.46	- 3.68
0.4535	0.01152	- 0.79	- 4.46
0.1601	0.00404	- 1.83	- 5.51

Table - 4 The LIX51 (2.5%) Experiments

Feed m_o (gr.)	Stripping rate R_2 (gr/hr)	$\ln m_o$	$\ln R_2$
1.7466	0.0537	0.56	- 2.92
0.8836	0.0388	- 0.12	- 3.25
0.4830	0.0290	- 0.73	- 3.54

Table -5 Constants of Equation ($y = a_1 x + a_0$) Used to Correlate ln R_2 vs ln m_0 Data

EXPERIMENT LIX	wt%	$a_0 \equiv (\ln k_2)$	k_2	$a_1 \equiv n$	Correlation Coefficient r^2
64N	2.5	- 3.33	0.036	0.71	0.97
64N	5	- 3.39	0.034	0.64	0.98
65N	2.5	- 3.97	0.019	0.79	0.98
51	2.5	- 3.19	0.041	0.48	1.00

IX.2 APPENDIX 2

(FIGURES)

Fig.23 The Equilibrium Curves:
FEED ---► LIX64N

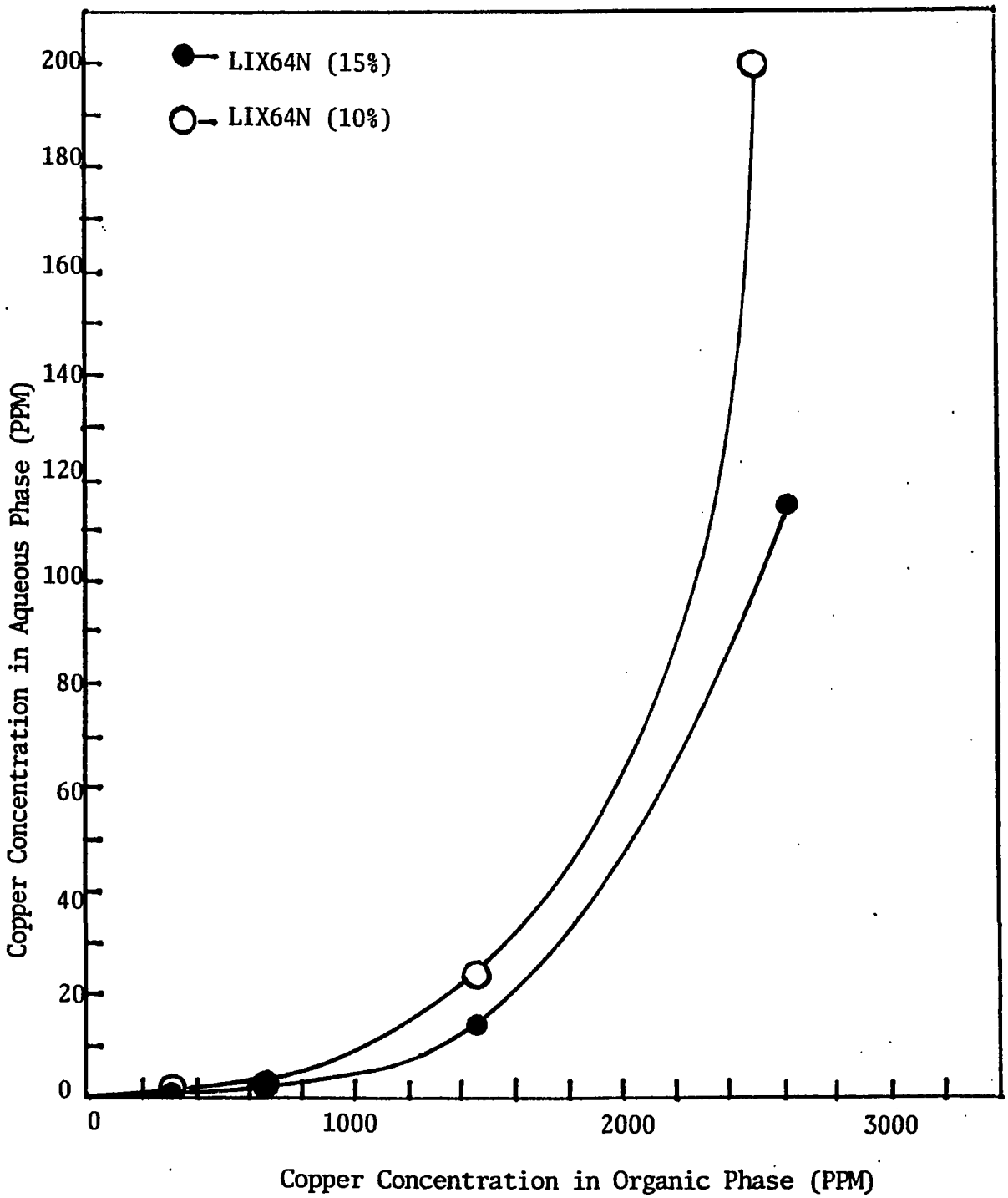

Fig. 24 The Equilibrium Curves :

