Stalkup, F. I., "The study of vapor-liquid equilibria at high pressure by gas-liquid partition chromatography," Ph.D. Thesis, Rice University, Houston, TX (1961).

Stalkup, F. I., and R. Kobayashi, "High pressure phase equilibrium studies by gas-liquid partition chromatography," *AIChE J.*, 9 (1), 121 (1963a).

Stalkup, F. I., and R. Kobayashi, "Vapor-liquid equilibrium constants at infinite dilution determined by gas chromatography: ethane, propane and n-butane in the methane-decane system," *J. Chem. Eng. Data*, 8 (4), 564 (1963b).

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Selective Electrorefining with Liquid Membranes

Liquid membranes containing macrocyclic polyethers can be used to electrorefine metals. This purification depends on the selective reaction of the polyether and the metal cation to produce a charged product. The amount of this product is found to be proportional to the square root of the amount of polyester present. Results for silver and copper purification illustrate the ideas involved.

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SCOPE

Electrorefining is a method of purifying metals using an electrolytic cell. An impure metal anode is dissolved, and purer metal is redeposited at the cathode. If the impurities are insoluable in the electrolyte, they fall to the bottom of the cell, and can be separated and further refined. Electrorefining is often used to remove insoluable noble metals from copper. However, it can not be used if the impurities also dissolve in the electrolyte and then reprecipitate at the cathode (Yannopoulous and Argawol, 1976).

This work explores the feasibility of using a liquid membrane to make electrorefining more selective. Such membranes are an organic solution of a mobile carrier, a water-insoluble solute which reacts selectively with a particular metal ion and facilitates its transport (Cussler and Evans, 1980). These membranes are analogs to those found in living systems (Eisenmen, 1975). They are frequently suggested as a route to commercially attractive separations, especially for heavy metals (Schwind et al., 1978; Cahn et al., 1980).

In this paper, we investigate two different membrane geometries suitable for selective electrorefining. First, we place a liquid membrane like those used for selective separations between the anode and the cathode of an electrocyclic cell. This geometry requires supporting this ultra thin, liquid membrane. Second, we coat the cathode itself with the liquid membrane. This method provides automatic membrane support but can be compromised by reaction of membrane components at the cathode.

CONCLUSIONS AND SIGNIFICANCE

We have developed liquid membranes which can selectively electrorefine silver and copper. The selectivity depends on the formation and diffusion of charged complexes of ions and a macrocyclic polyether, 18-crown-6 or benzo-15 crown-5. The key feature of these complexes is their ionic charge necessary for the electrorefining. Previously reported complexes used in other types of membrane separations were usually ion pairs with no net charge (Hochhauser and Cussler, 1975; Christensen et al., 1980). Obtaining ionic complexes requires carefully balancing membrane properties like the solvent dielectric constant, the cation-carrier reaction, and the solubility of available anions.

The results for a liquid membrane mounted in solution between anode and cathode are in agreement with theoretical predictions developed in this paper. These predictions assume that the rate limiting step in the process is the ion transport across the liquid membrane caused by an electrical potential, and so are accurate only for thick membranes and reversible electrodes. We emphasized this case because we wanted to focus on the membrane properties, rather than on the electrode reactions. The results for a liquid membrane coating the cathode show that silver can be transported across this membrane and deposited in pure form. This process is often compromised by electrode reactions of the membrane solvent or the mobile carrier.

Thus we have demonstrated the technical feasibility of selective electrorefining using liquid membranes. Achieving commercial operation will require developing a thin, stable membrane with selectively high electrical conductivity. We do not feel that making the membrane thin and stable will be a major problem: membrane technology for these attributes is well developed. We do feel that developing a membrane which is both selective and conductive is harder, for our experience suggests that high selectivity often means low conductivity, and *vice versa*.

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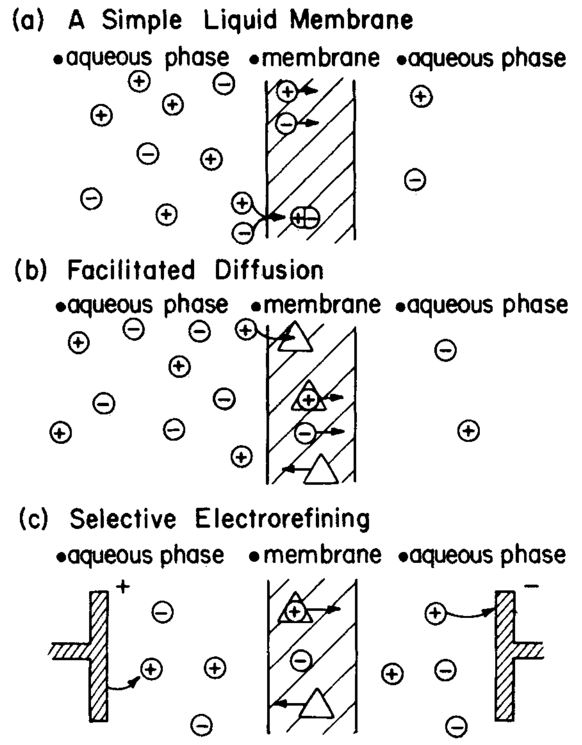

