$$<T^*>^{(2)} = \frac{\sum_i \sum_j x_i x_j q_i \dfrac{\epsilon_{ij} q_i}{c_i k} r_j \sigma_{ji}^3}{\sum_i \sum_j x_i x_j q_i r_j \sigma_{ji}^3} \tag{B5}$$

$$<T^*>_L = \frac{\sum_i x_i q_i \dfrac{\epsilon_{ii} q_i}{c_i k}}{\sum_i x_i q_i} \tag{B6}$$

and the constants $(C_J)_m$ have been fitted to the J_2 integral [Equation (34)] evaluated by Smith et al. (1970). Equation (B2) and the first term in Equation (B4) give the random mixing result. The second and third terms in Equation (B4) correct the random mixing approximation for clusters of two and three molecules, respectively.

The third- and fourth-order terms have been derived, they are of a form similar to Equations (28) and (29). These are not useful, however, because they require the higher-order distribution functions $g^0(1234)$, etc., which are unknown. A good approximation can be made for these terms by writing them in the form of Equation (B4) and including only the correction for clusters of two molecules. This provides the dominant correction for mixture nonrandomness. The result is

$$\frac{A^{(3)}}{NkT} = \sum_m \frac{A_{3m}}{v^m} <cT^*v^*><T^*>^{(2)}<T^*>^{(3)}<v^*>^{m-1} + \sum_m \frac{A_{2m}}{3v^m} [<cT^{*3}v^*> - <cT^*v^*><T^*>^{(2)}<T^*>^{(3)}]<v^*>^{m-1} \tag{B7}$$

$$\frac{A^{(4)}}{NkT} = \sum_m \frac{A_{4m}}{v^m} <cT^*v^*><T^*>^{(2)}<T^*>^{(3)}<T^*>^{(4)}<v^*>^{m-1} + \sum_m \frac{A_{3m}}{4v^m} [<cT^{*4}v^*> - <cT^*v^*><T^*>^{(2)}<T^*>^{(3)}<T^*>^{(4)}]<v^*>^{m-1} \tag{B8}$$

where

$$<cT^{*n}v^*> = \sum_i \sum_j x_i x_j c_i \left[\frac{\epsilon_{ij} q_i}{c_i k}\right]^n \frac{r_j \sigma_{ji}^3}{\sqrt{2}} \tag{B9}$$

$$<T^*>^{(3)} = \frac{\sum_i \sum_j x_i x_j q_i \dfrac{q_i}{c} \dfrac{\epsilon_{ij} q_i}{c_i k} r_j \sigma_{ji}^3}{\sum_i \sum_j x_i x_j q_i \dfrac{q_i}{c_i} r_j \sigma_{ji}^3} \tag{B10}$$

$$<T^*>^{(4)} = \frac{\sum_i \sum_j x_i x_j q_i \left[\dfrac{q_i}{c_i}\right]^2 \dfrac{\epsilon_{ij} q_i}{c_i k} r_j \sigma_{ji}^3}{\sum_i \sum_j x_i x_j q_i \left[\dfrac{q_i}{c_i}\right]^2 r_j \sigma_{ji}^3} \tag{B11}$$

These complex equations allow calculation of mixture properties when the molecules differ in size, shape or intermolecular potential energy.

For athermal solutions, the perturbed-hard-chain theory yields the Flory-Huggins combinatorial entropy of mixing for chain molecules, while for mixtures of spherical molecules of the same size, perturbed-hard-chain theory becomes essentially equivalent to Guggenheim's quasichemical approximation. Perturbed-hard-chain theory, in effect, interpolates between these two well-established theories of mixtures.

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Selective Copper Recovery with Two Types of Liquid Membranes

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Copper can be selectively separated and concentrated by diffusion across liquid membranes. These membranes are effective either as thin films supported by porous polymer sheets or as liquid microcapsules or liquid surfactant membranes.

SCOPE

This paper shows how two different liquid membranes can selectively separate and concentrate copper or nickel ions. In other words, it demonstrates how copper or nickel can be removed from a dilute solution and concentrated in a more acidic solution. As such, the work is another effort in this laboratory aimed at making mass transfer fast and selective.

These membranes contain liquid ion exchangers which function as the mobile carriers so often postulated in biophysics (Stein, 1967). These carriers react with the solutes of interest and diffuse with them across the membrane. The criteria which these carriers must fulfill to be effective are described elsewhere (Cussler and Evans, 1974; Schultz et al., 1974).

This paper directly compares two different membrane geometries capable of effecting these separations. In the

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first, a solution of liquid ion exchanger is supported on a thin, highly porous polymer film. This membrane, which is similar to some described previously (Cussler, 1971; Choy et al., 1974; Caracciolo et al., 1975), can be used continuously. Its operation on a large scale would be similar to membranes developed for stack gas cleanup (Ward et al., 1970; Matson et al., 1977).

In the second membrane geometry, the solution of ion exchanger is reformed as small spherical shells or liquid surfactant membranes (Li and Shrier, 1972; Li, 1971; Meteluvicious and Li, 1974). This system essentially is a water-in-oil-in-water emulsion. It consists of small droplets of strong acid (in water) coated with the ion exchanger solution (the oil) and suspended in dilute copper solution (in water). Because this method involves a large surface area of thin membranes, it can give a faster flux than the supported films. Because the liquid surfactant embranes are an emulsion, they can be less stable than the supported films.

CONCLUSIONS AND SIGNIFICANCE

This work reports experiments on liquid membranes containing the copper selective liquid ion exchangers LIX-64N and LIX-65N. The experiments show that the selectivity of these membranes can be quantitatively predicted from equilibrium measurements of ion distribution.

When these membranes are supported by porous polymer films, they provide a reliable method for continuously separating and concentrating copper. The copper flux in such a device is characteristically about $2 \cdot 10^{-4}$ g cm^{-2} hr^{-1} or $2 \cdot 10^{-3}$ g hr^{-1}/cm^3 of feed treated. These values are similar to those found in other independent experiments (Baker et al., 1977). While the membrane thickness (about $3 \cdot 10^{-3}$ cm) currently limits this flux, much thinner membranes may not give much higher fluxes because of concentration polarization.