LIX64N ----→ H^+

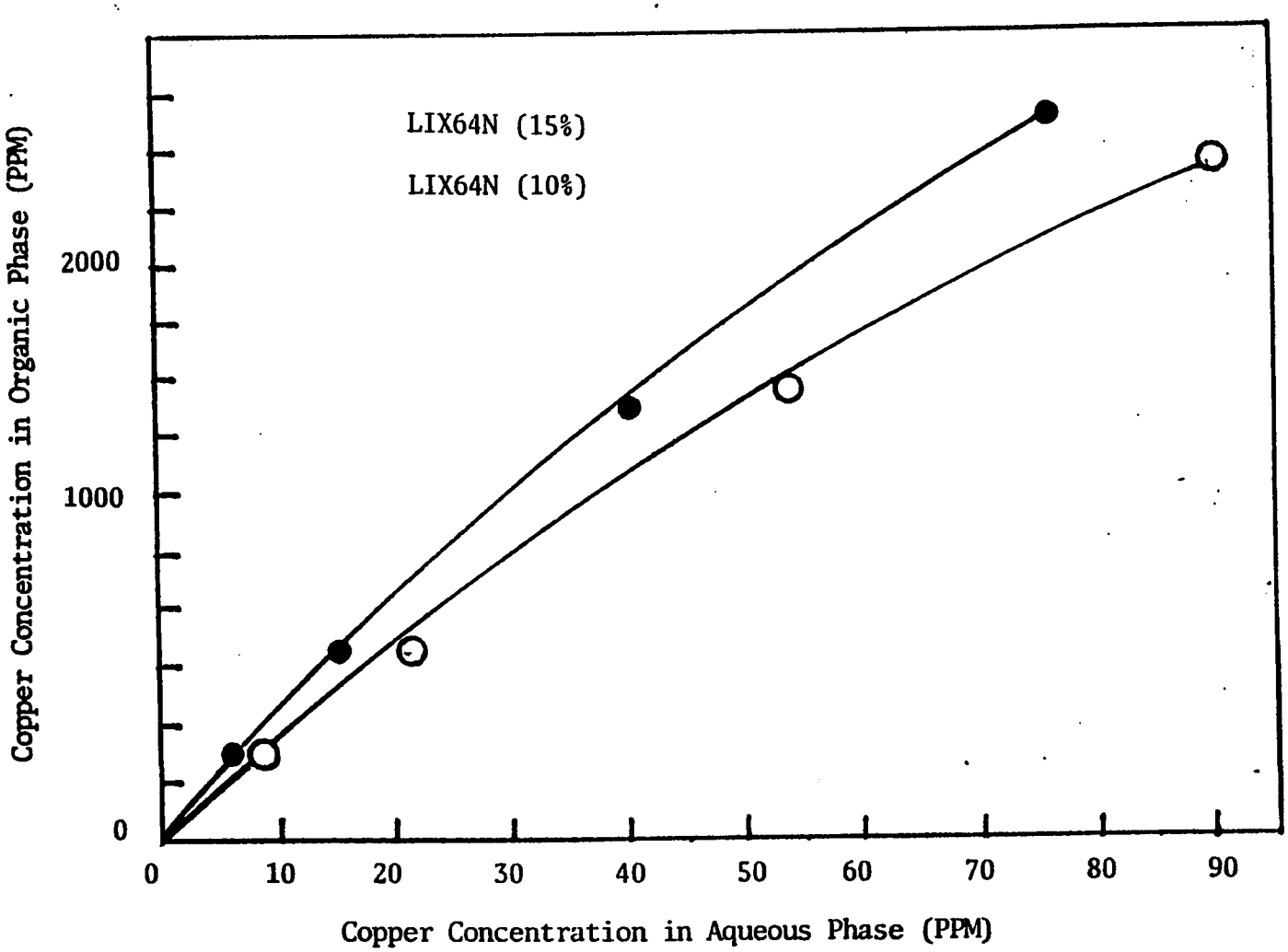

Fig.25 The Equilibrium Curves :

Feed ⟶ LIX64N

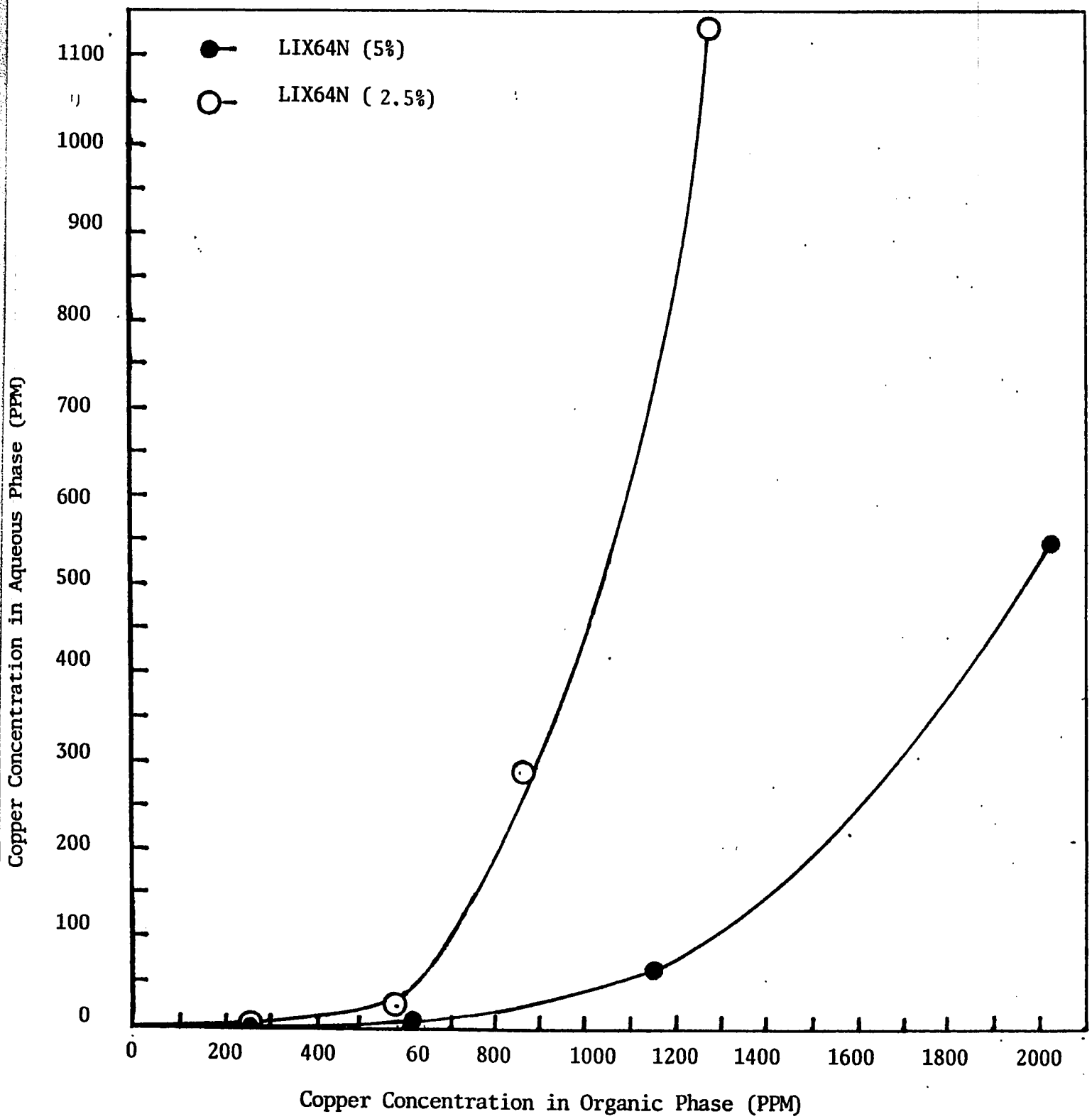

Fig. 26 The Equilibrium Curves:

