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Extraction of Copper by Liquid Membranes

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Abstract

Important variables governing the permeation of copper ion through liquid membranes and their effects on the separation process are described. These variables are membrane viscosity, treatment ratio (volume ratio of emulsion to feed in mixer), complexing agent concentration, internal droplet size, internal phase leakage, and copper concentration in the internal phase. The information is needed for scaling-up of equipment and further process development. The economic evaluation based on bench-scale pilot plant runs shows this process is 40% cheaper than solvent extraction.

INTRODUCTION

Liquid membranes were invented in 1968 (*1*). They are made by forming an emulsion of two immiscible phases and then dispersing the emulsion into a third phase (the continuous or "feed" phase). Usually, the encapsulated phase and the continuous phase are miscible. The continuous phase in the emulsion, or membrane phase, must not be miscible with either if the emulsion is to remain stable. The emulsions can be of the oil-in-water or of the water-in-oil type, although only the latter will be discussed here. To maintain the integrity of the emulsion during the separation process, the continuous phase or membrane usually contains surfactants, additives, and a base material which is a solvent for all the other membrane ingredients. Hence, for specific applications, liquid membranes must be "tailor-made."

When the emulsion is dispersed by agitation in the continuous phase, globules of emulsion are formed which are stable and do not disintegrate. Their sizes depend on the nature and concentration of the surfactants in the emulsion, the emulsion viscosity, and the mode and intensity of mixing. Normally, the size is controlled in the range of 0.2 to 2 mm diam-

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eter. Each emulsion globule contains many tiny encapsulated droplets with a typical size of 1–10 μm in diameter. A large number of globules of emulsion can easily be formed to produce a correspondingly large membrane surface area for rapid mass transfer from either the continuous phase to the encapsulated phase or vice versa. A drawing of a water-in-oil emulsion dispersed in an aqueous phase is shown in Fig. 1.

Processes utilizing liquid membranes offer several separation mecha-

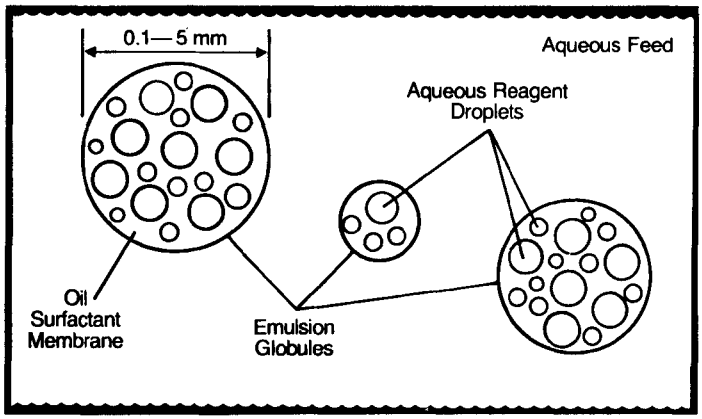

FIG. 1. Dispersion of LM emulsion.

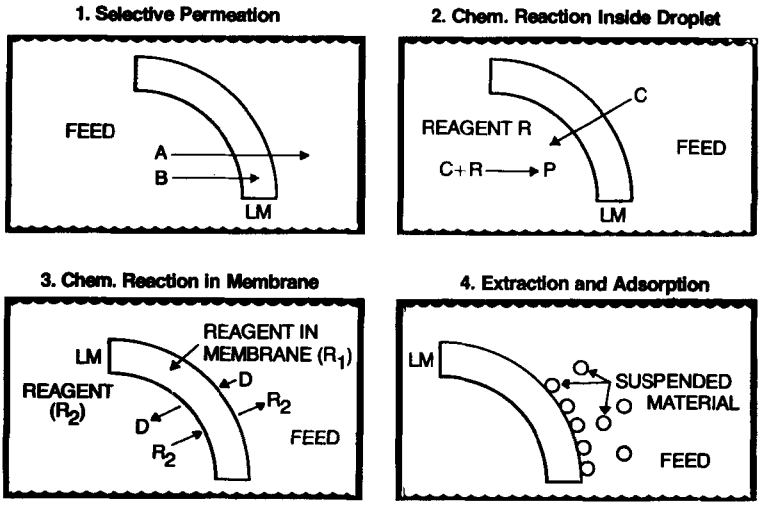

FIG. 2. Various LM mechanisms.