Liquid surfactant membranes give fluxes of about $2 \cdot 10^{-3}$ g hr^{-1}/cm^3 of feed treated, comparable with those obtained with the supported films. We found that these membranes can be very difficult to make reproducibly. Unless their stability can be improved over that found here, they seem to us an uncertain alternative to supported films.

The manner in which the membranes used in this work function is illustrated in Figures 1 and 2. In the experiments reported in Figure 1 (Lee, 1977), a supported liquid membrane separates a dilute basic stream from a concentrated acid stream. The base flows with a constant space time of 5 min; that is, the length of the membrane divided by the velocity of the base equals 5 min. It enters with 165 ppm copper but leaves with about 50 ppm copper because of diffusion across the membrane. At the same time, the acid enters containing no copper but can leave with more than 700 ppm copper because of this diffusion.

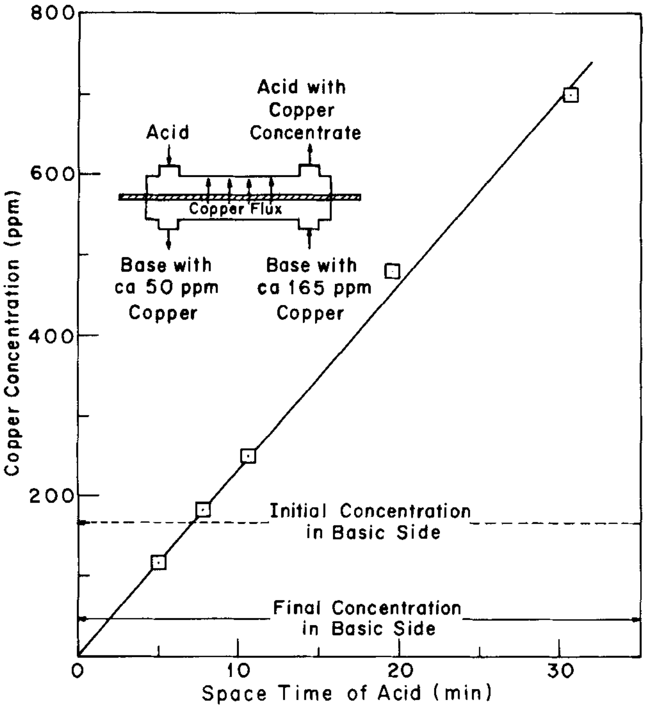

Fig. 1. Copper stripping with a supported liquid membrane. Copper is selectively concentrated by diffusion across a liquid membrane supported by a porous polymer film.

In the experiments reported in Figure 2, the membranes are very different, but the effects are similar. The membranes involved, commonly called liquid surfactant membranes (Li and Shrier, 1972; Li et al., 1974), are an oil coating on small drops of acid; the resulting droplets are suspended in dilute base. The base originally contains 165 ppm copper. The acid, which originally contains no

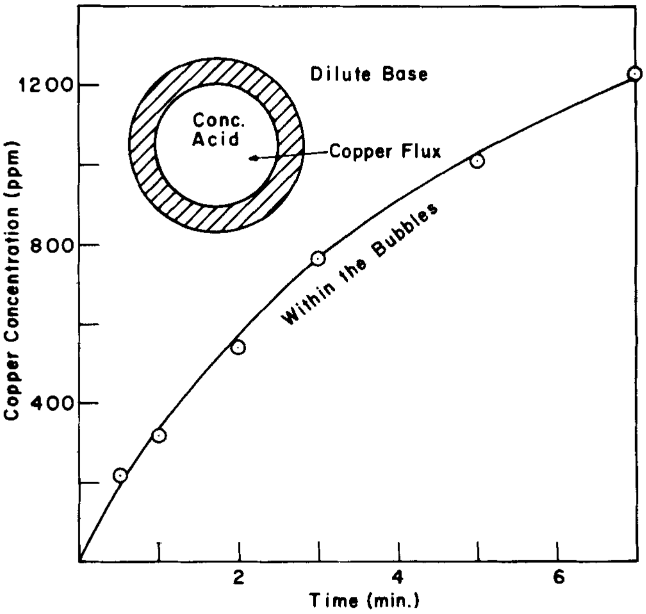

Fig. 2. Copper stripping with liquid surfactant membranes. Copper is concentrated in the interior of small liquid bubbles which are stabilized with surfactants.

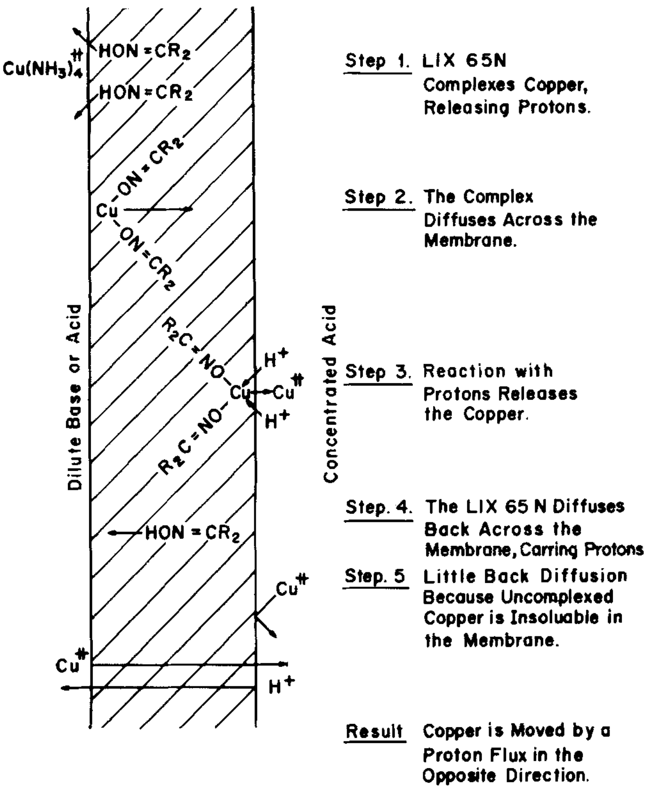

Fig. 3. How the membranes work. The copper is concentrated by means of the steps shown.

copper, accumulates over 1 200 ppm copper in just 7 min. Again, this copper accumulation is the result of diffusion across the liquid surfactant membranes.