Figure 1. Selective electrorefining with liquid membranes. When an organic liquid membrane separates two aqueous solutions, mass transfer involves parallel transport of ions and ion pairs, as shown in (a). The former route is central in this paper. This transport can be made selective using mobile carriers, shown schematically in triangles in (b). These features of membrane diffusion are combined with an electrical potential for selective electrorefining, as shown in (c).

INTRODUCTION

In this research, we want to develop liquid membranes suitable for selective electrorefining. Such a membrane should conduct an electric current as ions. It should be selective, permeable to some metal ions but not to others. It should be chemically inert, and not decomposed by any electrode reactions.

These requirements stand in contrast to the existing liquid membrane separations shown schematically in Figure 1. In the simplest case, shown in Figure 1(a), an organic liquid membrane separates two aqueous solutions containing different concentrations of electrolyte. The electrolyte in these solutions diffuses from left to right, that is, from high to low concentration. This process includes two parallel transport mechanisms, diffusion of free ions and diffusion of ion pairs. At high dilution, the electrolyte will remain dissociated and the dominant mechanism will be diffusion of free ions. At more moderate concentration, the ions will associate, and the important route can be the diffusion of ion pairs. One interesting consequence of these parallel mechanisms is the variation of the electrolyte's flux with its concentration difference across the membrane. At high dilution, the flux varies linearly with this difference, but in more concentrated solution it can vary with the difference squared (Duffey et al., 1978).

In our experiments dealing with electrorefining, the membrane still separates two aqueous solutions but it now functions in a different way. The aqueous solutions contain the same concentration of electrolyte. This electrolyte is not transported by diffusion, but moves under an applied electric field. Both ions and ion pairs are present; but only the ions carry charge. The fraction of electrolyte present as ions depends on both the electrolyte itself and the organic membrane solvent. In the organic membrane, large singly charged ions like tetraphenylboride do dissolve mostly as ions, but small, multiply charged ions like cupric are present mostly as ion pairs. Ion pair formation is also a very strong function of the dielectric constant of the membrane solvent. For example, at a concentration of 10^{-3} M, ions can remain ionic in a solvent whose dielectric constant is 20, but may almost completely associate if this constant is 10. Thus one task must be the selection of appropriate ions and solvents.

We also want the liquid membrane to be highly selective. In previous membrane separations, such selectivity has depended on mobile carrier mechanisms like that shown in Figure 1(b). As before, an organic liquid membrane separates two aqueous solutions containing different concentrations of electrolyte. As before, the electrolyte diffuses from the high concentration at the left to the lower concentration at the right. Now, however, electrolyte diffusion is enhanced by a mobile carrier, shown schematically as the triangles. This mobile carrier is soluble in the organic membrane but not in the adjacent solutions. It reacts with a specific electrolyte to form a complex which then diffuses across the membrane, a process called "facilitated diffusion." Because the carrier can react much more strongly with some electrolytes than with others, the process can be highly selective, much more than the transport of individual ions or of ion pairs. Thus our second task must be the choice of a mobile carrier.

The chief characteristics of the membrane system developed here are shown in Figure 1(c). As in the earlier separations, we plan to use an organic membrane separating electrolyte solutions. The membrane will contain a mobile carrier capable of selective reaction. Much of the electrolyte within the membrane will remain ionic, relatively free from ion pairs. We will use the same electrolyte solution on both sides of the membrane. As a result, ion transport will not depend on diffusion, but on a voltage drop between the two electrodes shown. The anode will be an impure metal bar and the cathode a purified bar. The chief ion being transported will be the cation of the metal being purified. In some of our experiments, we will replace both the anode and the cathode with reversible electrodes. Analyzing the behavior of this process is the subject of the following theory. In later sections of the paper, we will discuss experimental studies.

THEORY

The system shown in Figure 1(c) involves transport of ions from the anode through an aqueous solution, across the liquid membrane, and through another identical aqueous solution to the cathode. To analyze this process, we assume the membrane is the limiting resistance in the system. The membrane is assumed to contain only three charged species, free cation m^+, complexed cation mc^+, and anion a^-. All of these species are assumed to have the same constant equivalent conductance λ. The membrane may also contain various ion pairs, but these do not appear explicitly in our analysis.