LIX64N ---→ H^+

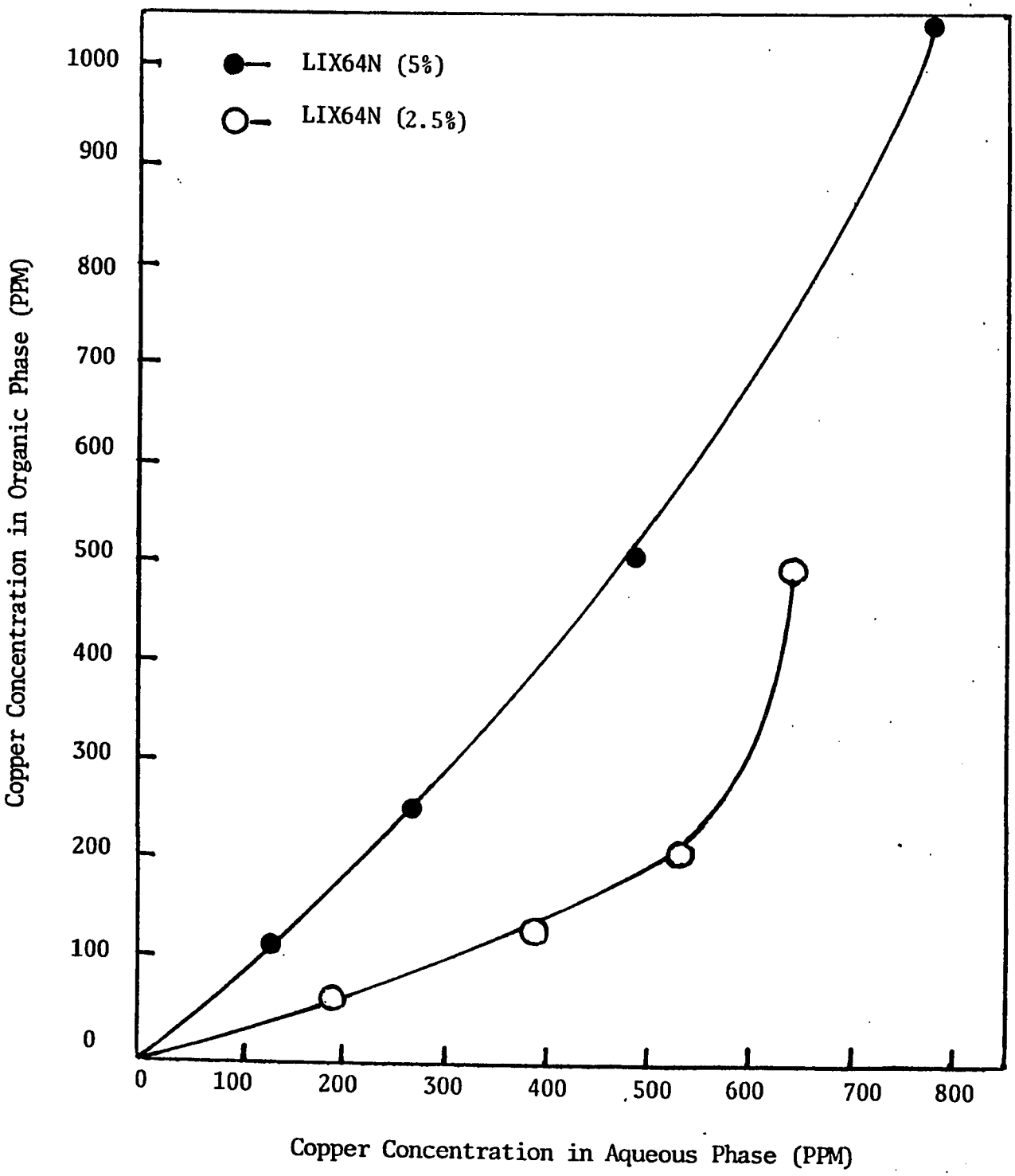

Fig. 27 The Equilibrium Curves :