The mechanism by which the membranes in Figures 1 and 2 function is shown schematically in Figure 3. In this figure, the membrane is shown as the two vertical lines. This membrane separates a dilute base or acid solution on the left from a concentrated acid solution on the right. Within the membrane, two molecules of the liquid ion exchanger first react rapidly and selectively with copper and transport it across the membrane. This reaction is favored because of the relatively high *p*H on the left. On the other, right-hand side of the membrane, the copper is stripped from the ion exchanger by the presence of acid. The two molecules of liquid ion exchanger then diffuse back to the other side of the membrane. This shuttling of the ion exchanger back and forth across the membrane is characteristic of a mobile carrier mechanism.

The net result of this mechanism is the movement of copper from left to right across the membrane. This movement can occur from a region of low copper concentration on the left into a concentrated copper solution on the right. The energy for this concentration comes from the diffusion of protons from right to left, as shown in step 4 in Figure 3. As such, this mechanism is qualitatively similar to other coupled facilitated transport systems based on mobile carriers.

THEORY

We now want to use the mechanism in Figure 3 as a basis for calculating the steady state flux of copper and nickel across a liquid film. In this calculation, we will make four key assumptions (Cussler, 1971; Hochhauser and Cussler, 1975): that the membrance contains only three diffusion species (ion exchanger, copper complex, and nickel complex), that the formation of the complexes takes place very rapidly at the membrane surface, that diffusion across the membrane is the only resistance to mass transfer, and that all species in the membrane have equal diffusion coefficients. The success of these assumptions clearly depends on the chemistry of the system. The first assumption requires that uncomplexed ions are very insoluble in the membrane, and the second implies a large Damköhler number within the membrane. Both these assumptions have been shown to be reasonable in other, similar systems (Schiffer et al., 1974). The third assumption, which has the greatest practical implications, requires that concentration polarization be negligible, that is, that the solutions adjacent to the membrane are well stirred. The fourth assumption is less critical than the others, since diffusion coefficients are constant within about ±20%, and the constants characterizing the reaction equilibria implicit in the first two assumptions are found to vary ±100%. While earlier papers have shown how these assumptions can be relaxed (Schultz et al., 1974), we focus here on the simpler results and so obtain a clearer physical picture of the membranes operation.

These assumptions imply that four overall reactions occur in the system, two on each side of the membrane. On the basic side, at $x = 0$, we assume that (Merigold et al., 1971; Merigold and Sudderth, 1973)

$$\mathrm{Cu(NH_3)_4^{++}} + 2\mathrm{OH^-} + \mathbf{2RH} \overset{K_1}{\rightleftarrows} \mathbf{R_2Cu} + 2\mathrm{H_2O} + 4\mathrm{NH_3} \tag{1}$$

$$\mathrm{Ni(NH_3)_4^{++}} + 2\mathrm{OH^-} + \mathbf{2RH} \overset{K_2}{\rightleftarrows} \mathbf{R_2Ni} + 2\mathrm{H_2O} + 4\mathrm{NH_3} \tag{2}$$

where the bold face species are within the organic membrane, the other species are in the adjacent aqueous solution, and the K_i's are a combined distribution constant and an equilibrium constant characterizing these over-all reactions. The equilibria of these two reactions is strongly shifted to the right. The ammonia is itself in equilibrium with ammonium hydroxide. On the acidic side at $x = l$, the reactions are equally straightforward:

$$\mathrm{Cu^{++}} + \mathbf{2RH} \overset{K_3}{\rightleftarrows} \mathbf{R_2Cu} + 2\mathrm{H^+} \tag{3}$$

$$\mathrm{Ni^{++}} + \mathbf{2RH} \overset{K_4}{\rightleftarrows} \mathbf{R_2Ni} + 2\mathrm{H^+} \tag{4}$$

The equilibria of these reactions is strongly to the left. Equations (1) to (4) parallel similar relations used in extractions based on these and similar ion exchangers.

In this work, we are concerned with both the transport of either copper or nickel and the competitive transport between these two species. For the transport of a single species like copper, the concentration of complex is small on the acid side of the membrane and large on the basic side. Indeed, we expect that the concentration of complex on the basic side approaches half the average concentration of ion exchanger in the membrane. In this limit, the copper flux becomes

$$j_{\mathrm{R_2Cu}} = \frac{D}{l}\left([\mathrm{R_2Cu}]_o - [\mathrm{R_2Cu}]_l\right) = \frac{D}{l}\frac{R}{2} \tag{5}$$

This result will be checked experimentally.

For the competitive transport of copper and nickel from strong base into strong acid, the concentrations of both complexes will be very small on the acid side of the membrane. As a result, the relative flux of these species will be

$$\frac{j_{\mathrm{R_2Ni}}}{j_{\mathrm{R_2Cu}}} = \frac{[\mathrm{R_2Ni}]_o}{[\mathrm{R_2Cu}]_o} = \frac{K_2[\mathrm{Ni(NH_3)_4^{++}}]}{K_1[\mathrm{Cu(NH_3)_4^{++}}]} \tag{6}$$

Thus, the relative transport is mainly governed by the relative product of equilibrium constant and concentration. This result will also be checked experimentally.

If the difference between acid and base concentrations is smaller, the results are similar but much more complex algebraically (Lee, 1977). For example, for copper transport

$$j_{R_2Cu} = \frac{D}{2l}\left\{ \frac{\sqrt{1 + \frac{8RK_3[Cu^{++}]_l}{[H^+]_l^2}} - 1}{4R\frac{K_3[Cu^{++}]}{[H^+]_l^2}} - \frac{\sqrt{1 + \frac{8RK_1[OH^-]^2[Cu(NH_3)_4^{++}]}{[H_2O]_o^2[NH_3]_o^4}} - 1}{\frac{4RK_1[OH^-]_o^2[Cu(NH_3)_4^{++}]_o}{[H_2O]_o^2[NH_3]_o^4}} \right\} \tag{7}$$

The result when two species are competitively transported is similar but still more complex. While Equation (7) will not be stringently tested in this paper, it is included here because practical development of this process will use the smaller pH differences than those required by Equations (5) and (6).

