Separation & Purification Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

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E. S. Matulevicius[a]; Norman N. Li[a]
[a] Exxon Research and Engineering Company, Linden, New Jersey

To cite this Article Matulevicius, E. S. and Li, Norman N.(1975) 'Facilitated Transport Through Liquid Membranes', Separation & Purification Reviews, 4: 1, 73 — 96

To link to this Article: DOI: 10.1080/03602547508066036

URL: http://dx.doi.org/10.1080/03602547508066036

SEPARATION AND PURIFICATION METHODS, 4(1), 73-96 (1975)

FACILITATED TRANSPORT THROUGH LIQUID MEMBRANES

E. S. Matulevicius and Norman N. Li

Exxon Research and Engineering Company
P. O. Box 45
Linden, New Jersey 07036

ABSTRACT

Liquid membranes, developed by Li,[1] offer a new and effective means for separation of mixtures. In order to maximize the utility of this concept, it is necessary to maximize the concentration gradient of the diffusion species across the membrane. This can be done in two ways:

Type 1 facilitation where the concentration gradient is maximized by causing an irreversible reaction to occur in the receiving phase, thereby, maintaining the permeate concentration effectively zero in that phase, and,

Type 2 facilitation where an additional species is added to the membrane capable of reversibly reacting with the permeate, thereby, increasing the concentration gradient by carrier mediation.

Facilitation of the first type is illustrated for the case of phenol removal from water. A model is presented which

describes the overall permeation process. The separation of hexane from heptane using cuprous ammonium acetate as the membrane carrier of hexane is used as an example of Type 2 facilitation.

INTRODUCTION

The separation of mixtures using semipermeable membranes has been the subject of much academic interest in the past decade. However, this concept has not met with much success in industrial applications since the polymeric membranes have generally suffered from low flux rates and low selectivities.[2] Thus, area and staging requirements become too great for any large scale process.

An alternative is to use liquid films for membranes. In general, liquids possess much higher selectivities than polymeric membranes, thereby reducing staging requirements markedly.[3,4] However, membrane systems based on thin liquid films have not been able to overcome the costs associated with achieving sufficient area to make a significant impact in the separation area. The liquid membrane concept, first proposed by Li,[1] overcomes this liability by generating the necessary surface area without the need for mechanical support.

In general, these liquid membranes are formed by first making an emulsion of two immiscible phases and then dispersing the emulsion into a third phase (continuous phase) by agitation. The liquid separating the encapsulated phase of the emulsion and the continuous phase is the semipermeable liquid membrane. Thus, two miscible liquids are separated by an immiscible film which, because of the small droplets formed through agitation, provides a large area for permeation. Separation can readily be achieved by selective diffusion of one component through this membrane phase into the liquid of lower concentration. Once separation is effected, the three phases can be separated first by settling the emulsion and continuous phase and then by breaking the emulsion (depending on process requirements, different means other than demulsification may be used to handle the used emulsion).

The most effective use of the liquid membrane process is achieved when the flux through the membrane phase and the capacity for the diffusing species in the receiving phase are maximized. Techniques for maximization of the flux and capacity are the subject of this paper. Briefly, the flux rate through the membrane phase can be achieved by maximizing the concentration gradient of the diffusing species across the film. This is readily achieved in two ways:

<u>Type (1)</u>: Minimization of the concentration of the following species in the receiving phase. This is normally done by reacting the diffusing species with some other constituent in the receiving phase to form a product incapable of diffusing back through the membrane. For example, in the removal of phenol from water, the phenol diffuses through a hydrocarbon membrane to a receiving phase of caustic solution. The phenol reacts with caustic to form sodium phenolate which is insoluble in the hydro-

carbon membrane and hence cannot diffuse back into the water phase from which the phenol is being removed. In this way, the concentration of phenol in the receiving phase is low, thus, facilitating its passage through the hydrocarbon membrane.[5,6,7]

Type (2): Carrying the diffusing species across the membrane by incorporating "carrier" compounds in the membrane. This concept of carrier-mediated transport is illustrated in Figure 1. Species A diffuses through the membrane both as dissolved A and as product AX. Upon reaching the receiving phase, AX dissociates into A and X. Component A dissolves into the receiving phase while X diffuses back to the other side of the membrane. Thus, concentration gradients shown in Figure 1 are set up in the membrane phase. Since the concentration of AX can be several orders of magnitude higher than A in the membrane phase, it can easily be seen that the flux rate can be substantially increased.[7,8,9]