FEED → { LIX65N
LIX51

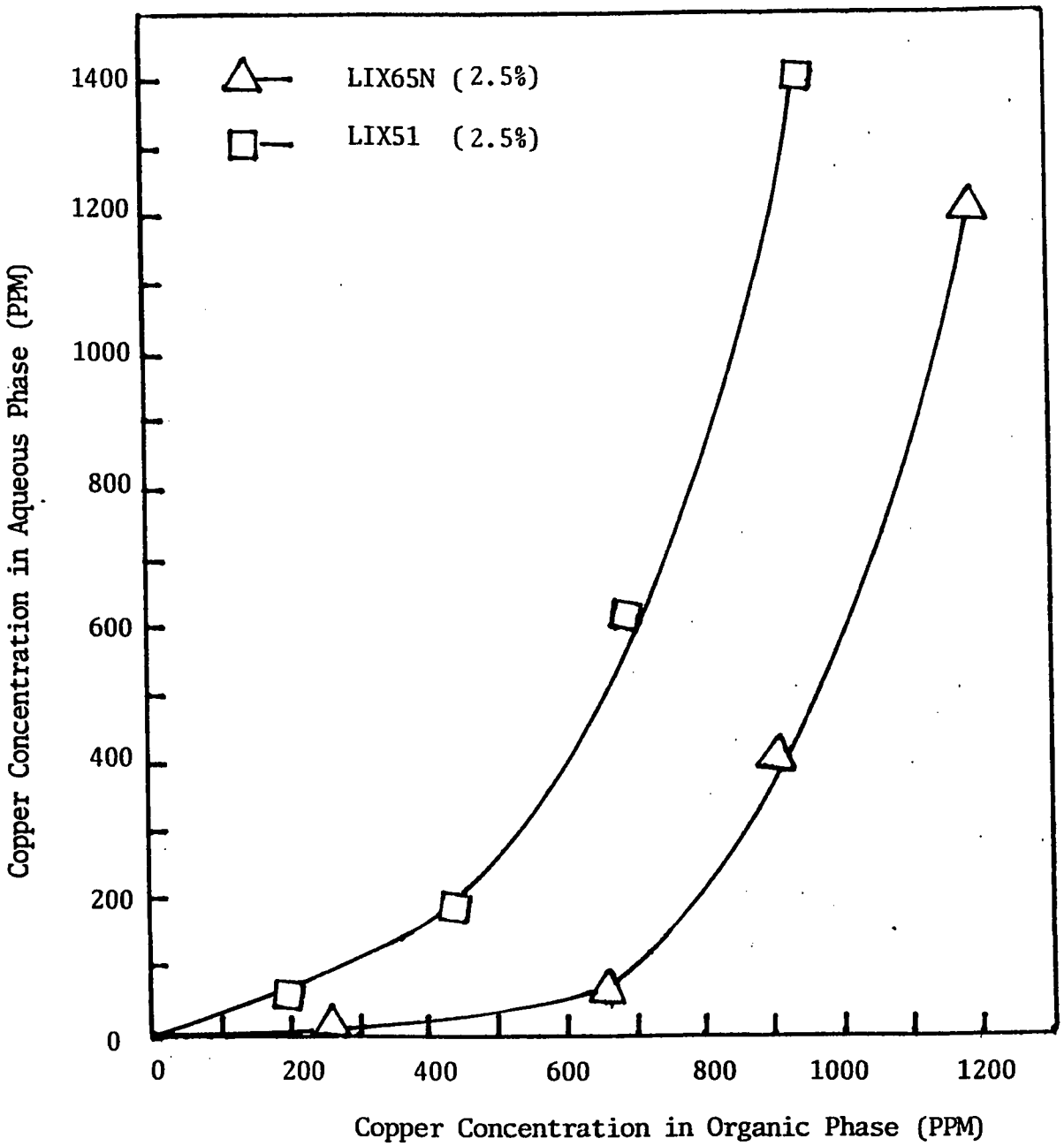

Fig.28 The Equilibrium Curves :

LIX65N
LIX51 } ⟶ H^+

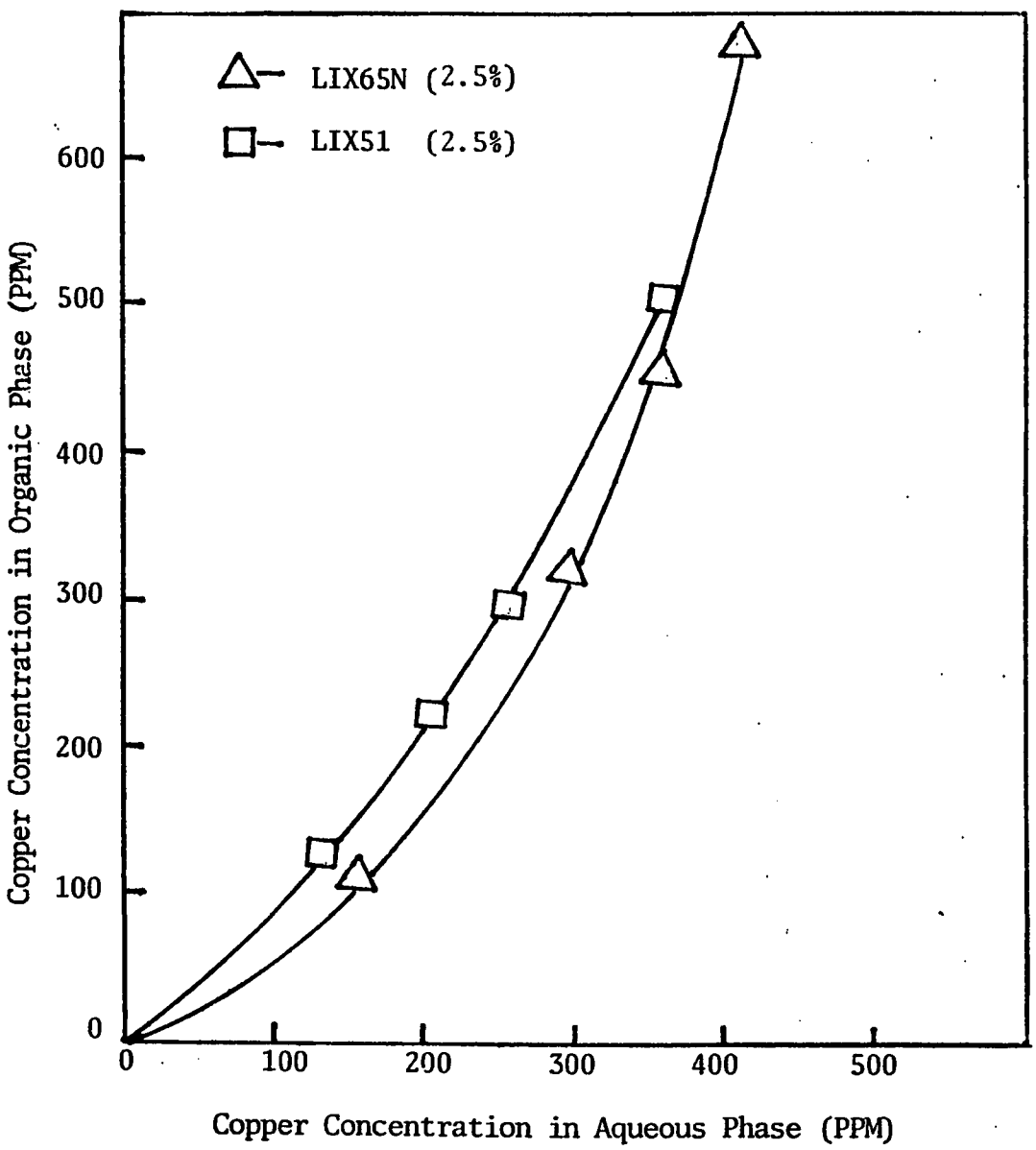

Fig. 29 Modelling of Extraction Phase

(LIX64N 5 wt %)