EXPERIMENTAL

Materials

Except as noted below, all salts and organic solvents were reagent grade and were used as received. The mobile carriers in the membranes used were either LIX-64N or LIX-65N (General Mills). LIX-64N is a mixture of α-hydroxy aliphatic oximes and benzophenoximes; LIX-65N consists only of the latter compounds (Merigold et al., 1971; Ashbrook, 1975). The membranes were sometimes thickened with polybutenes (Indopol Polybutene L-100, Amoco) or with light mineral oil (Fisher); liquid surfactant membranes were stabilized with sorbitan monooleate (Span 80, ICI America). All solutions of these materials were prepared by weight. Before use, all membrane solutions were saturated with water, and all aqueous solutions were saturated with the appropriate membrane solution.

Supported Liquid Films

Supported liquid membranes were based on a porous polymeric support of polypropylene (Celgard 2500, Celanese). This support is 25μ thick and 45% voids and has an average pore size of 0.04μ. Because this film has a critical surface tension of 35 dyne/cm, it is wet by octanol but not by water.

The pores in this polymer support were filled with the membrane solution by putting the film under vacuum and then immersing it in the membrane solution. Releasing the vacuum forces the membrane solution into the pores. When the pores were not filled in this fashion, results were erratic. The membrane was then clamped in a Teflon flow dialysis unit (Technicon #105-B018-01). Our unit has a volume of 2 cm^3, a flow channel 228 cm long, and a surface area for mass transfer of 30 cm^2. In most experiments, 1N H_2SO_4 saturated with octanol flowed above the membrane, and the basic solution containing copper and/or nickel and saturated with octanol flowed countercurrently below the membrane. Both flows were controlled with Harvard infusion pumps; putting the acid below and the base on top reversed the direction but not the size of the metal ion fluxes. All concentrations were analyzed by atomic absorption spectroscopy, using a Varian model 1100 spectrophotometer.

Liquid Surfactant Membranes

These membranes are essentially the oil phase in a water-in-oil-in-water emulsion. Such an emulsion was made as follows. Except as indicated below, a membrane solution was prepared consisting of 2% of the surfactant sorbitan monooleate; 0.5 to 2% of the carrier LIX-64N; 17% of the solvent hexachloro-1,3-butadiene, added to improve carrier solubility; and 80.5 to 79% of the membrane base, light mineral oil. Thirty cubic centimeters of this membrane solution were stirred in a 250 ml beaker with 10 cm^3 of aqueous acid, most commonly 0.1M H_2SO_4. Stirring was at 1 800 rev/min with a 1.5 in., three vane marine type of impeller with a 5 deg pitch and with a Bodine NSH-12R, 1/70 hp, nonsynchronous shunt wound motor regulated with a Minarik SH-14 speed controller.

To make a diffusion experiment, the resulting 40 cm^3 of water-in-oil emulsion was mixed in a 600 ml beaker with 100 ml of basic solution containing copper and/or nickel. This mixing, most commonly at the slower speed of 200 rev/min, used a 2 in., three vane marine type of mixing propeller with a 50 deg pitch attached to the same motor and controller. Higher speeds tended to rupture the membranes. The result is a water-in-oil-in-water emulsion, in which the oil phase acts as a liquid membrane. To monitor the diffusion of metal ions across this membrane, the stirring was stopped so that the original acid-in-oil phase rose to the top of the beaker. Two milliliter samples of the base and of this emulsion were taken and the emulsion broken by adding petroleum ether. Acidic and basic solutions were then analyzed as before.

Before we decided on the membrane composition given above, we made a large number of experiments with other compositions (Lee, 1977). We tested the stability of these membranes by using 1M $K_2Cr_2O_7$ as the phase within the bubbles and measuring the color change with time of the continuous water phase with a Perkin-Elmer model 139 UV-VIS spectrophotometer. The amount of color change in this continuous phase is taken as a measure of the stability of the formulation. That used in the bulk of the experiments was the most stable on this basis.

Equilibrium Constants

The equilibrium constants in Equations (1) to (4) were measured by shaking equal volumes of the appropriate membrane and aqueous solutions. Final concentrations were measured as before. The values obtained for these constants varied a factor of two over tenfold variations in concentrations. This variation shows that the use of concentrations rather than activities in Equations (1) to (4) is not exact. However, other simple chemical descriptions gave apparent equilibrium constants which varied still more widely. We decided to assume the chemistry implied by Equations (1) to (4) and to test this assumption by experiment.

RESULTS AND DISCUSSION

Before presenting specific results, we should review the limitations and predictions of the arguments given above:

1. The equations apply when the membrane is the only limit to mass transfer.
2. Except in very dilute solutions, the flux of copper should vary linearly with carrier concentration but should be independent of copper concentrations, as in Equation (5).
3. The ratio of copper and nickel fluxes should be consistent with the equilibrium measurements suggested by Equation (6).

These predictions are most easily discussed first for the supported liquid films and then for the liquid surfactant membranes.

Supported Liquid Membranes

For these films, the variation of copper flux with flow and concentration is exemplified by the data in Figure 4. The copper flux increases with flow until the base side velocity is about 0.4 cm/s. Below this velocity, the flux is reduced by significant concentration gradients in the basic solution; above it, the membrane itself limits the metal ion flux. As a result, we must test Equations (5) and (6) at velocities above this value. In addition, we varied the velocity of the acid stream on the other side

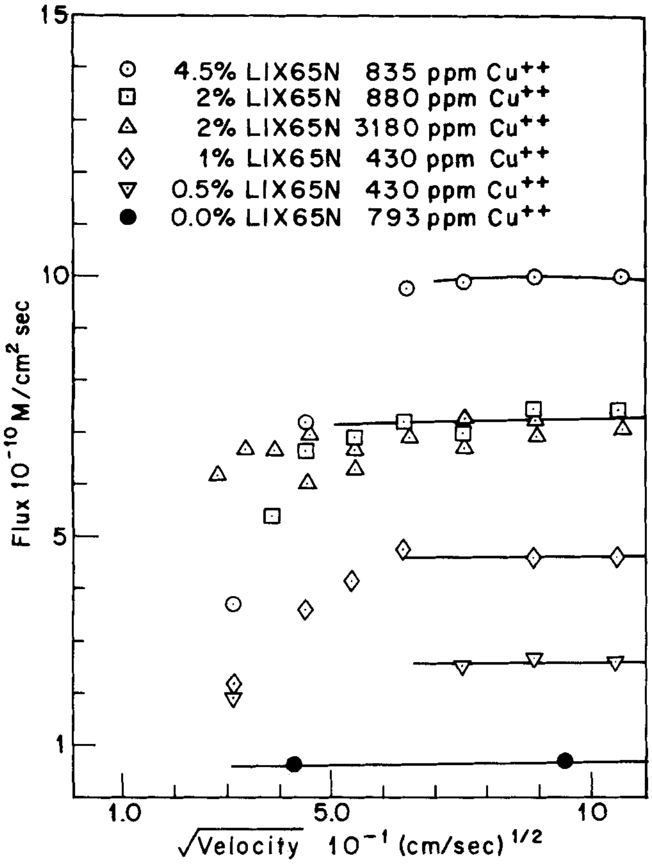

Fig. 4. Concentration polarization in supported liquid films. At very low flows, the flux depends on the velocity of the basic stream in Figure 1.

of the membrane and found no effect on the metal ion flux, even at low acid flow. This result shows that resistance to mass transfer is apparently negligible on the acid side of the membrane.