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nisms, four of which are shown in Fig. 2 (*2*). These serve to illustrate the versatility of this technique. A great variety of separations is possible. The simple separation mechanism is that of selective permeation (Fig. 2–1), which depends solely on the differential permeation rate through the membrane. This mechanism has been used successfully in the laboratory for the separation of hydrocarbons (*3*, *4*). Significant improvements in rates and selectivities can be achieved by encapsulating a reactive species inside the membrane microdroplet which will convert the extracted species into a nonpermeable derivative (Fig. 2–2). For example, encapsulated aqueous bases have been used to trap acidic compounds such as phenol (*5*), H_2S, and HCN (*6*), and drugs such as phenobarbital and acetylsalicylic acid (*7*). By this procedure the organic acids, which have significant oil solubility in their undissociated form, permeate through the membrane to the basic internal phase where they are trapped as their oil-insoluble anions. In a similar manner, basic materials such as ammonia may be trapped by aqueous acids (*8*). For such applications the internal aqueous droplets essentially act as sinks for the material to be extracted by converting it into a nonpermeable species.

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Another improvement in transport rates can be achieved by incorporation of a transport facilitator or "carrier" in the membrane phase (Fig. 2–3). Such additives reversibly react with the permeating species, thereby enhancing its solubility in the oil phase (*9–14*). The complex of carrier and extracted species diffuses through the membrane to the internal phase where the latter is removed by an appropriate, aqueous "stripping" agent, R_2. This technique has been used successfully for the separation of oil-insoluble materials such as heavy metal ions like Hg^{2+}, Cr^{6+}, and Cd^{2+} (*8*), and, of special interest to this paper, of Cu^{2+} (*8*, *10*, *15–22*). Some typical results of metal ion extractions, which serve to illustrate the versatility of this method, are shown in Fig. 3 (*8*). The utility of this method, in fact, is limited only by the ability to find suitable ion carriers and stripping agents.

The fourth mechanism for liquid membrane extraction (Fig. 2–4) involves simply the adsorption of water-insoluble particles on the membrane surface, and is of no concern here. In this paper we will discuss some of the parameters affecting facilitated transport of copper ions through liquid membranes.

Chemistry of Copper Extraction by Liquid Membranes

A conceptualized drawing of a liquid membrane "globule" for copper extraction is given in Fig. 4. The example shown is the removal of Cu^{2+} according to the equations (*22*):

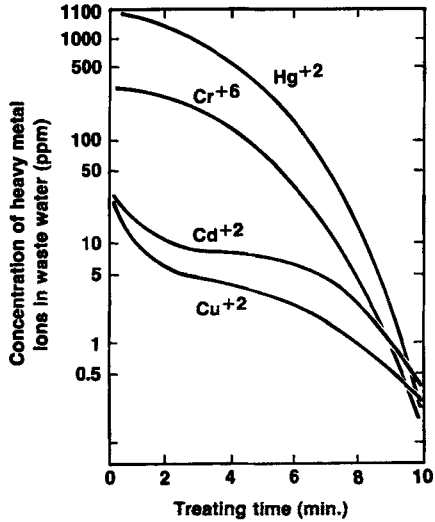

FIG. 3. Metal removal by LM.

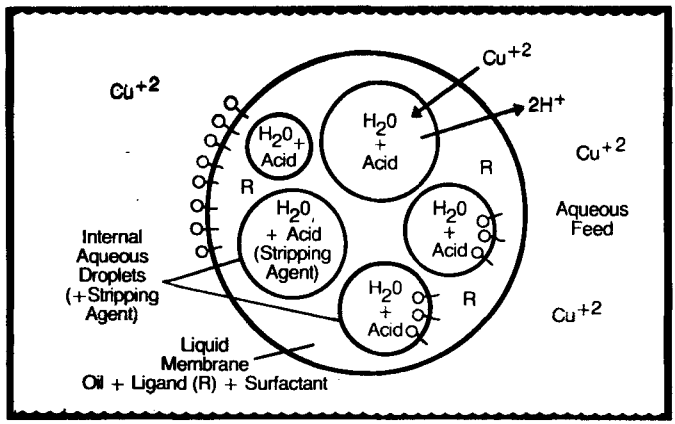

FIG. 4. Cu transfer in LM globule.

Extraction:

$$\underset{\text{Org}}{2RH} + \underset{\text{Aq}}{Cu^{2+}} \rightleftarrows \underset{\text{Org}}{R_2Cu} + \underset{\text{Aq}}{2H^+} \qquad (1)$$

Stripping:

$$\underset{\text{Aq}}{2H^+} + \underset{\text{Org}}{R_2Cu} \rightleftarrows \underset{\text{Aq}}{Cu^{2+}} + \underset{\text{Org}}{2RH} \qquad (2)$$

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where RH represents the protonated form of a liquid exchange agent which is used as the carrier or "transport facilitator." Among the most useful for copper extraction are the oxime type (LIX reagents) produced by General Mills (*8*).