The current across this membrane depends on the number of ions carrying charge. If only uncomplexed and complexed metal cations are involved, the current density i_e is (Robinson and Stokes, 1959; Newman, 1973)

$$i_e = \frac{\lambda}{l}([m^+] + [mc^+])\Delta\psi \qquad (1)$$

where l is the membrane thickness, $\Delta\psi$ is the electrochemical potential, and $[s]$ is the concentration of species s in the membrane. If both cations and anions carry charge, the current density i_r is

$$i_r = \frac{\lambda}{l}([m^+] + [mc^+] + [a^-])\Delta\psi \qquad (2)$$

However, because of electrical neutrality,

$$[m^+] + [mc^+] = [a^-] \qquad (3)$$

and

$$i_r = 2\frac{\lambda}{l}([m^+] + [mc^+])\Delta\psi \qquad (4)$$

For the assumptions made here, the current with anion and cation transport is just twice that with cation transport alone.

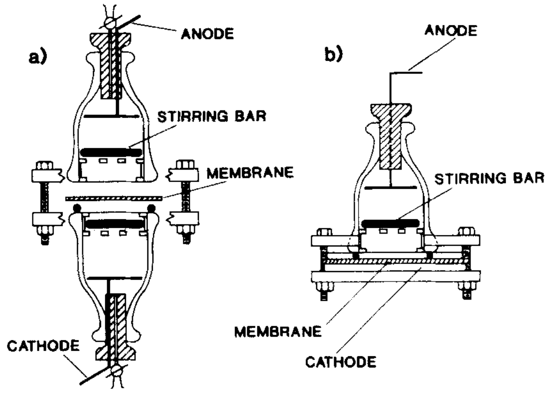

Figure 2. Electrorefining cells. In the cell on the left, the liquid membrane is mounted between two well stirred aqueous solutions, each of which contains an electrode. This cell is used for all results except those in Figure 7. In the cell on the right, the liquid membrane coats one electrode. Both geometries are similar to diaphragm cells used in diffusion experiments.

We want to rewrite the current in terms of experimentally accessible quantities like the metal ion concentration in aqueous solution and the total carrier concentration in the membrane. To do so, we recognize that the following equilibrium holds at each membrane interface,

$$[m^+][a^-] = k^+k^-[M^+][A-] \qquad (5)$$

in which k^+ and k^- are the partition coefficients of individual ions and $[M^+]$ and $[A^-]$ represent the cation and anion concentration in aqueous solution. If only one electrolyte is present,

$$[M^+] = [A^-] \qquad (6)$$

We also expect that the reaction between the free metal ion and the mobile carrier is so rapid that it approaches equilibrium

$$[mc^+] = \{K[c]\}[m^+] \qquad (7)$$

in which K is an equilibrium constant and $[c]$ is the concentration of uncomplexed carrier. We expect in many of our experiments that the carrier will be present in excess, so we assume that $[c]$ is approximately equal to the total carrier concentration. We use Eq. 6 to eliminate $[A^-]$ from Eq. 5, solve Eqs. 5 and 7 for $([m^+] + [mc^+])$, and insert the result into Eq. 1 to obtain:

$$\frac{i_e}{\Delta\psi} = \left(\frac{\psi\sqrt{k^+k^-}}{l}\right)(1 + \{K[c]\})^{1/2}[M^+] \qquad (8)$$

The current per potential shown on the left hand side of this equation is equal to the reciprocal of the resistance of the membrane; the current for both cation and anion transport is double this. Note that in both cases, the results do not explicitly depend on ion pair formation.

This equation suggests two characteristics of the liquid membrane which may be tested by experiment. First, it says that the current is proportional to the potential difference and varies inversely with the membrane thickness. This is a consequence of our assumption that the membrane is the limiting resistance in the system. Second, Eq. 8 predicts that the current will be proportional to the square root of the carrier concentration when the carrier-complex formation is strong. This is because any metal complex mc^+ must involve an anion a^-, a factor which has not been central to earlier, more complete theories (Sandblom, 1969; Solner, 1971; Eisenman, 1975). These characteristics will be checked experimentally later.

EXPERIMENTAL

All salts were reagent grade and were used as received. Membrane solvents were also reagent grade but were usually distilled once, taking a fraction which boiled within 0.03°C. Macrocyclic polyethers were either synthesized using the methods of Pedersen (1978), or were purchased from the Parish Chemical Company.