PROPERTIES OF LIQUID MEMBRANES

As mentioned previously, liquid membranes are made by forming an emulsion of two immiscible phases and then dispersing the emulsion into a third phase (continuous phase). Usually, the encapsulated phase and the continuous phase are miscible. The membrane phase must not be miscible with either if it is to remain stable.[1] Therefore, the emulsion is of the oil-in-water or of water-in-oil type, depending on the nature of the continuous and encapsulated phases. To maintain the integrity of the emulsion during the separation process, the membrane phase

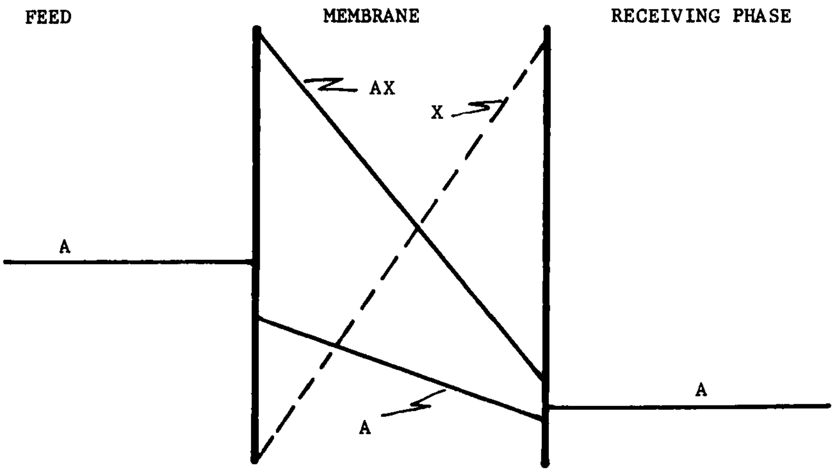

Figure 1. The Concept of Facilitated Transport.

usually contains surfactants, additives, and a base material which is a solvent for all the other ingredients. Hence, for specific applications, liquid membranes must be tailor-made.

When the emulsion is dispersed by agitation in a continuous phase (the third phase), many small globules of emulsion are formed. Their size depends strongly on the nature and concentration of the surfactants in the emulsion, emulsion viscosity, and the mode and intensity of mixing. In most of our laboratory runs, the globule size is controlled in the range of 0.1 to 0.2 mm in diameter. Thus, an enormously large number of globules of emulsion can easily be formed to produce equally large membrane surface area for rapid mass transfer from either the continuous phase to the encapsulated phase or vice versa. It should be noted that many much smaller droplets approximately 1μ in diameter are encapsulated within each globule.[6]

The large number of liquid systems from which liquid membranes can be made renders this an extremely useful process. It is applicable to aqueous and hydrocarbon separations, which include applications in waste water treatment,[5,6,7,9] minerals recovery,[5,6,7,9] and "artificial kidney" treatment.[10] It can also be used in gas separations. In the latter case, the membrane system is a foam containing an encapsulated gas dispersed in another gas phase[11] or a liquid.[12,13] The blood oxygenation application (artificial lung) uses a gas/liquid liquid membrane system.[12] Introducing various means of facilitation to the liquid membrane system to increase the flux and capacity makes it truly an efficient and general separation process. For example, in water treating, some of the contaminants which can be separated by the liquid membrane technique are:[6]

Organic Acids	Cations	Anions
Phenol	Cupric	Sulfide
Acetic Acid	Mercuric	Nitrate
Citric Acid	Ammonium	Phosphate
	Silver	Cyanide

In this paper, the removal of phenol from water will be used to illustrate the facilitated transfer in a liquid membrane system by the use of an encapsulated reactive solution (Type 1 Facilitation). The separations of inorganic compounds and/or ions from water and olefins from paraffins can be readily achieved using carrier-mediated transport through, respectively, oil-type and aqueous-type liquid membranes. It is the latter case which will be considered in more detail in this paper to demonstrate the carrier-mediated type of process (Type 2 Facilitation).