The equilibrium between the various species can be expressed by the simple equation:

$$\frac{[R_2Cu]_{org}[H^+]_{aq}^2}{[RH]_{org}^2[Cu^{2+}]_{aq}} = K \tag{3}$$

where the equilibrium constant K is not only a function of the specific liquid ion exchange agent selected, but also depends on the properties of the organic solvent in which it is dissolved.

Extraction (Eq. 1) occurs at the membrane–external aqueous phase interface, while stripping (Eq. 2) occurs at the membrane–internal aqueous phase interface. The overall reaction represents an exchange of a copper ion for two hydrogen ions. The copper is effectively trapped in the interior of the liquid membrane by the large excess of hydrogen ions, which does not allow the oil-soluble Cu-form of the complex to form, according to equilibrium (Eq. 3).

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EXPERIMENTAL SECTION

General Procedure for Preparation of Liquid Membrane Emulsions

A solution of the internal aqueous phase (150 g) was added dropwise to a stirred solution of surfactant in oil (total of 100 g) contained in a baffled 2-L resin kettle with a marine propeller. The resulting emulsion was stirred at 1000–2000 rpm for 10–20 min at ambient temperature to ensure complete encapsulation. The oil phase of the emulsions was similar to those described previously (*1, 6, 8*). A typical formulation was 2.0% by weight of a nonionic polyamine (*6, 8*) used as surfactant and strengthening agent, 2.5% by weight of LIX 64N (obtained from General Mills Corp.) which served as the copper carrier, and 95.5% of S100N, an isoparaffinic solvent manufactured by Exxon (*1, 6*). In some instances, mixtures of isoparaffinic solvents were employed to afford a range of viscosities of the oil phase. The internal, aqueous phases of the emulsions were solutions of various amounts of $CuSO_4 \cdot 5H_2O$ in 20% H_2SO_4. The external or "feed" phase was a synthetic copper ore leachate consisting of 38.6 g of $MgSO_4$, 56.6 g of $Al_2(SO_4)_3 \cdot 18H_2O$, 6.5 g of $FeSO_4 \cdot 7H_2O$, 2.4 g of $Fe_2(SO_4)_3 \cdot XH_2O$, and either 2.0 g (500 ppm Cu) or 8.0 g (2000 ppm Cu) of $CuSO_4 \cdot 5H_2O$ in 1 L of water. The feed was adjusted to a pH of 2.5 with H_2SO_4.

Laboratory Test Procedure

The appropriate liquid membrane emulsion was added to a 2-L baffled resin kettle containing the synthetic ore leachate solution to be extracted. The two-phase system was stirred by means of a variable speed mixer equipped with two marine-type propellers with three blades each. Mixing speed ranged from 200 to 400 rpm. The uptake of the copper was monitored by removing samples of the feed solution periodically for analysis. Atomic absorption and colorimetric techniques were used for copper determinations.

RESULTS AND DISCUSSION

The effectiveness of the liquid membrane system for extraction of copper is illustrated by the typical data shown in Table 1. The "fresh" liquid membrane formulation shown here was able to remove 99% of the copper from synthetic mine water containing 2 g/L copper in 10 min with a concentration factor

$$\left(\frac{\text{conc Cu in internal phase}}{\text{conc Cu in external phase}}\right) = 440$$

The second set of data in Table 1 shows typical extraction of copper with

TABLE 1

Extraction of Copper from Synthetic Mine Water by Liquid Membranes

Contact time (min)	Concentration of Cu^{2+} External (feed) phase[a] (g/L)	Internal phase (g/L)	% Extracted
	I. With Fresh Emulsion		
0	2.0	—	—
2	0.61	9.3[b]	70
4	0.30	11.4	85
6	0.20	12.1	90
10	0.03	13.2	99
	II. With Preloaded Emulsion		
0	0.50	30.0	—
2	0.07	33.6[c]	85
4	0.02	34.0	96
6	0.01	34.1	98

[a]Present as $CuSO_4$ in synthetic mine water.

[b]Based on external phase/internal phase ratio of 6.7.

[c]Based on external phase/internal phase ratio of 8.3.

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a liquid membrane emulsion *already containing* 30 g/L of copper. Even against this extreme concentration gradient the liquid membrane formulation extracted 98% of the copper from the external or feed phase in 6 min. The concentration factor in the second run was 3460.

Factors Affecting Transport through Liquid Membranes

There are a number of parameters which can affect the transport of metal ions across the liquid membrane barriers. In the following sections, several of the more important will be discussed. Some of these have very large effects on transport rates and efficiency. Others, somewhat surprisingly, have relatively little influence.