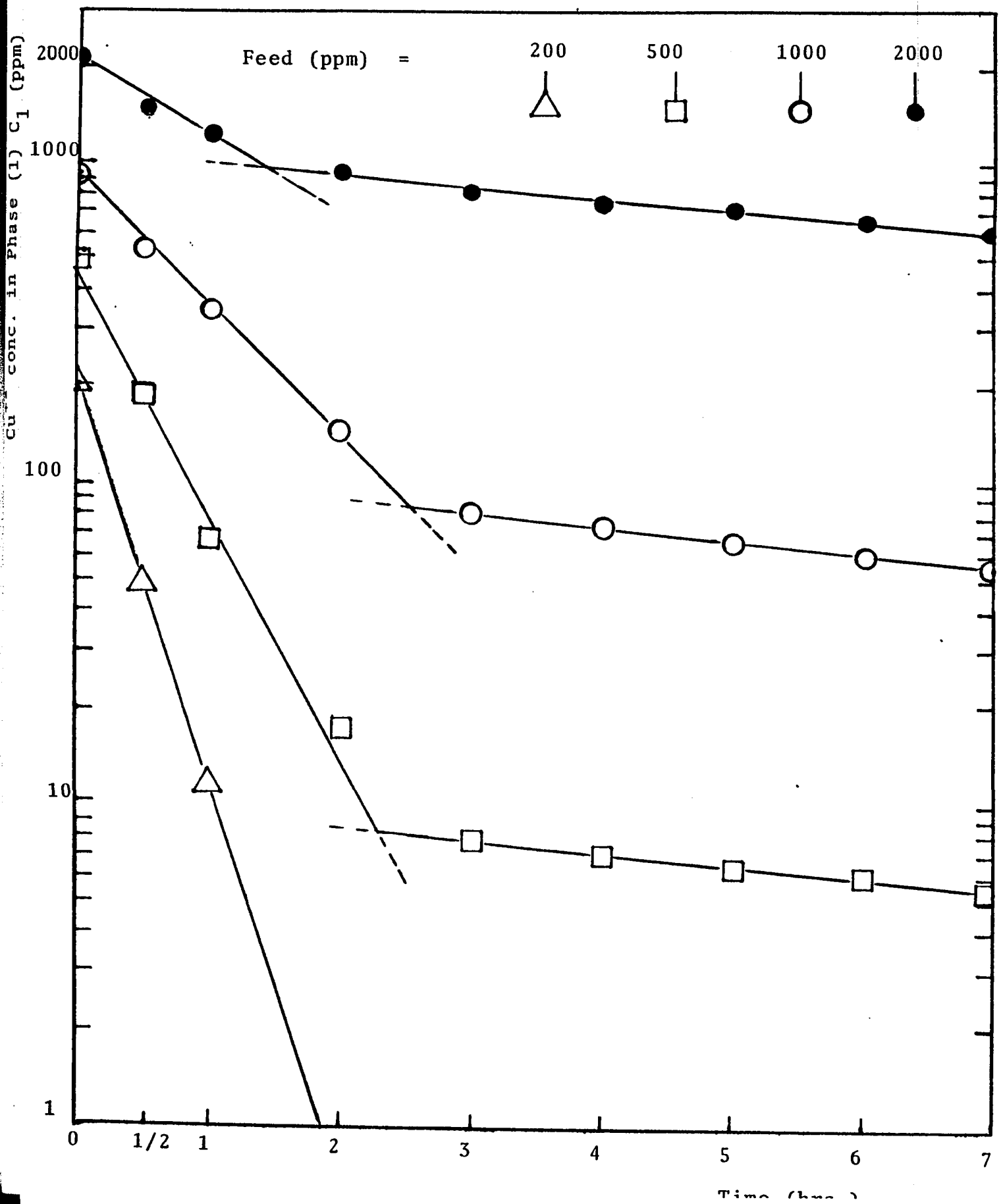

Fig. 30 Modelling of Extraction Phase

(LIX65N 2.5 wt %)