All liquid membranes were supported with films of a microporous polypropylene (Celgard 2400 or Celgard 2500, Celenese Plastics Co.). These films have effective pore diameters of 0.02 μ and 0.04 μ, and porosities of 35% and 45%, respectively. Their effective diffusion path is much greater than their thickness of 25 μ, apparently because of unusually tortuous pores (Lee et al., 1978). These pores were filled with the membrane solutions using the method of Duffey (Duffey et al., 1978). The membranes were mounted in the cells shown in Figure 2. The cell on the left, identical with diaphragm cells used in earlier experiments (Choy et al., 1974), has the membrane clamped between two aqueous solutions. Each solution contains a silver-silver chloride electrode or pure metal electrode used to apply an electrical potential. The cell on the right has one aqueous solution replaced with a flat metal cathode, which serves as an electrode. Potential between the electrodes in both cells was applied over a range of 0–1.0 V and currents of 0–400 ma with a DC power supply (Semi-Conductor Circuits, Inc., model 401). The surface of the metal cathode was analyzed by both ESCA and Auger spectroscopy (Associated Electronics model 200A and Physical Electronic Industries model 545, respectively). Details of the operation of these cells are given elsewhere (Hodgson, 1979; Gökalp, 1981).

RESULTS AND DISCUSSION

In this section, we describe the development of liquid membranes suitable for electrorefining, and show how these membranes behave consistently with the analysis given above. In this development, we wanted to explore technical feasibility rather than produce specific inventions. Accordingly, we decided to focus on the electrorefining of silver in the presence of copper and nickel, for the membrane transport properties of these species have been reported previously (Reusch and Cussler, 1973; Lee et al., 1978). This system is of course the reverse of the commercial process for electrorefining copper in the presence of noble metals like silver, a process which does not use the liquid membranes.

Our first task was the choice of an appropriate membrane solvent and of an anion soluble in this solvent. One criterion for this choice is that the cation be very soluble; a second, less obvious criterion is that the cation should not associate to form ion pairs. We originally and carelessly thought that solubility was paramount. We found organic solutions which contained as much as 0.5 M cation, often solubilized with the help of large amounts of macrocyclic polyether. We were dismayed to discover that these solutions had resistivities of megohm cms, indicating that only a very small fraction of cation was present as charged species.

We found that the best solvents were higher alcohols like n-hexanol and n-octanol. These solvents are not very soluble in water. They have a relatively low volatility and a relatively high viscosity, and so yield stable liquid membranes. They dissolve significant amounts of electrolyte yet have a dielectric constant of around 15, so much of the dissolved electrolyte remains ionic. Finally, they are relatively inert chemically, and do not react on the cathode (Weinberg, 1975).

We found that many other solvents were less satisfactory for a variety of reasons. We were concerned that too much water dissolved in other alcohols like phenol, m-cresol, benzyl alcohol, cyclohexanol, furfural, and 2 ethyl 1-3 hexanediol. Other solvents which were very insoluble in the aqueous phases often dissolved few free ions. These included chloroform, nitrotoluene, o-chlorophenol, chlorobenzene, trioctylphosphate, 3-pentanone, and carbon disulfide. Solvents which were both water-insoluble and dissolved free ions often reacted at the cathode. Examples of this group are pyridine, nitrobenzene, nitroanisole, butyronitrile, benzyl cyanide, and tetrahydrofuran (Hodgson, 1978; Gökalp, 1981).

We also tested a variety of anions, looking for species which would enhance the dissolution of cations. In these tests, we usually added the appropriate sodium salt to both sides of the membrane, and using silver-silver chloride electrodes to find the current under a fixed voltage. Some of the results are given in Figure 3. The anions which gave the greatest current were either surface active (like dodecylsulfate or cholanate) or capable of distributing charge (like tetraphenylboride or perfluorooctanoate). We were concerned that the surface active ions might be forming inverted micelles which

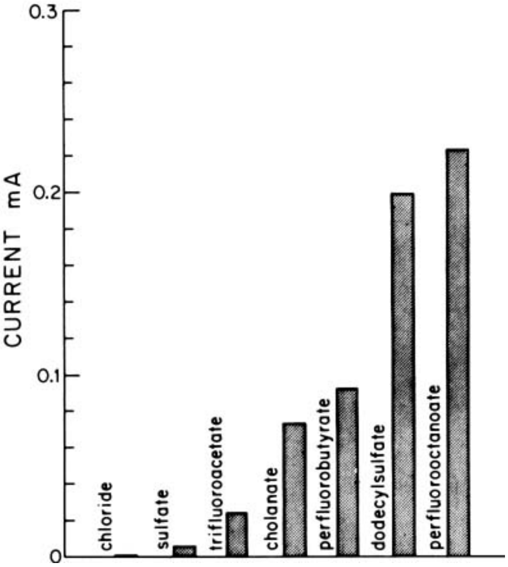

Figure 3. Anion effects across liquid membranes. The current across the octanol membrane is affected by the anions present because the membrane permeability depends on a geometric average of ionic partition coefficients (cf. Eq. 8). The anion concentrations were 0.1 N except for cholanate, which is 0.02 M. Silver-silver chloride electrodes were used, but a mobile carrier *was not*.