PHENOL REMOVAL FROM AQUEOUS STREAMS - TYPE 1 FACILITATION

1. Experimental Procedure

In a typical laboratory experiment, a water-in-oil type of emulsion containing a 0.5 percent by weight NaOH solution is first made. A typical oil-type liquid membrane could contain Span-80 (sorbitan monooleate) as the surfactant, ENJ-3029 (polyamine) as the membrane-strengthening additive, and S100N (isoparaffinic oil with an average carbon number of 35) as the solvent.[5,6,7,9] The concentrations of the surfactant and the additives in the membrane phase usually are quite low, such as within 1 to 5%. The balanced weight percent is that of the solvent. The W/O emulsion is dispersed in a simulated waste water phase containing phenol in a mixer. At various times throughout the test, agitation is stopped and small samples of the continuous phase are withdrawn and analyzed. Because the liquid membrane coated drops coalesce when mixing is stopped, (thereby, reducing drastically the total membrane surface area for mass transfer), the amount of phenol diffusing into the membrane during the sampling period is negligible. The mixing is continued until most of the phenol is removed from the water. The results of phenol removal vs. time are then plotted as shown in Figure 2.

It should be noted that the strength of caustic in the emulsion is such that virtually all of the phenol is reacted to

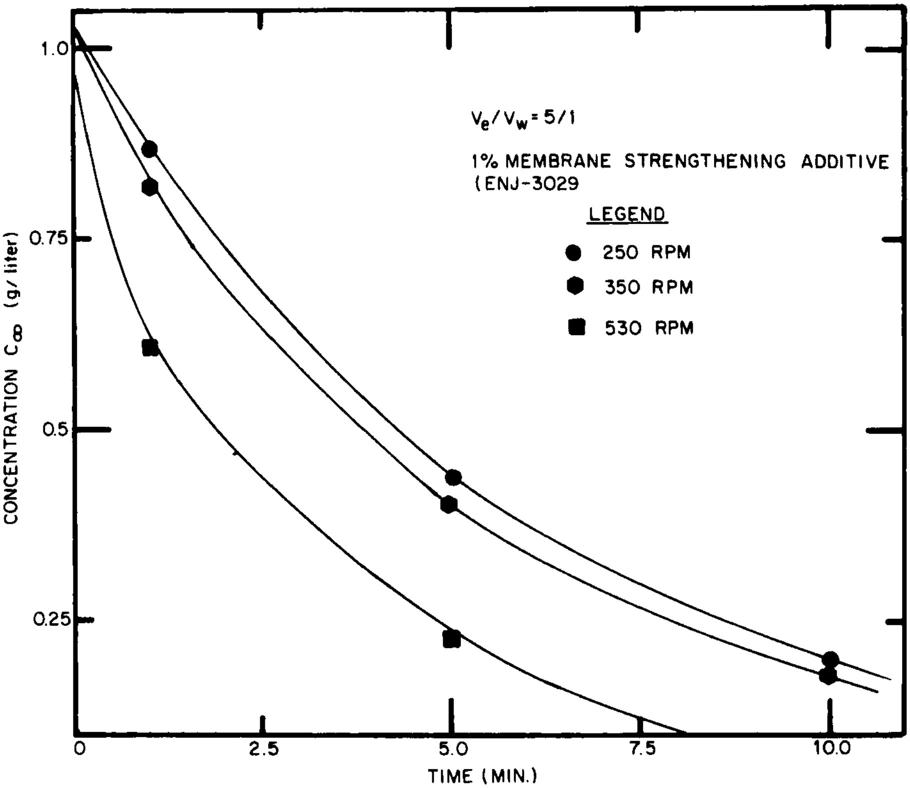

Figure 2. Phenol Removal from H_2O.

sodium phenolate, i.e., the concentration of phenol in the dispersed emulsion phase was effectively negligible throughout the experiment. Hence, the concentration driving force was maximized. Depending on process requirements, the concentration of the encapsulated NaOH solution can be much higher than 0.5%.[6]

2. Discussion of Results

A model describing the process was constructed[1,6] with the following assumptions:

1. The continuous water phase and emulsion are well mixed.
2. The process is mass transfer limited in the liquid membrane phase.
3. Each emulsion droplet is an agglomerate of reactive droplets in a hydrocarbon phase. However, diffusion of phenol is limited, from gradient considerations, to the outer droplets only. This is equivalent to a large membrane droplet shown in Figure 3.
4. The emulsion droplet remains intact once formed.