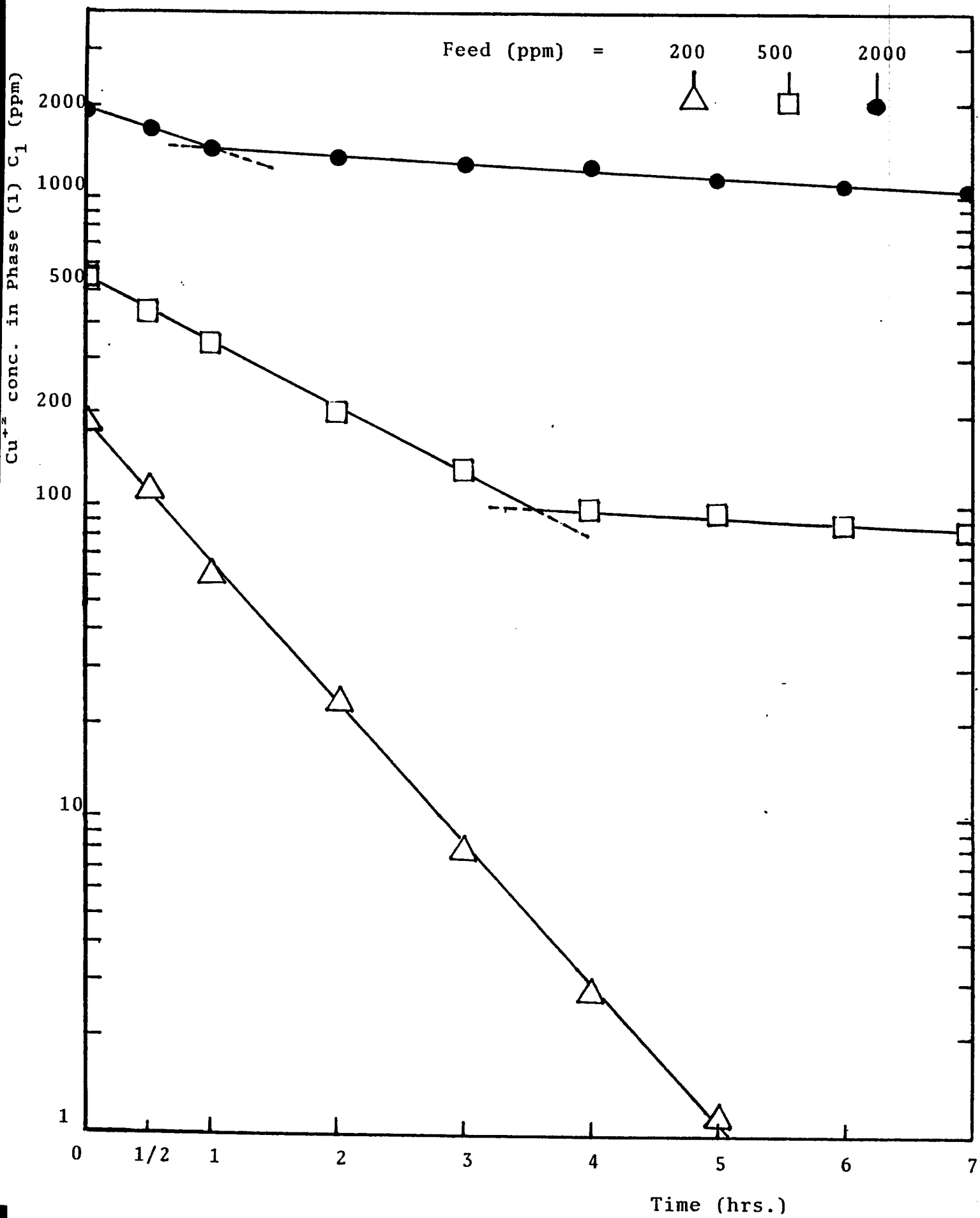

Fig. 31 Modelling of Extraction Phase
(LIX51 2.5 wt %)

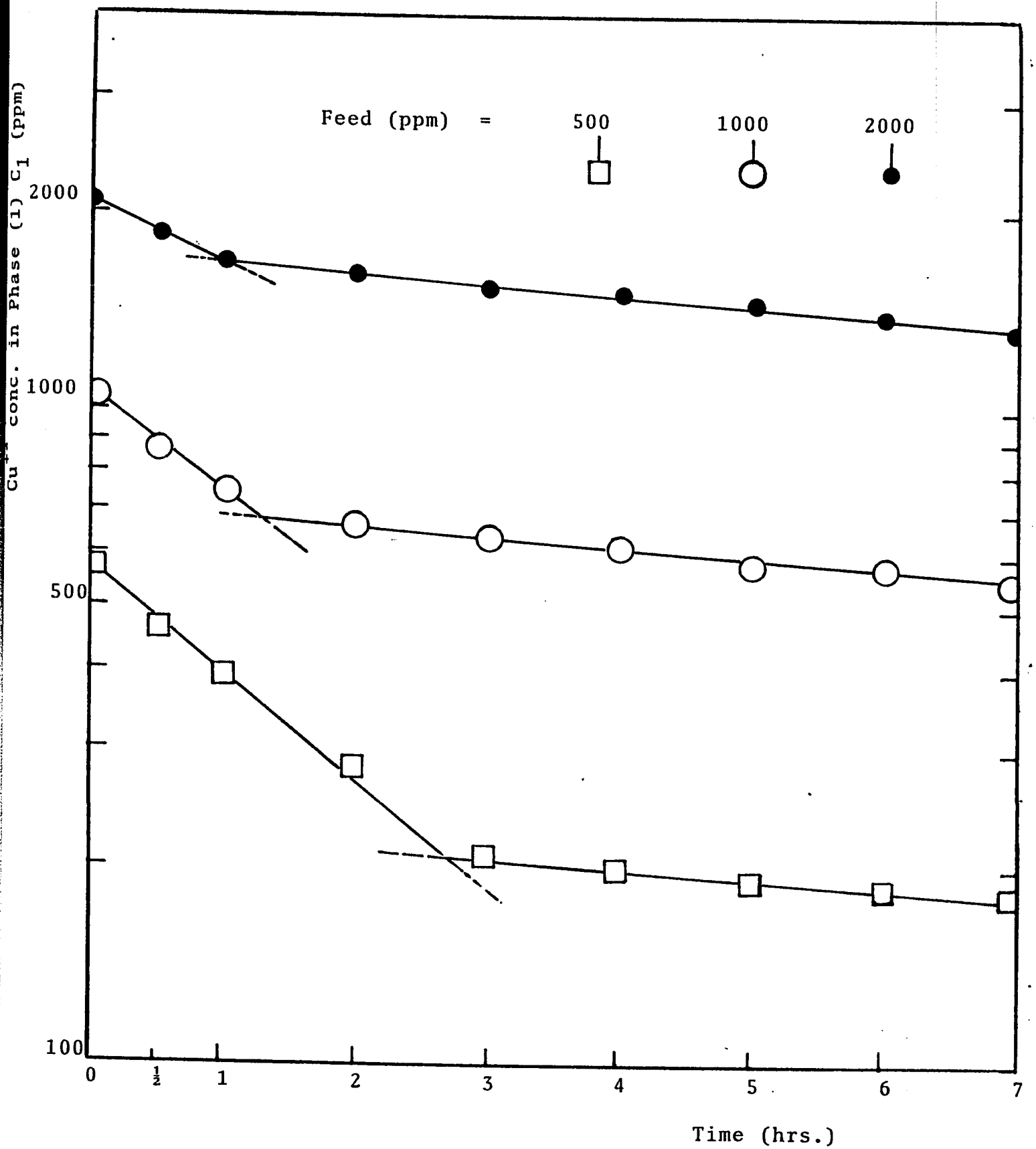

Fig. 32 Stripping Rate Behaviour

(LIX64N 5 wt %)