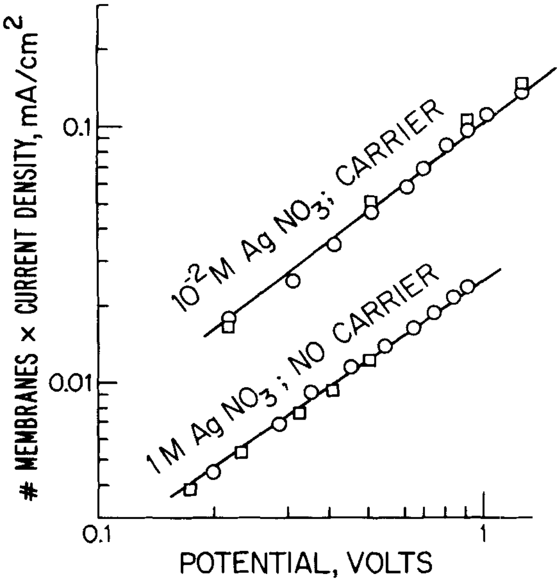

Figure 4. Current vs. potential. The current is directly proportional to the potential and inversely proportional to the membrane thickness, so the membrane limits the current. The circles are for one layer of a Celegard membrane support, and the squares are for two Celegard membranes clamped together. Note the effect of mobile carrier: the current using 10^{-2} M AgNO$_3$ and a hexanol membrane containing the carrier 18-crown-6 and supported with Celegard 2400 is six times greater than that using 1 M AgNO$_3$ and an octanol membrane without carrier supported with Celegard 2500, which is twice as permeable.

were non-selective, so we did not study these species further. We found tetraphenylboride was unstable. For future work, we recommend using perfluorooctanoate, which is soluble in organics, reticent about forming ion pairs, and stable.

Our next task was the selection of a mobile carrier capable of transporting silver across the membrane. The most obvious alternatives for this choice are the chelating agents used for liquid-liquid ion exchange. These agents have been used for diffusion-based membrane separations (Schiffer et al., 1974). However, we found that they usually involved uncharged complexes which are not suitable for electrorefining. Instead, we decided to use the crown ethers, macrocyclic compounds which are not charged yet selectively complex cations (Schwind et al., 1978). We found that the most common of these compounds, dibenzo-18-crown-6 and dicyclohexane-18-crown-6 were sparingly soluble in higher alcohols and produced solutions with very high resistivities, probably because of ion pair formation (Evans et al., 1972).

More successful experiments using polyether-containing membranes are shown in Figures 4–5. All experiments used solu-