Equation (5) can be tested with the data in Table 1. The first four columns describe the state of the basic solution below the membrane, and the fifth column gives the carrier concentration within the membrane. The experimentally measured fluxes are shown in the sixth column. The range over which Equation (5) is valid is shown in Figure 5. At the lower carrier concentrations, the values of flux fall along a straight line of slope $1.5 \cdot 10^{-5}$ cm/s. Equation (5) predicts this slope should equal $D/2l$, the diffusion coefficient divided by twice the effective membrane thickness. The diffusion coefficient estimated from the Stokes-Einstein equation or the Wilke-Chang correlation (Sherwood et al., 1975) is about $7 \cdot 10^{-7}$ cm²/s, so the effective membrane thickness is 0.02 cm, almost ten times the actual membrane thickness of 0.0025 cm.

We were not sure whether this large effective thickness was characteristic of the liquid membrane or the porous

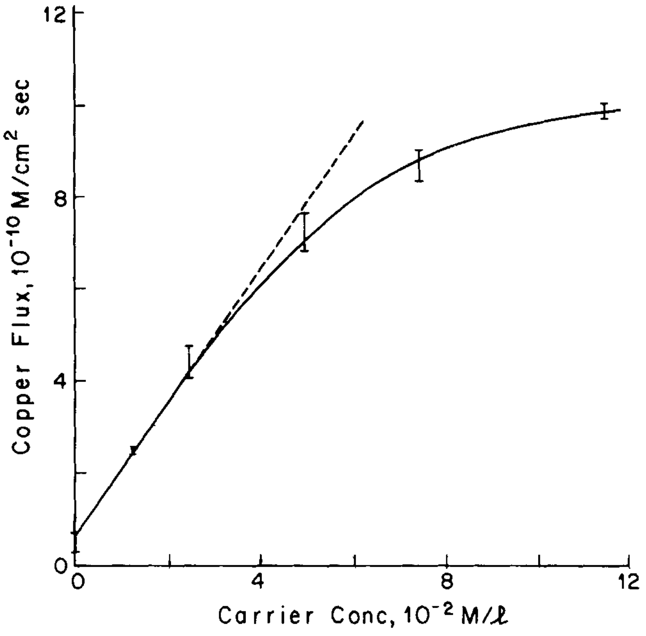

Fig. 5. Copper flux across supported membranes. The dotted line is that consistent with the mechanism in Figure 3.

Table 1. Initial Copper Flux Results

Cu^{++} (10^{-3} M/l)	OH^- (10^{-3} M/l)	NH_3 10^{-1} M/l	Flow vel. (10^{-1} cm/s)	R (10^{-2} M/l)	Cu flux (10^{-10} M/cm² s)
8.4	1.44	7.12	3.4	11.5	9.8_2
9.91	1.91	7.08	5.6	11.5	9.9_2
10.9	1.91	7.04	7.8	11.5	10_0
11.4	2.90	7.04	11.0	11.5	10_1
9.9	0.85	7.00	4.0	7.5	8.4_3
12.5	2.30	6.99	11.0	7.5	8.8_2
12.4	2.15	6.99	11.0	7.5	9.0_8
49.0	1.19	5.50	5.6	5.0	7.0_1
49.1	1.21	5.50	5.6	5.0	6.9_3
49.0	1.19	5.50	5.6	5.0	7.1_4
49.6	1.33	5.49	7.8	5.0	7.4_2
49.6	1.31	5.48	7.8	5.0	7.0_5
12.7	2.43	6.99	11.0	5.0	7.6_7
12.7	1.53	6.96	11.0	5.0	7.5_2
3.9	1.12	7.27	2.9	2.5	4.1_6
4.43	1.92	7.30	4.0	2.5	4.8_1
5.3	2.24	7.27	5.6	2.5	4.5_5
5.6	2.08	7.26	7.8	2.5	4.6_3
6.1	2.43	7.24	11.0	2.5	4.6_7
6.0	1.84	7.24	5.6	1.23	2.5_7
6.2	2.08	7.23	7.8	1.23	2.5_9
6.4	2.34	7.23	11.0	1.23	2.60
4.6	2.53	7.56	5.6	0.0	0.37
11.8	1.10	7.21	2.0	0.0	0.78
3.9	1.15	7.67	2.0	0.0	0.52

TABLE 2. SELECTIVE TRANSPORT ACROSS SUPPORTED LIQUID MEMBRANES*

$Cu^{++} \times 10^3$	$Ni^{++} \times 10^3$	$OH^- \times 10^3$	NH_3	$R \times 10^2$	j_{Cu}	j_{Ni}
11.1	14.3	1.80	0.641	5.0	6.8_9	0.3_9
11.3	14.9	1.39	0.637	5.0	5.8_6	0.2_4
6.3	22.3	1.42	0.620	5.0	5.5_6	0.8_6
5.0	24.8	1.72	0.612	5.0	5.4_5	1.2_7
4.7	24.9	1.42	0.613	5.0	5.1_9	1.1_1
4.4	26.0	1.24	0.611	5.0	4.7_2	1.2_8
3.9	26.0	1.34	0.611	5.0	4.4_9	1.4_6
3.6	30.0	1.52	0.539	5.0	3.8_7	1.4_4
3.2	29.7	1.74	0.596	5.0	4.1_5	1.8_2

* All these experiments were made at a base flow and an acid flow greater than 0.78 cm/s. All concentrations are in moles per liters; all fluxes are in 10^{-10} mole/cm² s.

polymer support. To check this, we measured the diffusion across the polymer support of tetrabutylammonium bromide dissolved in methanol. We found $D/l = 4.6 \cdot 10^{-4}$ cm/s. Since the diffusion coefficient in this system is $1.2 \cdot 10^{-5}$ cm²/s (Kay et al., 1965) the effective membrane thickness is 0.027 cm, again about ten times the actual membrane thickness. Thus, the effective length is characteristic not of the liquid membrane but of the polymer support.