Influence of Membrane Viscosity

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The effects of the viscosity of the oil phase on liquid membrane permeation are illustrated by the extraction rate data in Table 2. The viscosity of the oil is controlled by changing the ratio of viscous and nonviscous solvent oils. Shown in Table 2 are data for both copper and ammonia extractions. The former is an example of "facilitated transport" while the latter represents the simple diffusion with an internal trapping agent mechanism. The rates are compared on the basis of the extraction rate constants which were calculated according to (*5*, *7*)

$$\ln \frac{C_{in}}{C_{out}} = D'(V_E/V_{aq})\theta \tag{4}$$

where C_{in} and C_{out} are the initial and final concentrations of the extracted

TABLE 2

Effects of Membrane Viscosity on Transport Rates

Extracted species	Viscosity (η) of oil phase (cP/100°F)[a]	Permeation constant (D') (min^{-1})[b]	$\eta D'$
Copper	3.75	4.0	15.0
	6.83	2.5	17.1
	7.13	3.1	22.3
	26.3	1.5	39.5
Ammonia	6.0	0.75	4.5
	11	0.48	5.3
	18	0.32	5.8
	24	0.23	5.5

[a]Controlled by adjusting amount of nonviscous solvent in oil phase of liquid membrane.

[b]Average value over several time intervals.

species, respectively, in a batch experiment, V_E/V_{aq} is the treatment ratio (volume of emulsion divided by volume of external, aqueous phase in the mixer), and θ is the contact time for the interval over which D' is calculated. It should be noted that when the liquid membrane formulation is changed, although the stirring conditions remain the same, the size of the emulsion droplets and globules may change somewhat due to the change of interfacial tension. Theoretically, this change of size should not affect D' since it includes the mass transfer area, as discussed in more detail in Eq. (5). However, whether D' is strictly independent of drop and globule size change will need to be examined in our future work (24).

The results clearly illustrate the rate enhancement possible with the use of oil-soluble complexing agents. The rate of the facilitated transport of copper is 3 to 7 times faster than the simple diffusion of ammonia through membranes of comparable viscosity. Of course, as pointed out above, Cu^{2+} ion does not diffuse through the membrane at all, or at best at extremely slow rates, in the absence of the ion carrier, LIX. If it did, we could not trap it by the present mechanism.

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Clearly, membrane viscosity plays an important role in controlling permeation through liquid membranes. In the case of simple diffusion of molecular species such as NH_3 (*5*, *8*), phenol (*5*), or organic acids (*7*, *23*), viscosity and solubility represent the two most important parameters. In such cases, the product of $\eta D'$ is a constant as is to be expected from correlations which equate the Stokes-Einstein group ($D\eta/T$) with molecular parameters. However, in the case of facilitated transport, where the diffusing species is the Cu-LIX complex, more complicated kinetics is involved and $\eta D'$ is not a constant as the membrane viscosity is changed. One possibility is that changing the membrane composition affected the LIX equilibrium constant, which in turn would affect the rate at which Cu will be carried through the membrane.

The data in Table 2 suggest that practical considerations would dictate as nonviscous a membrane as possible. Up to a point, this is true. However, membrane stability must also be considered. Very nonviscous oils tend to produce less stable membranes with enhanced leakage of the internal phase, especially at long contact times. This has been observed previously in studies of phenol extraction (*5*) and is illustrated in the case of copper by the curves in Fig. 5. One of the two membranes was purposely formulated to be weak by employing low viscosity oils and a minimum quantity of surfactant. It is interesting to note that the initial extraction rate is significantly faster with the low viscosity membrane. However, at longer contact times, its inherent instability results in partial membrane rupture and spillage of the trapped copper back into the external phase at a rate exceeding the emulsion's ability to reabsorb it. The more viscous mem-

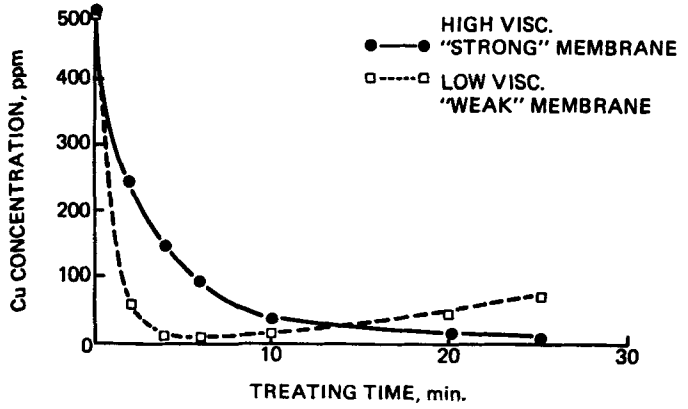

FIG. 5. Effect of viscosity/stability.