Using these assumptions, diffusion through the liquid membrane can be described by the following equations:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \qquad (1)$$

$$\begin{array}{lll} \text{at} & r = R_i & c = 0 \\ & r > R_o & c = c_\infty \\ & r = R_o & c = kc_\infty \end{array} \qquad (2)$$

$$\begin{array}{lll} \text{Initially,} & r < R_o & c = 0 \\ & r > R_o & c = c_{\infty i} \end{array} \qquad (3)$$

Assuming a particle size distribution function

$$\frac{n}{N} = fdR_o \qquad (4)$$

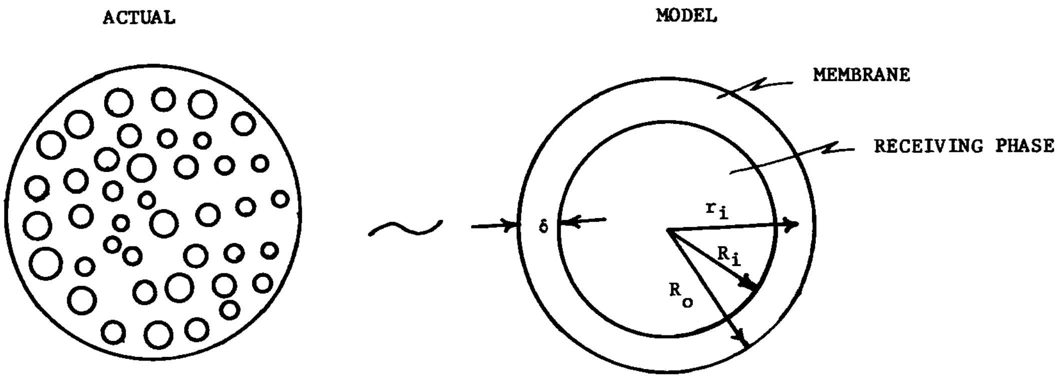

Figure 3. Model of Liquid Membrane.

where f is an unspecified distribution function, the above equations can be solved for the case where the film thickness is much smaller than the aggregate radius. It can be shown that

$$M = 6\,\phi \sum_{n=1}^{\infty} \frac{\exp(-q_n^2\,\tau)}{3\,\phi + 9\,\phi^2 + q_n^2} \qquad (5)$$

where $q_n = 3\,\phi \cot(q_n)$ (6)

and ϕ = constant = function of

Ve/V_w, k, δ, and f (7)

Solutions for Equations 5 and 6 are shown in Figure 4. The phenol concentration in the continuous phase is described by two parameters, the Fourier Mass Transfer Number, τ, and the rate parameter, ϕ. For each experiment, constants ϕ and τ were determined by a trial-and-error technique.[14] Figure 5 shows very good agreement of some of the data with this model.

In order to determine whether such a correlation is fortuitous, both the volume of hydrocarbon membrane phase to receiving phase and the composition of the hydrocarbon phase was varied. In this way, the membrane "thickness" distribution coefficient of phenol, and the surface tension effects were changed making the probability of chance correlation relatively remote. Under all conditions, the correlation proved accurate lending credibility to the validity of the model.

The product, $3\,\phi\,D/\delta^2$ can be directly related to the convention mass transfer rate, K wherein