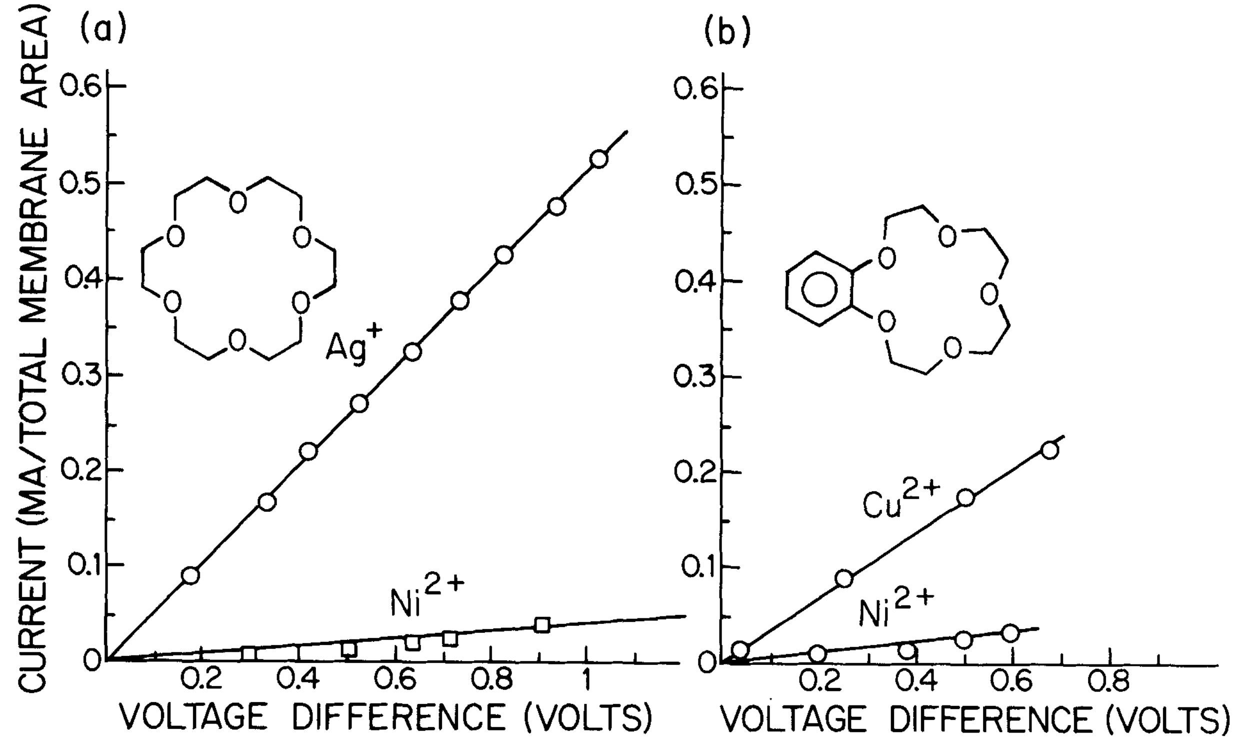

Figure 5. Selective membranes. The silver flux across the liquid membranes is significantly greater than that of the other ions. In (a), the membrane was a hexanol solution of 18-crown-6 (shown in inset) and the aqueous solutions had metal ion concentration of 10^{-2} M and a pH of 7. In (b), the membrane was a hexanol solution of benzo-15-crown-5 (shown in inset) and the aqueous solutions had metal ion concentrations of 10^{-2} M and a pH of 3.

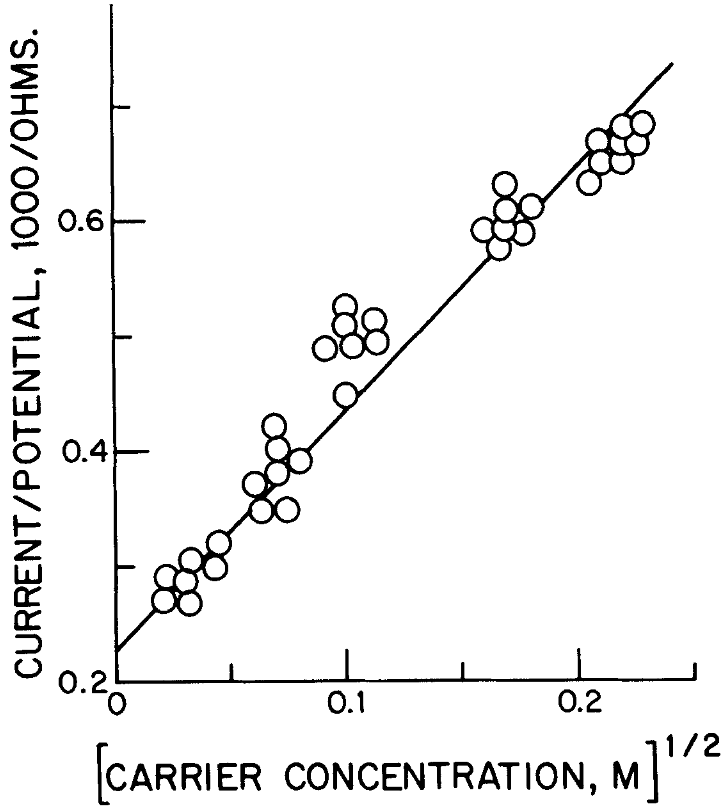

Figure 6. Current/potential vs. carrier concentration. The resistance across a liquid membrane varies with the square root of the concentration of the mobile carrier, 18-crown-6, as predicted by Eq. 8. The membrane, a hexanol solution supported by microporous polypropylene, had an area of 5 cm^2 and a thickness of 0.0025 cm. The aqueous solutions both contained 0.01 M $AgNO_3$ at a pH of 7. Potentials were between 0.20 and 0.92 V.

tions of $AgNO_3$, $CuCl_2$, or $NiCl_2$ in the diaphragm cell apparatus in Figure 2(a). The results in Figure 4, obtained with reversible silver-silver chloride electrodes, compare the current obtained with 10^{-2} M $AgNO_3$ solutions and a membrane containing the polyether 18-crown-6 with 1.0 M $AgNO_3$ solutions and a membrane without carrier. The current across the polyether containing membrane is six times larger, even though the aqueous concentration is one hundred times less. Thus the polyether has increased the silver transport six hundred times.