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brane maintains its integrity considerably longer and may give better overall extraction.

Concentration of Complexing Agent

Varying the concentration of the carrying agent (LIX) over a fairly wide range has only a minor effect on extraction rates (Table 3). Between 7.5 and 2%, nearly a 4-fold change in carrier concentration results in only a 20% reduction in the extraction rate.

A plot of extraction rate constants vs LIX concentration is given in Fig. 6 and compared with the curve expected if the rate were directly proportional to carrier concentration. The curves indicate a break at about 2% LIX. This suggests the optimum carrier concentration for

TABLE 3

Effects of Carrier (LIX) Concentration on Copper Extraction

	LIX conc[a] (wt-%)						
	0.5	1.0	1.5	2.0	2.5	5.0	7.5
Treatment time (min)	ppm Cu	ppm Cu	ppm Cu	ppm Cu	ppm Cu	ppm Cu	ppm Cu
0	2016	2016	2016	2016	1350	1350	1700
2	69	42	10	4	14	9	8
3	65	45	15	4	9	5	21
Extraction rate const, D'[b]	3.6	4.2	5.1	6.6	6.8	7.5	8.0

[a]In oil phase of membrane.
[b]Corrected for pH effects.

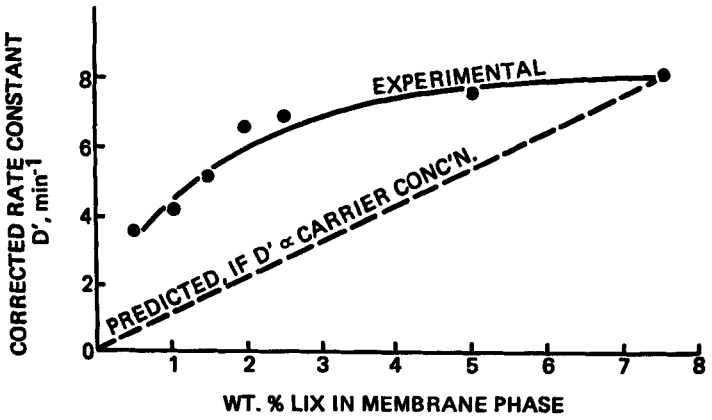

FIG. 6. Effect of carrier concentrations.

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copper extraction lies in the 2% range. This type of analysis is quite useful in determining optimum membrane formulations. This optimum will vary for each metal ion–carrier combination and may also depend on the metal ion concentration in the feed solution.

Effects of Concentration of Extracted Species in Internal Phase

For economic reasons it is usually desirable to "load" the internal phase of the liquid membrane emulsion to the greatest extent possible consistent with maintaining good extraction rates. An important feature of liquid membranes is that, in many instances, extremely high loadings can be attained.

The effects of internal phase copper concentration on extraction rates are shown in Table 4, where the emulsions were preloaded with copper sulfate at various levels. An equimolar amount of H_2SO_4 was backed out with each increment of copper. Thus the internal phase became increasingly higher in copper concentration and lower in acid. It is apparent that, up to loadings of 50 g/L, the permeation rate is relatively unaffected by copper loading. In fact, it appears that the only important factor is that an appreciable pH gradient between external and internal phases be maintained. It should be noted that with the internal phase of 50 g/L, a copper extraction coefficient ((conc Cu internal phase)/(conc Cu external phase)) of over 2000 is obtained in 6 min.

Influence of Treatment Ratio

For most extraction processes, a high $((V_{\text{external phase}})/(V_{\text{emulsion}}))$ ratio is desirable to minimize equipment size and costly chemical losses.

TABLE 4

Effect of Composition of Internal Phase on Extraction Rate

Treatment time (min)	Treatment ratio[a] g external phase / g emulsion	Copper concentration: External phase (ppm)	Copper concentration: Internal phase (g/L)[b]	% Extracted	Average permeation const (min^{-1})
0		500	0		
4	$\frac{8}{1}$	30	8.8	94	
6		7.5	9.2	99	5.6
0		500	10.0		
4	$\frac{8}{1}$	25	18.9	95	
6		9	19.1	98	5.7
0		500	50.3		
4	$\frac{8}{1}$	42	58.8	92	
6		30	61.1	94	4.4

[a]Ratio of (external phase/internal phase) = 18.7; this value used to calculate loading of internal phase after contacting.

[b]Preloaded value, equivalent amount of H_2SO_4 backed out.