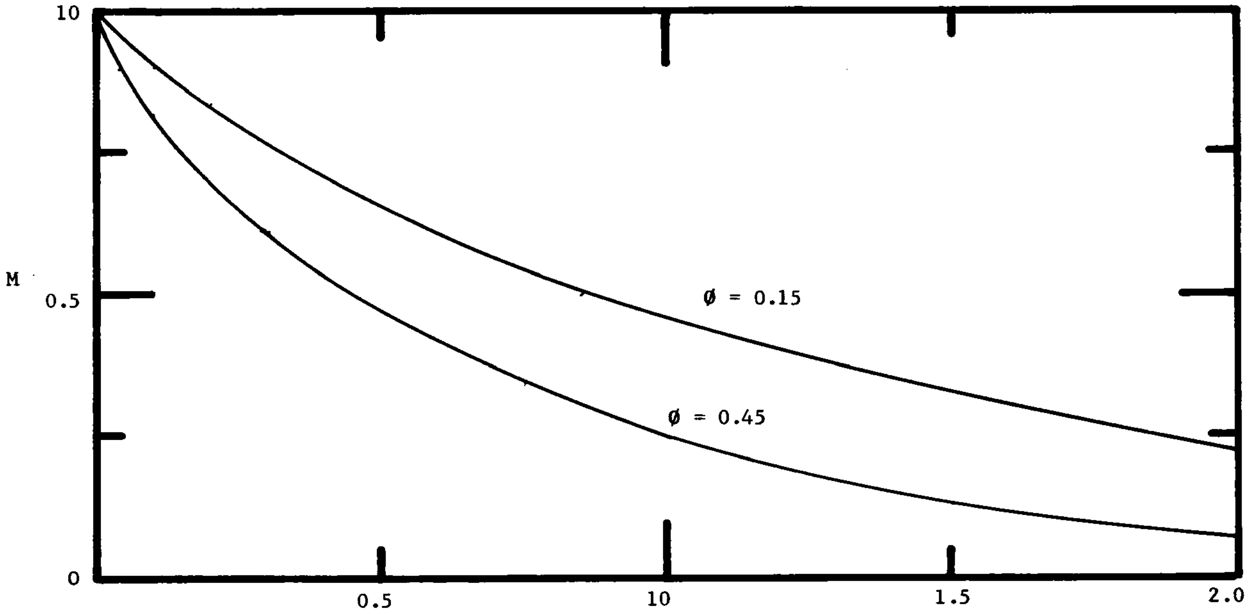

Figure 4. M vs τ as a Function of the Rate Parameter, ϕ.

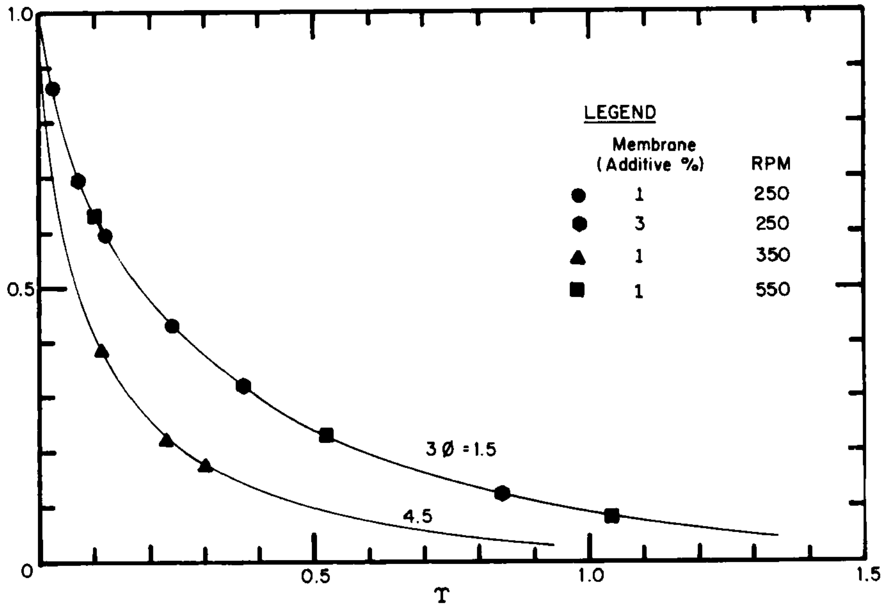

Figure 5. Phenol Extraction from Water.

$$J = K\ (\Delta C) \qquad (8)$$

In Figure 6, the rate constant, K, is plotted vs. the stirrer speed for increasing membrane additive concentration. A similar plot is shown in Figure 7 for the case of varying the Ve/V_w ratio. From these figures, it can be seen that

$$K = a\ RPM^3 + b \qquad (9)$$

The coefficient, a, is due to two factors, the solubility change of phenol in the hydrocarbon phase due to an increase in the membrane strengthening additive and, the change in dispersion of the emulsion phase. It would be expected that the solubility would increase with increase additive. However,