That this increased transport is selective is shown by the results in Figure 5. In these experiments, electrodes of the appropriate metal wire were used. The two solutions were separated by a liquid membrane containing a macrocyclic polyether. The polyether used in the silver and nickel experiments, 18-crown-6, has a cavity of 1.3 Å, close to the ionic radius of 1.26 Å for Ag^+, but well above that of 0.69 Å for Ni^{++}. This polyether effects a silver flux ten times greater than that of nickel, as shown in Figure 5(a). The polyether used in the copper and nickel experiments, benzo-15-crown-5, has a cavity of 0.81 Å, slightly closer to the size of Cu^{++} (0.72 Å) than to Ni^{++} (0.69 Å). Even this difference causes a copper flux six times larger than nickel, as shown in Figure 5(b).

We recognize that exotic polyethers cost a lot, and so make this process more expensive. However, the situation here is much more promising than for diffusion-based membrane separations. There, liquid membranes are used to treat large volumes of dilute solutions which are discarded after treatment. Valuable membrane components will almost inevitably be lost in this discarded material. Here, the liquid membranes and adjacent solutions will be used again and again to refine metal bars, so loss of valuable membrane materials should be much less.

We now turn to the experimental tests of the analysis which led to Eq. 8. The prediction that the current varies directly with the potential and inversely with the membrane thickness is verified by the data in Figure 4. The data for two membranes tightly clamped together fall within experimental error of the data for one membrane, whether or not mobile carrier is present. Such dependence on membrane thickness justifies our assumption that the membrane resistance limits the current. In addition, the potential gradients involved apparently do not spark free convection, probably because the viscous forces in the membrane's pores are too high (Plonski et al., 1979).

The prediction that the current can vary with the square root of carrier concentration is verified by the results in Figure 6. We should stress that it is a consequence of the transport of ions, and not of the formation of ion pairs. At the same time, we should remember that this simple variation requires strong association between cation and carrier, and that transport of free cations may still be important in some cases (Gökalp, 1981).

Finally, we report in Figure 7 preliminary experiments with a membrane supported directly by the appropriate metal cathode. We used a liquid membrane of octanol but without carrier, for we wanted to avoid any possible carrier-electrode reactions. We used either chloride or nitrate as an anion; for copper and nickel, both anions gave results identical within experimental error. We found that the current again was proportional to the potential, but varied less sharply with the membrane thickness; this means that both the membrane and the electrode reaction contribute to the overall resistance to the process (Hodgson, 1979). Indeed, the current here is roughly correlated with the electrochemical potential of each metal. We analyzed the cathode surfaces with both ESCA and Auger spectroscopy, but found spectra identical with the pure metal, and no trace of product of any other electrochemical reactions. In passing, note that the relative selectivity of copper and nickel shown without carrier in Figure 7 is the reverse of that shown with carrier in Figure 5(b).

Thus we have shown that liquid membranes can be used to make electrorefining more selective. This selectivity, which depends on the membrane solvent, the anion, and the mobile carrier, requires complexing the metal as a free ion. If this is done, the metal flux will vary with the square root of mobile carrier concentration. These results suggest strategies by which more practical processes can be developed.

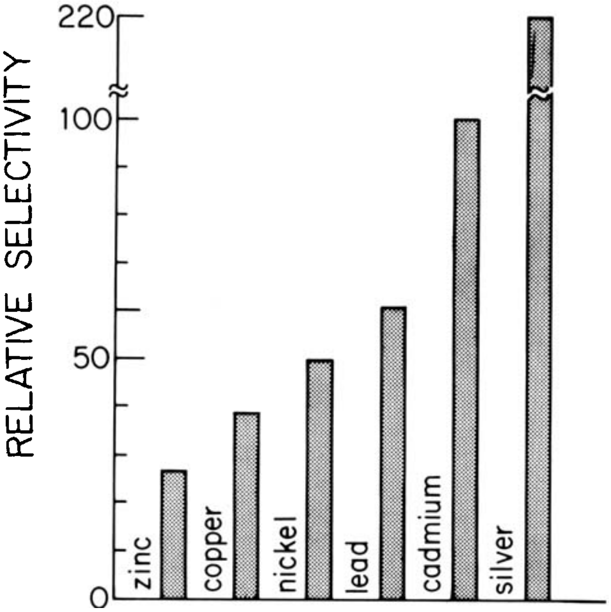

Figure 7. Current to a membrane-coated cathode. These data were obtained using the cell in Figure 2(b) with an octanol membrane without mobile carriers. In each case, the cathode was a pure sheet of the metal indicated, and the electrolyte was the appropriate nitrate. The currents reported are in arbitrary units relative to a value of 100 for cadmium.