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The effects of this ratio on copper extraction are shown in Table 5. Although the overall rate of copper uptake slows with increasing external phase, the effect is not very large. Even at a 10/1 ratio, 95% of the total copper in the external phase is removed in 6 min. It should be emphasized that this is against a concentration gradient of over 60/1 at the start of the extraction since all the internal phases of the emulsions were preloaded to 30 g/L copper. In fact, at a feed ratio of 10/1, the concentration gradient after 4 min becomes over 600/1 (60 ppm in the external phase vs 40,000 ppm in the internal phase).

It is interesting to note the average rate constants, D', increase slightly with increasing feed ratio. Since Eq. (4), which defines D', includes a treatment ratio term, these constants should not vary. This observation is discussed below as part of the derivation of the rate equation.

Variation in Extraction Rate with Internal Droplet Size

An interesting, unique feature of liquid membranes is the variation in their properties with the size of the internal microdroplets. As mentioned above, droplets typically range from about 1 to 20 μm in diameter. The average size can be controlled by the way in which the membranes are formulated and the emulsions are prepared.

The average size of these droplets exerts an important influence on extraction rate. This is illustrated by the curves in Fig. 7. About a 30%

TABLE 5

Effects of Treatment Ratio of Copper Extraction

External phase/ Emulsions[a]	Time (min)	Cu in external phase (ppm)	% Extracted	Average extraction rate constant D' (min^{-1})
3/1	0	500		
	2	44	91	2.9
	4	11	98	
	6	6	99	
5/1	0	500		
	2	74	85	
	4	18	96	4.0
	6	13	97	
8/1	0	500		
	2	108	78	
	4	42	92	5.2
	6	14	97	
10/1	0	500		
	2	195	61	
	4	60	88	5.0
	6	25	95	

[a]v/v: emulsion internal phase preloaded to 30 g/L Cu.

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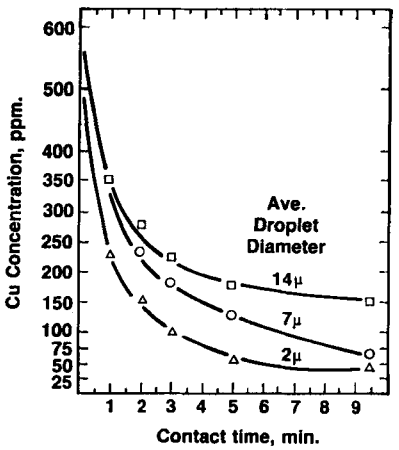

FIG. 7. Effect of I.P. droplet size.

increase in rate is obtained by reducing the average droplet size from 14 to 2 μm. The reason for this is related to the efficiency of extraction and stripping which is better with the smaller microdroplets since the surface

area for diffusion is greatly increased. Also, membrane stability is enhanced by having small microdroplets, and leakage is retarded. Since the measured permeation rate is the difference between extraction and "leakage" (see below), the apparent rate would be less for weaker membranes due to larger droplet size.

Extraction Rate Equations for Liquid Membrane Permeation

A simplified rate equation for process design and scale-up calculations, which covers both the simple diffusion and the facilitated transport mechanism, is derived as follows (*5*). The rate of permeation for any constituent from the external aqueous phase to the internal aqueous phase is defined as

$$dN/d\theta = (D)(\text{area})(\Delta c/\Delta x) \tag{5}$$

where Δc is the concentration difference of the permeating species on either side of the membrane, Δx is the membrane thickness, and D is the diffusion coefficient of the permeating species. Since the area available for permeation and Δx are difficult to measure for a liquid membrane system, the group $(D)(\text{area})/\Delta x$ can be replaced by $D'(V_E/V_{aq})$. Essentially, Δx has been combined into D', and it has been assumed that when the emulsion breaks up into globules, the area available for permeation is proportional to the amount of emulsion used in the treatment per unit of external phase.

Equation (5) is easily rearranged and integrated to give

$$\ln \frac{C_{in}}{C_{out}} = D'(V_E/V_{aq})\theta \tag{4}$$

The equation is valid for batch extraction runs only.

The permeation rate constants at various time intervals for two different extraction runs are shown in Table 6. The rates for a very strong but viscous liquid membrane are slower but are fairly constant throughout the run. In the case of less viscous membranes, considerable variation occurs.