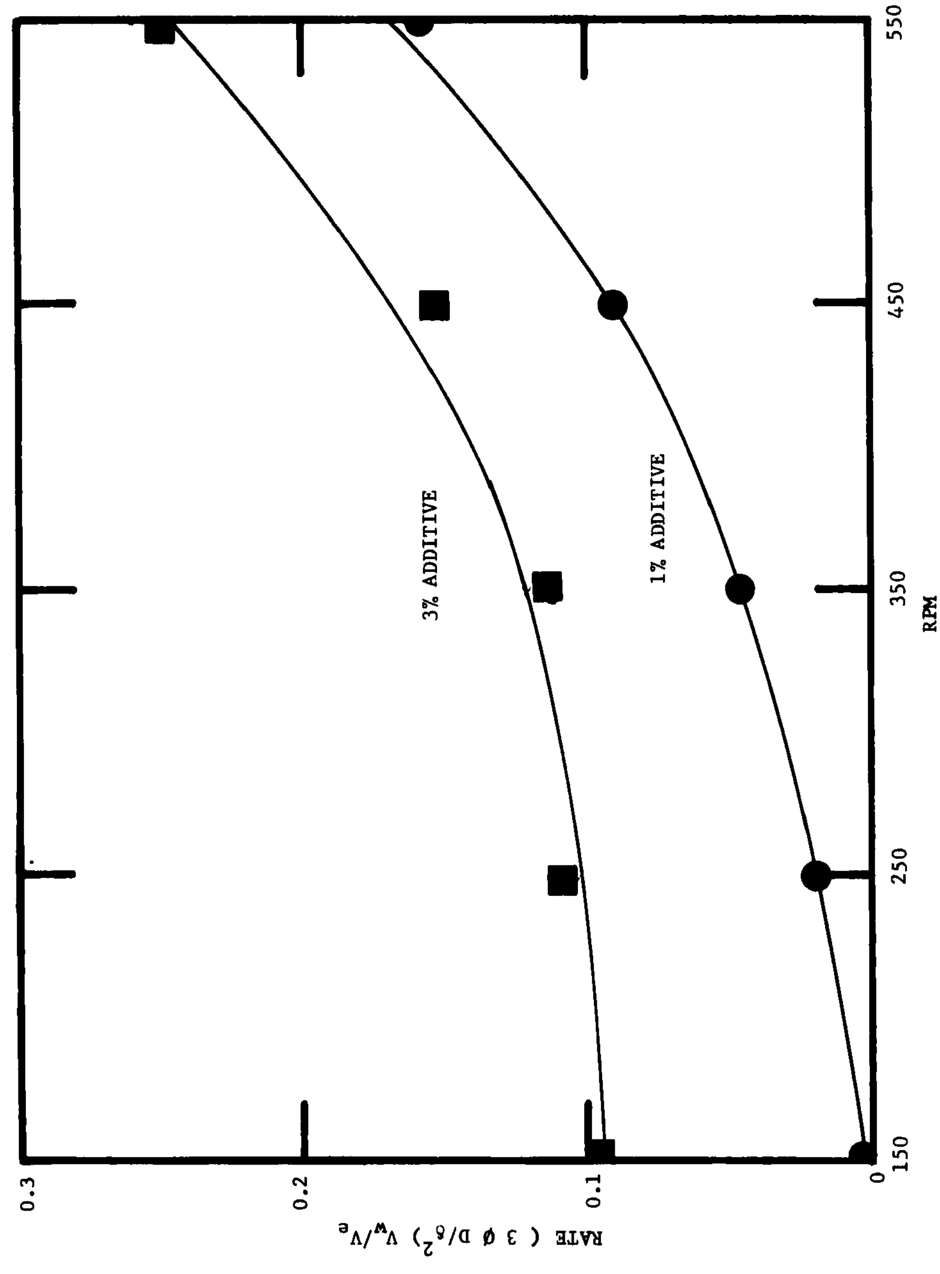

Figure 6. Rate vs Stirrer Speed.

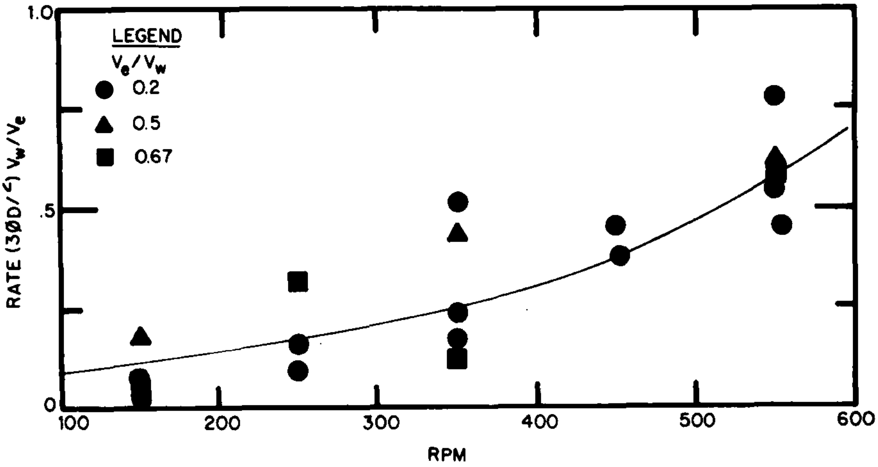

Figure 7. Rate vs RPM for Varying V_e/V_w.

since the viscosity increases with increasing additive (polyamine) the mean diameter of the emulsion should decrease. Separation of these effects at present is not possible since no work was done on drop size distribution.