This large effective thickness suggests that the membrane fluxes could be improved by using other, thinner porous polymer films. Such films already are used for gas separations (Matson et al., 1978). However, for liquid separations, different films will give dramatically higher fluxes only if the fluid velocity is increased still further so that the membrane remains the chief resistance to mass transfer.

At higher carrier concentrations, the flux no longer varies linearly with carrier concentration. The reasons for this are unclear. Our first suspicion was that we were wrong to assume that the reactions in the membrane are fast. A plethora of theories have effectively advertised the pitfalls of this assumption (for example, Ward, 1970; Smith et al., 1973; Schultz et al., 1974; Donaldson and Quinn, 1975). However, after some thought, we believe that these reactions are always fast and that the failure to predict all aspects of Figure 5 results from chemical factors other than slow reaction rates. There are two reasons for this belief. First, if the reactions are slow, they must have half-lives much greater than l^2/D. In our system, this implies a half-life of several hundred seconds. But these are acid base reactions which are often very fast (Addison, 1967), so it seems unlikely that they will not approach equilibrium.

The second reason for our belief comes from the negative deviation from linearity in Figure 5. If the reactions were rate limiting and first or higher order in carrier concentration [see Equations (1) to (4)], then the flux should increase more than the straight line in Figure 5. Instead, the flux increases less than the straight line, implying that the reactions are made slower by adding more carrier. Such behavior seems unlikely.

We suspect the results in Figure 5 are better explained by assuming that the reactions are fast but that molecules of the mobile carrier aggregate. While such aggregation is often called inverted micelle formation, it probably occurs less abruptly in the organic solutions like this membrane than in aqueous solutions (Mittal, 1975). Such aggregation would reduce the concentration of species capable of serving as mobile carriers and hence is qualitatively consistent with the data given here. Testing this suspicion will require more experiments.

The membranes developed in this work are selective for copper over nickel as shown by the data in Table 2 and Figure 6. In the table, the first four columns report the concentrations on the basic side of the membrane, and the fifth gives the total carrier concentration with the membrane. The final two columns give the experimentally measured fluxes across the membrane. The fluxes are selective, as Figure 6 clearly shows. For example, when the nickel concentration difference of nickel across the membrane is five times greater than the copper difference, the nickel flux is four times smaller than the copper flux.

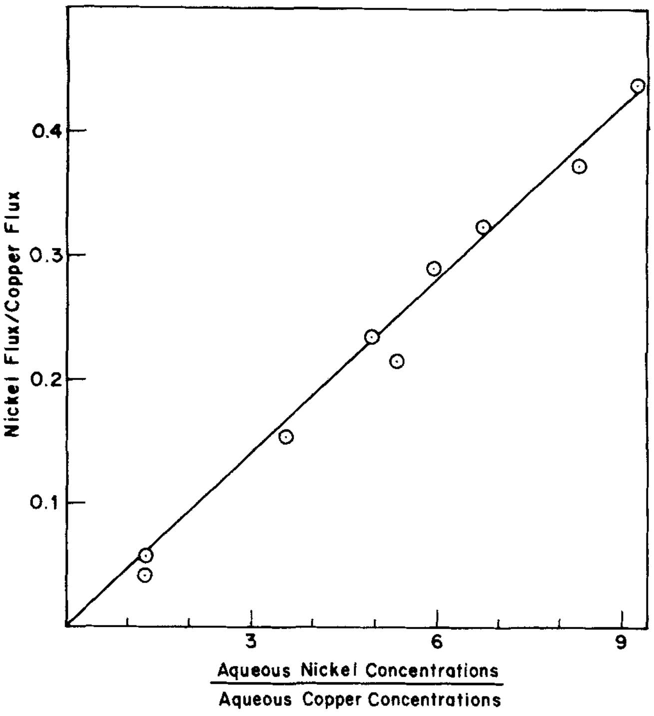

Fig. 6. Selectivity of supported liquid membranes. The solid line is predicted from the mechanism in Figure 3.

The measured fluxes do correlate closely with those predicted by Equation (6). The slope in this figure, equal to 0.046, should equal the ratio K_2/K_1. From equilibrium experiments, we found $K_1 = 3.10^{11}$ $(M/l)^2$ and $K_2 = 1.4 \cdot 10^{10}$ $(M/l)^2$. The ratio is 0.047, in surprisingly good agreement. This result shows that equilibrium measurements can provide an effective guide for diffusion based membrane separations.

Liquid Surfactant Membranes

Published experiments using these membranes have been extremely dramatic, suggesting the possibility of very rapid, selective separations. As a result, this type of membrane has attracted considerably more attention than the liquid membranes using an inert support and discussed above.