ACKNOWLEDGMENTS

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NOTATION

$a-$ = anion in membrane
A^- = anion in aqueous solution
c = carrier in membrane
i_e = current density for cation transport
i_r = current density for cation and anion transport
k^+,k^- = partition coefficients for cation and anion, respectively
K = equilibrium constant (Eq. 7)
l = membrane thickness
m^+ = metal ion in membrane
M^+ = metal ion in aqueous solution
mc^+ = metal ion complex in membrane
λ = ionic conductivity
ψ = electrochemical potential

LITERATURE CITED

Cahn, R. P., J. W. Frankenfeld, and N. N. Li, "Extraction of Copper with Liquid Membranes," 73rd AIChE Annual Meeting, Chicago (Nov., 1980).

Choy, E. M., D. F. Evans, and E. L. Cussler, "A Selective Membrane for Counter-transporting Sodium Ion Against its Gradient," *J. Am. Chem. Soc.*, **96**, 7085 (1974).

Christensen, J. J., R. M. Izatt, and J. D. Lamb, "Selective Transport of Metal Ions Through Liquid Membranes Containing Macrocyclic Carriers," 73rd AIChE Annual Meeting, Chicago (Nov., 1980).

Cussler, E. L., and D. F. Evans, "Liquid Membranes for Separations and Reactions," *J. Memb. Sci.*, **6**, 113 (1980).

Duffey, M. E., D. F. Evans, and E. L. Cussler, "Simultaneous Diffusion of Ions and Ion Pairs," *J. Memb. Sci.*, **3**, 1 (1978).

G. Eisenmen, ed., *Membranes*, **1-3**, Dekker, NY (1975).

Evans, D. F., S. L. Wellington, J. A. Nadis, and E. L. Cussler, "The Conductance of Cyclic Polyether-Cation Complexes," *J. Soln. Chem.*, **1**, 499 (1972).

M. Gökalp, "Membrane Reactors," Ph.D. Thesis, Carnegie-Mellon Univ. (1981).

Hochhauser, A. M., and E. L. Cussler, "Concentrating Chromium with Liquid Surfactant Membranes," *AIChE Symp. Ser.*, **71**, 136 (1975).

Hodgson, K. T., "Selective Electrowinning," M.S. Thesis, Carnegie-Mellon Univ. (1979).

Lee, K. H., D. F. Evans, and E. L. Cussler, "Selective Copper Recovery with Two Types of Liquid Membranes," *AIChE J.*, **24**, 860 (1978).

Newman, J., *Electrochemical Systems*, Prentice Hall, Englewood Cliffs (1973).

Pedersen, C. J., *Synthetic Multidentate Macrocyclic Compounds*, R. M. Izatt and J. J. Christensen, eds., Academic Press, New York (1978).

Plonski, J. W., and J. F. Hoburg, D. F. Evans, and E. L. Cussler, "Mixing Liquid Membranes with Electric Fields," *J. Memb. Sci.*, **5**, 371 (1979).

Reusch, C. F., and E. L. Cussler, "Selective Membrane Transport," *AIChE J.*, **19**, 736 (1973).

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London (1959).

Sandblom, J., "Liquid Ion Exchange Membranes with Weakly Ionized Groups," *J. Phys. Chem.*, **73**, 249 (1969).

Schiffer, D. K., A. M. Hochhauser, D. F. Evans, and E. L. Cussler, "Concentrating Solutes with Membranes Containing Carriers," *Nature*, **250**, 484 (1974).

Schwind, R. A., T. J. Gilligan, and E. L. Cussler, "Commercial Potential of Macrocyclic Molecules," *Synthetic Multidentate Macrocyclic Compounds*, R. M. Izatt and J. J. Christensen, eds., Academic Press, New York (1978).

Sollner, K., "The Basic Electrochemistry of Liquid Membranes," *Diffusion Process*, **2**, J. N. Sherwood, A. V. Chadwick, W. M. Muit and F. L. Swinton, Gordon and Beech, New York, 655 (1971).

Weinberg, N. L., "The Technique of Electroorganic Synthesis Part II," John Wiley & Sons Inc. (1975).

Yannopoulous, J. C., and J. C. Agarwal, *Extractive Metallurgy of Copper*, Metallurgical Society of AIME, New York (1976).

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