Since the power per unit volume, P, necessary to disperse the emulsion is proportional to RPM^3, this indicates that

$$K \alpha a P \qquad (10)$$

Power per unit volume is a common unit to correlate mixing processes.[15] This indicates that the amount of internal circulation with the emulsion droplet is relatively small compared to the overall rate process. For if it were not, a much higher coefficient than 3 in Equation 9 would be expected. Therefore, the assumption that the rate limiting step is diffusion of phenol to the <u>external</u> layer of droplets in the emulsion globule is valid. Thus, Type 1 facilitation occurs when the concentration gradient of the diffusing species between continuous phase and receiving phase is maximized by irreversible chemical reaction in the receiving phase.

This example illustrates that the liquid membrane process can be characterized into a diffusion process into rigid spheres of some size distribution, f. This can be the basis of engineering process scale-up. The model seemingly does not take into account parameters such as the "well mixedness" of the reactor nor the various film resistances to mass transfer. However, much of this is accounted in the parameter, ϕ, of Equation 7.

THE SEPARATION OF HEXENE FROM HEPTANE - TYPE 2 FACILITATION

1. Description

The separation of olefins from paraffins is used as an example of Type 2 Facilitation. Here, a certain additive (Cuprous ammonium acetate) is added to the aqueous membrane phase which reacts selectively with the olefin to form weak complexes. The purpose is to increase the effective solubility of the olefin in the membrane phase and thus promote its transfer rate through the membrane.

In general, the solubilizing additive or complexing agent selected should be soluble in the aqueous liquid surfactant membrane and not substantially soluble in either the organic solvent or the organic feed phases. It also should be chosen to be compatible with the surfactant since it is imperative that the solubilizing additive and the surfactant do not interact to substantially weaken the liquid surfactant membrane. That is, the surfactant should not react with the additive to destroy the effectiveness of the membrane. For example, ester or ether-type surfactants will be hydrolyzed with strong basic or acid additives.[8]

Several complexing additives can be used to separate various organic mixtures. Examples of some successful systems are given in Table 1. Complexing additives for separating inorganic mixtures will be discussed in detail in future papers. In general, the separations of inorganic compounds or ions from their aqueous solutions can be achieved by using oil-type liquid membranes containing suitable complexing agents or carriers. PH difference across the membrane can be used as the driving force for the selective permeation or ion exchange involved. It should be noted that in such a membrane system, describing specific solutes permeating "against their concentration gradient" or "pumping" could be confusing.[16] It is true that the specific solutes are concentrated from a dilute external aqueous phase to a much higher concentration in the aqueous phase on the other side of the membrane. However, it is best to picture this happening because of favorable equilibria being established at the two interfaces (by suitable adjustments of pH or displacing ion concentration), which will then allow the solute to diffuse across the membrane along its normal concentration gradient. Transfer across the interfaces occurs due to differences in chemical potential. The carrier, therefore, not only serves to move the ion across the membrane along its normal concentration gradient, but also allows the desired equilibria to be established at the respective interfaces.

It should be noted that the conventional interpretation of facilitated transfer refers to the Type 2 facilitation described here. In other words, it is for the situation where a carrier is added to the membrane phase to substantially increase the flux across the membrane beyond that attributable to purely molecular diffusion.

In order to illustrate the Type 2 facilitation, a 50 weight percent mixture of hexene and heptane was used as a model. This mixture was emulsified with an aqueous phase containing various amounts of cuprous ammonium acetate. The aqueous phase formed a thin liquid film around the hexene/heptane mixture through which the hexene and heptane could diffuse. The emulsion was then mixed with a n-octane phase. Periodically, samples of the n-octane phase were removed and analyzed for the amount of heptane/hexene present. The detail experimental conditions have been described elsewhere.[8] The ratio of hexene to heptane in the n-octane phase to the ratio of hexene to heptane in the interior of the emulsion phase was computed. The separation factor as a function of increasing cuprous ammonium acetate concentrations is shown in Table 2.