Table 3. Results for Liquid Surfactant Membranes*

	Membrane composition (% by wt)†								
	PO	TE	TR	PA	HE	DE	LX	SP	Cu^{++} (10^{-3} M/l)
(1)	73.5	9.8	9.8	—	—	—	4.9	2.0	3.15
(2)	73.5	9.8	9.8	—	—	—	4.9	2.0	7.79
(3)	73.5	9.8	9.8	—	—	—	4.9	2.0	1.57
(4)	73.5	9.8	9.8	—	—	—	4.9	2.0	1.57
(5)	68.6	14.7	9.8	—	—	—	4.9	2.0	3.15
(6)	49.0	24.5	19.6	—	—	—	4.9	2.0	1.57
(7)	73.5	9.8	9.8	—	—	—	6.8	1.9	3.15
(8)	70.3	9.4	9.4	—	—	4.3	4.9	1.9	7.79
(9)	46.7	—	—	—	—	46.7	4.7	1.9	7.79
(10)	32.2	—	—	—	65.4	—	0.8	1.6	11.65
(11)	—	9.8	6.9	78.4	—	—	2.9	2.0	3.15
(12)	—	9.8	6.9	78.4	—	—	2.9	2.0	7.87
(13)	—	—	—	80.5	17.0	—	0.5	2.0	1.57
(14)	—	—	—	80.5	17.0	—	0.5	2.0	5.98
(15)	—	—	—	80.5	17.0	—	0.5	2.0	11.80
(16)	—	—	—	80.0	17.0	—	1.0	2.0	5.90
(17)	—	—	—	80.0	17.0	—	1.0	2.0	5.90
(18)	—	—	—	80.0	17.0	—	1.0	2.0	11.67
(19)	—	—	—	80.0	17.0	—	1.0	2.0	5.76
(20)	—	—	—	80.0	17.0	—	1.0	2.0	5.67
(21)	—	—	—	80.0	17.0	—	1.0	2.0	5.71
(22)	—	—	—	80.0	17.0	—	1.0	2.0	4.57
(23)	—	—	—	80.0	17.0	—	1.0	2.0	11.96
(24)	—	—	—	80.0	17.0	—	1.0	2.0	11.72
(25)	—	—	—	79.0	17.0	—	2.0	2.0	11.80
(26)	—	—	—	79.0	17.0	—	2.0	2.0	11.80
(27)	—	—	—	79.0	17.0	—	2.0	2.0	11.80

* Emulsification for 15 min at 1 800 rev/min.

† PO = polybutene, TE = tetrachloroethane, TR = trimethylpentane, PA = paraffin oil, DE = decyl alcohol, LX = LIX64N, SP = Span 80, HE = hexachloro-1,3-butadiene.

** HNO_3 used instead of H_2SO_4.

*† NaOH used instead of H_2SO_4.

Table 4. Initial Flux Measurements

Membrane composition	NH_3 concentration	Initial pH Basic	Initial pH Acid
2% Span 80 93.1% Polybutene 4.9% LIX64N	1.57 M/l	11.4	2.5

Run	Time (min)	Ni^{++} conc. (10^{-3} M/l)	Initial flux (10^{-6} M Ni^{++}/min)
1	0	1.70	35.0
	0.5	1.53	
	1.5	1.22	
	3	1.05	
	6	0.81	
2	0	1.70	19.0
	0.5	1.61	
	1.5	1.43	
	3	1.27	
	6	1.02	
	10	0.69	
3	0	1.70	13.0
	1.5	1.53	
	3	1.29	
	6	1.03	
	10	0.76	
	15	0.51	
4	0	1.70	17.0
	1.5	1.60	
	3	1.27	
	6	0.92	
	10	0.51	

In this work, we want to compare as directly as possible liquid surfactant membranes and supported films. We made experiments with over one hundred different liquid surfactant membrane compositions. The most stable of the resulting membranes and the copper fluxes across them are given in Table 3. In most of the cases shown, we made no systematic study of membrane transport. However, we include these fragmentary experiments because most past publications on this subject have seldom reported detailed formulations.

We found that reproducible data can be difficult to obtain on these systems, as illustrated by the results in Table 4. These four experiments are identical; they used the same solutions, the same membrane preparation, and the same analytical procedure. This procedure gave a reproducible stability, as defined by the chromate experiments described above. Copper separations in four experiments looked qualitatively the same, without any experimental surprises. However, when the samples were analyzed, the measured fluxes differed by a factor of four, fifty times the variation found with the supported liquid films. While these data are an extreme case, they do illustrate the potential problems of working with emulsion based membranes.

As shown in Figure 7, the copper flux across these membranes varies with copper and ammonia concentrations for liquid surfactant membranes, although it did not do so for supported liquid films. This flux varies linearly with carrier concentration only below 0.03% carrier as LIX-64N. In contrast, the flux varied linearly with carrier concentration to over 2% carrier as LIX-65N in supported liquid films.

OH^- (10^{-3} *M/l*)	NH_3 (*M/l*)	Acid conc. (N H_2SO_4)	Initial flux (10^{-5}M cu/min)
4.47	1.55	0.5	5.82
3.72	1.53	0.5	4.82
5.01	1.56	1.0**	5.15
3.72	1.56	0.5	4.02
4.47	1.55	0.5	6.71
3.72	1.56	0.5	9.18
4.47	1.55	0.5	6.71
3.72	1.53	0.5	6.50
3.72	1.53	0.5	17.98
4.17	1.52	0.5	11.99
4.47	1.55	0.5	6.61
3.72	1.53	1.0**	5.91
2.00	1.55	0.5	3.31
2.63	0.75	0.5	5.24
5.63	1.84	0.5	5.03
2.63	0.75	0.5	8.63
2.51	0.75	0.5	7.57
1.26	0.72	0.5	3.95
0.03_5	0.49	0.5	1.29
4.47	0.75	0.5	8.55
2.24	0.45	0.5	7.48
0.12_0	0.53	0.5	8.41
3.89	1.20	0.5	7.04
1.82	0.57	2.0	14.00
5.62	1.84	0.5	8.84
2.45	0.73	0.5	8.86
2.45	0.73	0.1*†	0.32

There seem to be three possible reasons why the same theory works less well for liquid surfactant membranes than for the supported liquid membranes. First, the reactions in Equations (1) to (4) may have a different stoichiometry because they use LIX-64N not LIX-65N as a carrier. However, the equilibrium constants measured for these two carriers agree with 20%, so that an altered stoichiometry seems unlikely.

The second explanation for the less successful theory is that the membrane resistance must contain factors besides those assumed above. These factors could include unsteady state effects, boundary layers in the basic solution surrounding the bubbles, or boundary layers within the acidic center of the bubbles. None of these seem likely. Unsteady state effects should be less significant in thin membranes than in thick ones (Mateluvicious and Li, 1974); thus they should be less important for thin liquid surfactant membranes than for supported liquid films (Steele and Halligan, 1974, 1975). Boundary layers surrounding the bubbles should be decreased by stirring the emulsion faster (Sherwood et al., 1975); in fact, the flux of copper is not changed by stirring the system faster. Boundary layers inside the bubbles might be important, but if they are, they should also be important in the experiments with supported liquid films. They aren't.

The third possible reason that the theory works less well for liquid surfactant membranes is that the area and thickness of the bubbles vary with carrier concentration. In other words, the carrier or its complex is changing the nature of the bubbles, so that increases in carrier concentration could produce thicker membranes surrounding larger bubbles.