The effects of the treatment ratio on D' are shown in Fig. 8. As pointed out above, D' is assumed to be independent of the treatment ratio in order to arrive at easily used equations for process design. However, Fig. 8 shows that D' is a function of the treatment ratio. This means that for process design, a different D' value should be used when the treatment ratio is changed, or D' should be correlated as a function of the treatment ratio. Also, D' may be correlated as a function of process temperature and mixing intensity in the extractor. For theoretical interest, much more complex mathematics were derived, which will be discussed in a future

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TABLE 6

Permeation Rate Constants for Various Liquid Membrane Treating Intervals

LM formulation[a]	Time interval (min)	θ (min)	C_{in}/C_{out} (ppm/ppm)	D' (min^{-1})[b]
A	0–2	2	500/244	1.79
	2–4	2	244/142	1.35
	4–6	2	142/91.5	1.10
	6–10	4	91.5/30	1.39
	0–2	2	500/142	1.57
	0–6	6	500/91.5	1.42
	0–10	10	500/30	1.41
B	0–2	2	500/57	5.43
	2–4	2	57/12	3.89
	4–6	2	12/7	1.34
	0–4	4	500/12	4.66
	0–6	6	500/7	3.56
	0–10[c]	10	500/10	1.95

[a]Formulation A is a strong membrane with a viscous (26 cSt) oil and 2% surfactant; Formulation B is a weak membrane with nonviscous (3 cSt) oil and 1% surfactant.

[b]Calculated from $D' = \ln (C_{in}/C_{out})1/(V_E/V_{aq})\theta$; $V_E/V_{aq} = 0.20$ for these runs.

[c]Obvious leakage of internal phase had occurred by 10 min.

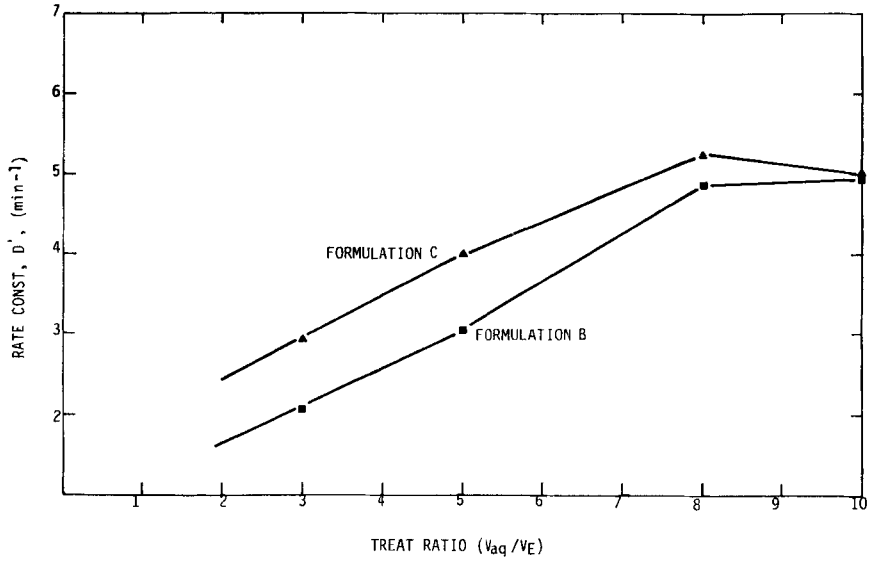

FIG. 8. Variation in rate constant D' with treat ratio.

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paper (*24*). In Fig. 8 the results of two membrane formulations (Formulations B and C) are shown. Formulation B is explained in Table 6. Formulation C is similar to Formuation B. It consists of a nonviscous oil (3 cSt) and 1% surfactant.

Refinement of Rate Equations by Considering Leakage Rate

The runs which show the greatest variation in D' values are those in which the weakest membranes are used (i.e., having the highest tendency to rupture or "leak" out the internal phase). Thus, one way to refine the permeation rate equation is to allow for such leakage. The basic rate equation for a system in which there is both permeation and leakage is

$$dC/d\theta = -Pt\Delta C + l \tag{6}$$

where C = concentration of permeating species in external phase
t = treatment ratio, V_E/V_{aq}
l = leakage rate expressed in terms of change in C per unit time
P = revised permeation constant
θ = contacting time

Equation (6) states that the rate of change of the permeating species in the external phase equals the difference between the rate of extraction ($-Pt\Delta C$) and the leakage rate (l). Solving for P,

$$P = \frac{1}{\theta t} \ln \frac{C_1 - \frac{l}{Pt}}{C_2 - \frac{l}{Pt}} \tag{7}$$

where C_1 and C_2 are the concentration of permeating species at the beginning and end of the contacting interval. Equation (7) can be solved for P by trial and error, if l is known, by following the concentration C of the permeating species as a function of θ. The leakage rate, l, can be determined for a given system by measuring the pH increase of the external phase with time and subtracting the calculated increase in H^+ concentration due to ion exchange with copper (Eq. 1) from the total H^+ increase. This, of course, assumes that leakage is due to membrane rupture and, therefore, that Cu^{2+} and acid "leak" at the same rate.