TABLE 1

Solubilizing Additives in Liquid Membranes to Facilitate Transfer of Organic Compounds

Solubilizing Additive	Feed Component
Cuprous ammonium acetate	C_1-C_{10} Diolefins or olefins
Sulfuric Acid	C_6-C_{20} Aromatics
Thiourea	C_1-C_{10} Olefins
Acetonitrile	C_1-C_{10} Diolefins
N-methylpyrrolidine	C_1-C_{10} Diolefins
Strong base	α-Acetylenes
Strong base	C_1-C_{10} Mercaptans
Sulfuric Acid	C_1-C_{10} Olefins
Weak Acids	C_1-C_{10} Amines

TABLE 2

Separation of Hexene from Heptane

Concentration of Cuprous Ammonium Acetate in Liquid Membrane	Separation Factor of 1-Hexene from n-Heptane
0	2.9
15	7.6
50	14.6

2. Discussion of Results

Cuprous ammonium acetate complexes reversibly with the olefin. Hence, the olefin diffuses across the aqueous membrane in both the complexed form and the dissolved form while the paraffin diffuses across as the dissolved species only. The increased diffusivity increases the mass transfer rate of hexene and consequently, the selectivity. Thus, this "Type 2 facilitation" can substantially increase the utility of the process by making aqueous membranes very much more selective than possible from differences in physical solubility.

In actual processes, the feed mixture of olefin/paraffin can be emulsified in an aqueous cuprous ammonium acetate solution and then mixed in a continuous phase of another solvent in a manner analogous to the phenol extraction case described previously. However, the mathematical analysis of such a process is substantially more complex because the distribution coefficients in both the encapsulated phase and continuous phase must be known as well as the parameters ϕ, D/δ^2. Further complexity is introduced by the fact that the cuprous ammonium acetate-hexene equilibrium is not linear with concentration. Hence, this resulting non-linearity of the "effective solubility" would complicate the model substantially, hence, making mathematical treatment exceedingly difficult. However, the true selectivity, i.e., the ratio of mass transfer rates of hexene and heptane must be determined by such an analysis. Without such a solution, a more simple case, that of diffusion from single drops, was chosen here to illustrate the effect of Type 2 facilitation.

CONCLUSIONS

The liquid membrane process is a very versatile separation process capable of separation in a wide range of liquid mixtures. However, in order to maximize its utility, it is necessary to maximize the flux rate of one constituent by a process of facilitation. In cases where separation is to be affected by the permeate's solubility in the encapsulated phase, e.g., removal of phenols from water, the incorporation in the receiving encapsulated phase of a reactive species capable of reacting with the permeate will ensure maximum mass transfer rates. Furthermore, the extent of removal is enhanced since much more of the permeate can be removed before the concentration driving force vanishes. In cases where such a reactive system for the encapsulated phase is not available or where the ratio of solubilities of the various constituents in the membrane are low, a reactive component or carrier can be added to the membrane phase which can selectively react with one constituent of the mixture, thereby, increasing the "effective solubility" of that constituent. Hence, efficient separation can be achieved.

The diffusion model developed for phenol removal was shown to be effective in correlating the data. A wide range of experiments have shown that mass transfer rates can be correlated effectively with the power imput per unit volume. These provide the basis for engineering evaluation and scale-up of the process for a given application.

NOMENCLATURE

a	constant = function of concentration of membrane additive, $\sec^{-1}$.
b	constant
c	concentration of permeate in membrane, mols/cm^3
c_∞	concentration of permeate in continuous phase, mols/cm^3
$c_{\infty i}$	initial concentration of permeate in continuous phase, mols/cm^3
D	diffusivity of permeate in membrane phase, cm^2/sec
f	drop size distribution function
J	flux rate of permeate into membrane, mols/sec cm^3
k	solubility of permeate in membrane phase cm^3/cm^3
K	mass transfer coefficient = $3\ \phi\ D/\delta^2$, $\sec^{-1}$
L	impeller diameter
M	ratio of concentration in continuous phase at time, t, to initial concentration, $c_\infty/c_{\infty i}$
n	number of drops of radius R_o
N	total number of drops of emulsion
P	power input per unit volume, Kw/sec
q_n	eigen value defined in Equation 6
r	radius, cm
R_i	internal emulsion drop radius, cm
R_o	external emulsion drop radius, cm
t	time, sec

V_e	volume of emulsion, cm^3
V_w	volume of continuous phase, cm^3
δ	equivalent membrane thickness, cm
ϕ	rate constant = function of V_e, V_w, R, F, δ
τ	Fourier Mass Transfer Number, Dt/δ^2

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