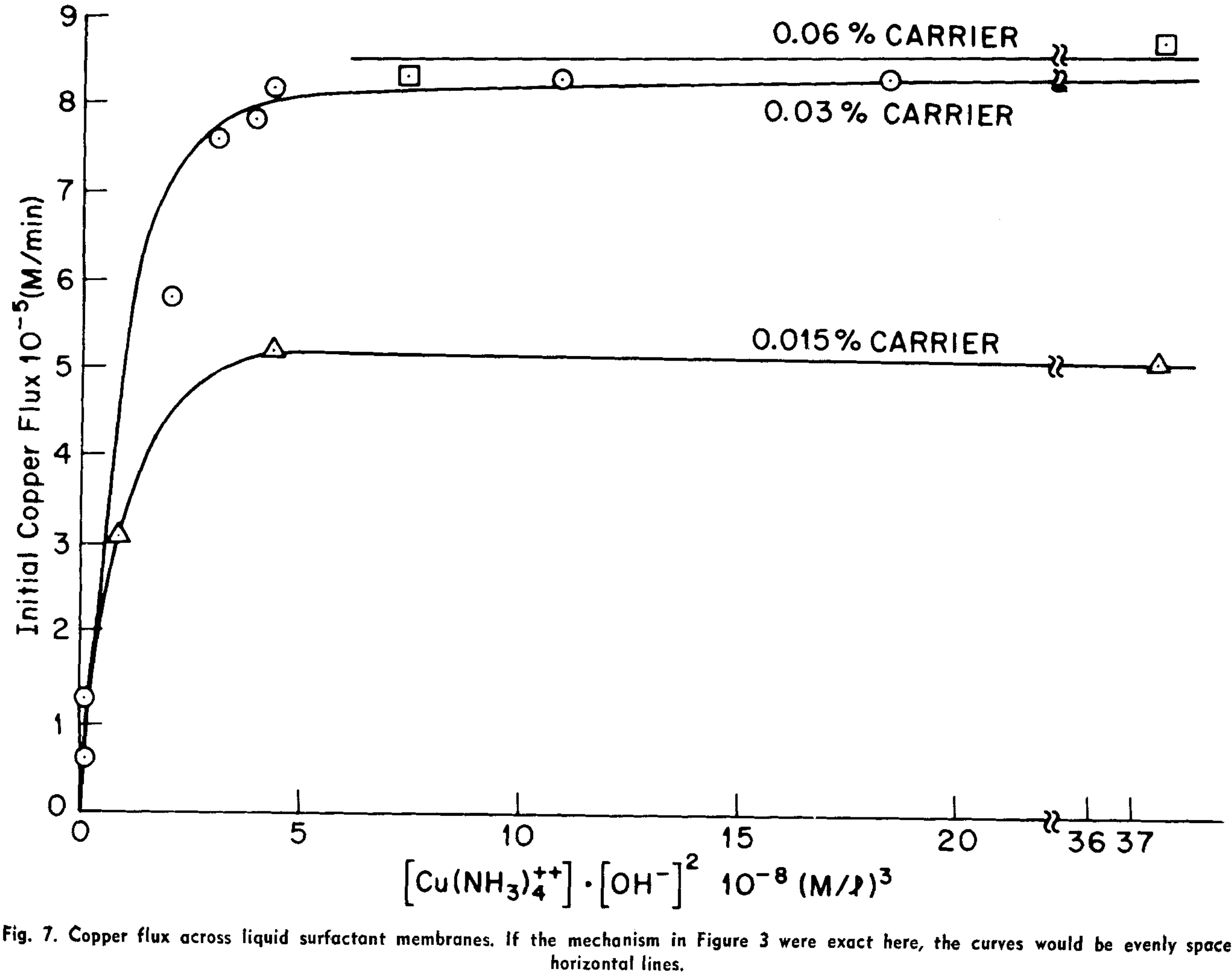

Fig. 7. Copper flux across liquid surfactant membranes. If the mechanism in Figure 3 were exact here, the curves would be evenly spaced horizontal lines.

We suspect this third explanation is most likely. In other, less systematic experiments (Lee, 1977), we found from photomicrographs that membrane thickness and area per volume varied with almost every other variable in the system, including *p*H and solute concentrations. This variation results from the well-known changes in the droplet size and stability of emulsion with changes in *p*H and ionic strength. Other workers have observed similar effects. Indeed, one group (Matsumoto et al., 1976) obtained more stable membranes by using two different surfactants, one on the acidic side of the membrane and one on the basic side. We considered this solution but were concerned because we did not see how the two surfactants could be easily recovered after the ionic separation was realized.

NOTE ADDED IN PROOF

A. Kopp has made the reasonable suggestion that there is convection of the encapsulated droplets.

Comparisons

We have shown that both supported liquid membranes and liquid surfactant membranes can selectively concentrate heavy metal ions. The behavior of the supported membranes can be quantitatively described over a reasonable experimental range using a simple theory. However, the behavior of the liquid surfactant membrane does not fit the same theory as well, perhaps because of unknown changes in membrane area and thickness.

Both types of membranes give similar fluxes in terms of the volume of material treated. Membranes supported by polymer films can easily be used in continuous plug flow reactor geometries, while the liquid surfactant membranes may be more easily used in continuous stirred-tank reactor geometries. The supported membranes produce a stream of concentrated product, but the liquid surfactant membranes must be separated and broken to recover the concentrated product. In both geometries, a major practical problem will be the slow loss of membrane material into the solutions being stripped. However, since much less ion exchanger is used in either of these liquid membranes than in more conventional extractions, this may not prove to be a limiting factor. How useful both these types of membranes become clearly depends on future economic developments; which type is most suitable depends on the specific application.

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NOTATION

D = diffusion coefficient, assumed equal for all species

j_i = flux of component i

K_i = overall equilibrium constant in Equations (1) to (4)

l = membrane thickness

R, RH, R_2Cu, R_2Ni = amounts of ion exchanger: total, uncomplexed, complexed with copper, complexed with nickel, respectively

x = distance within membrane

$[i]$ = concentration of species i in aqueous solution

$[\mathrm{i}]$ = concentration of species i within membrane

Subscripts

l = evaluated on acid side of membrane

o = evaluated on basic side of membrane

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