Equation (7) was checked by applying it to a series of runs with varying treatment ratios. The emulsion used was specifically formulated to exhibit a "fairly" high leakage rate (i.e., 10–20%/h). The P values were calculated for each of the 2-min time intervals for three cases, assuming leakage rates of 0% ($P = D'$), 10, and 25%/h. The results are shown in Table 7.

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TABLE 7

Calculated Values of P
(permeation rate constant including leakage)

Treatment ratio V_E/V_{aq}	Time interval (min) 0–2	2–4	4–6	Average	Range (%)
			0% *Leakage*		
1/3	3.65	2.08	0.91	2.21	±60
1/5	4.78	3.53	0.81	3.04	±70
1/8	6.13	3.78	4.69	4.87	±25
1/10	4.71	5.89	4.38	4.99	±15
			Overall	3.78	±80
			10% *Leakage*		
1/3	3.96	4.12	6.06	4.71	±25
1/5	4.99	4.65	3.22	4.29	±20
1/8	6.30	4.33	6.39	5.68	±20
1/10	4.83	6.25	5.34	5.47	±15
			Overall	5.04	±25
			25% *Leakage*		
1/3	4.5	8.25	14.9	9.22	±55
1/5	5.34	6.63	7.07	6.35	±15
1/8	6.55	5.19	9.2	6.98	±30
1/10	5.00	6.78	6.85	6.21	±15
			Overall	7.19	±50–100

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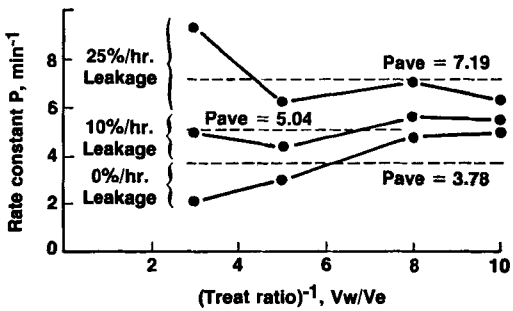

FIG. 9. Effect of l on V_E/V_W effect.

They suggest that an assumed leakage rate of 10% gives significantly more constant P values over the various time intervals. The variation of P values with treatment ratio for the three cases is shown in Fig. 9. The plot for Case 2 (10% leakage) is clearly closer to the theoretical curve (dashed lines in Fig. 9). In independent experiments, measuring the pH change of the external phase in contact with this emulsion, leakage rates

of 10–20%/h were estimated, in good agreement with the "best fit" case in Table 7. The leakage rate is dependent on the membrane formulation as discussed below.

Significantly better extraction rate calculations can be made by applying this correction to formulations where leakage occurs. In actual practice, formulations with very low leakage rates (<5%/h) are employed. In such cases (e.g., Formulation A, Table 6), P and D' are essentially the same except for very low values of C. Nonleaking emulsions can easily be formulated by choosing the proper oil, surfactant, and conditions of emulsion preparation. However, determination of leakage and overall extraction rates as described above are quite helpful in arriving at the optimum liquid membrane formulation for a given application.

Process Economics

Economics estimates were made by Davy McKee Co. in the United Kingdom. Using a basis of plant production of 36,000 tons copper/year from an acid leaching solution of 2.5 g copper/L, Davy McKee shows a 40% investment savings for liquid membrane as compared to solvent extraction. The operating cost for both processes is about the same. The estimates are summarized in Table 8 (*25*). Part of the economic study was based on the results of a continuous run that lasted 9 d in which real leach liquor was used. Copper extraction of 92% was achieved after 10 min residence time of the liquor in the liquid membrane extraction unit (*26*). The leakage rate was 1%/h. The liquid membrane selectivity of Cu vs Fe during extraction was good, varying from 70 to 325, with an average of 130 (*26*, *27*).

TABLE 8

Estimated Cost of Copper Recovery from Ore Leachates

	Solvent extraction	Liquid membrane
Copper recovered (kt/yr)	36	36
Stages	5	1
Plant investment, M$[a] (major savings: reduction of stages)	13	8
Organic inventory, M$	2	1
Direct operating cost, ¢/lb	1.8	1.7

[a]Includes facilities to make and break emulsion in LM case. The investment in both cases only includes the facilities to extract the copper from the clarified leach liquor and to concentrate it into the electrolysis liquor. Not included are preparation and conditioning of the leach liquor, nor the copper electrolysis plant.

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