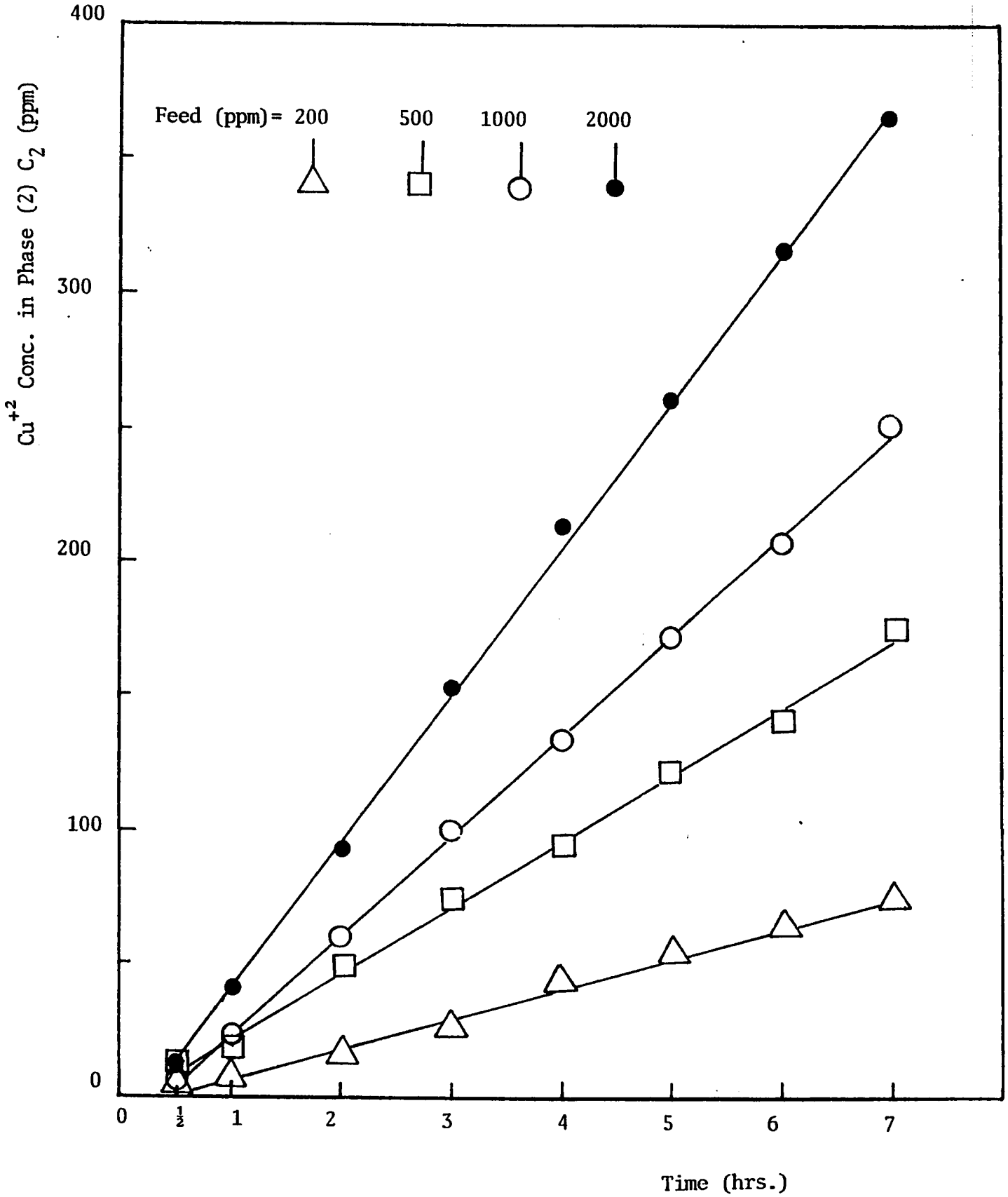

Fig.33 Stripping Rate Behaviour

(LIX65N 2.5 Wt %)

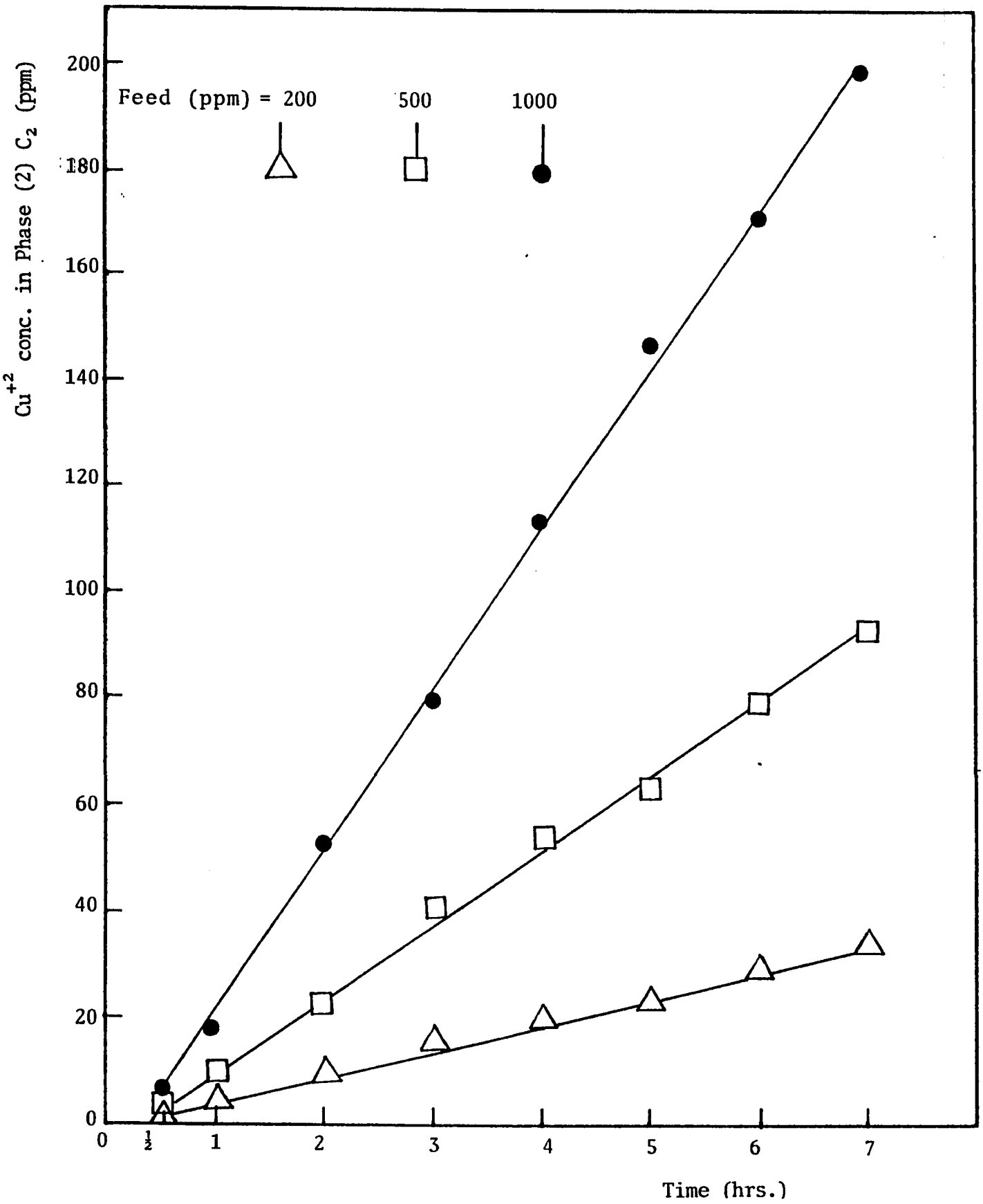

Fig. 34 Stripping Rate Behaviour

(LIX51 2.5 wt%)

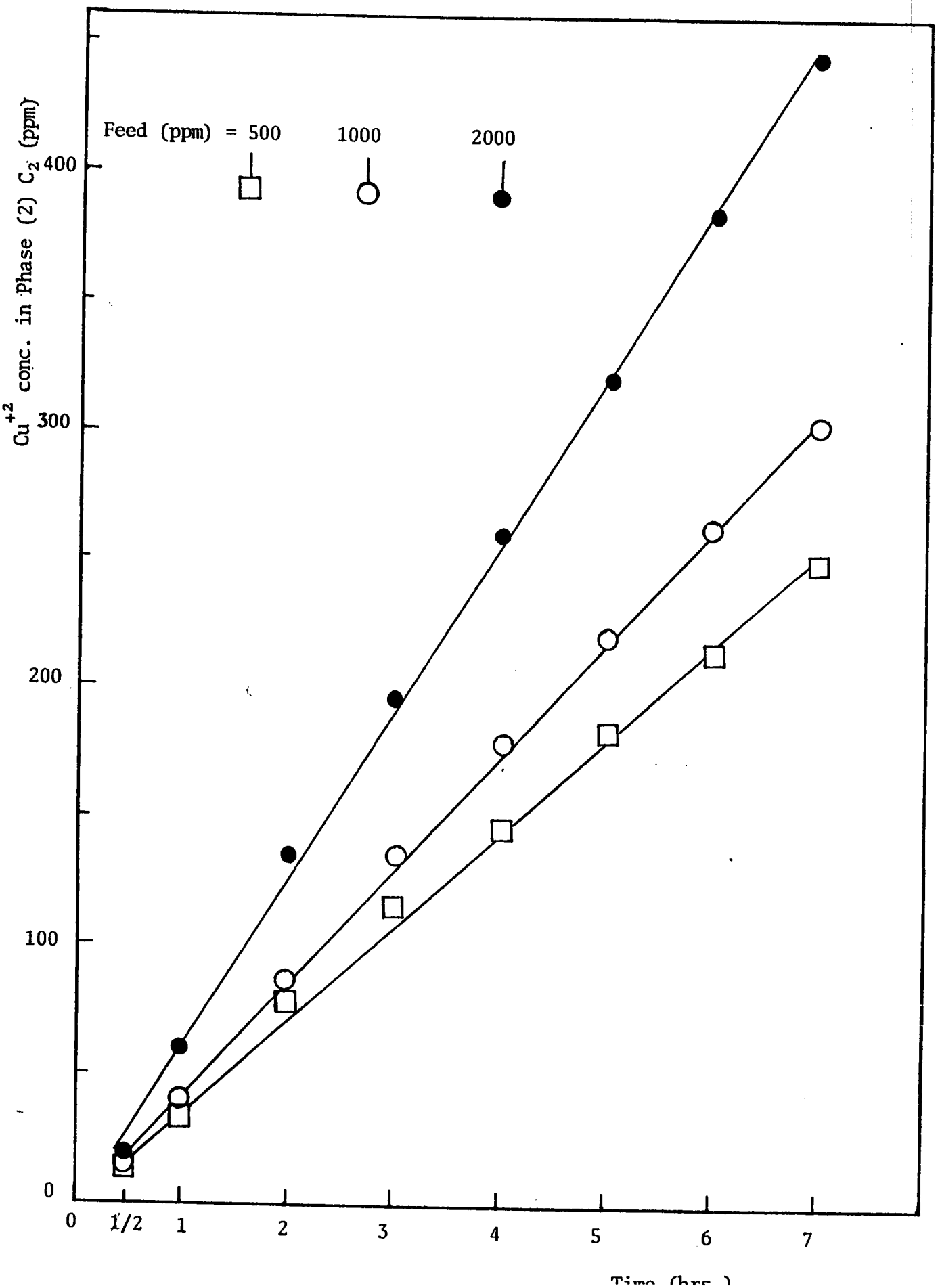

Fig. 35 The Diffusion Experiment
Aqueous Phase Concentration/Distance Profiles
at room temperature at different times