Solvent Extraction with Microporous Hydrophilic and Composite Membranes

Dispersion-free solvent extraction using microporous hydrophobic membranes has been extended to hydrophilic and composite hydrophobic-hydrophilic membranes. Excess phase pressure conditions, if needed for dispersion-free operation, have been identified. Boundary layer and membrane resistances to solute transport have been isolated and simple relations developed for the overall mass transfer coefficient in such systems. A variety of flat microporous membranes have been utilized. Previous investigations by others had interpreted the membrane mass transfer resistance using the notion of unhindered diffusion through tortuous pores of the membrane. We have studied here the applicability and limitations of such a model for a number of membrane-solute-solvent systems.

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Introduction

Highly efficient dispersion-free techniques using microporous hydrophobic membranes are increasingly being considered for a variety of conventional equilibrium continuous contact operations. A few of the candidate operations studied are gas absorption (Qi and Cussler, 1985a) and separation of volatile materials from liquids (Qi and Cussler, 1985b; Imai et al., 1982). Solvent extraction without dispersion has also been studied recently using a microporous hydrophobic membrane (Kiani et al., 1984; Prasad et al., 1986). In this technique, the interface of the immiscible aqueous and organic phases is immobilized at the pore mouths of a microporous hydrophobic membrane wetted by the organic solvent by maintaining the aqueous phase at a pressure higher than that of the organic phase. Several advantages of this technique with membranes in a hollow-fiber configuration have been pointed out (Kiani et al., 1984; Qi and Cussler, 1985a; Prasad and Sirkar, 1987). These are: very high interfacial area per unit extractor volume, ability to handle solids, no need to have a difference in phase densities, well-defined interfacial area, independent variation in phase flow rates, and therefore lack of flooding and ease in scale-up due to modular nature. The application of this technique with Celgard microporous hydrophobic hollow fibers has been illustrated in a fermentor-extractor where alcohol is locally extracted from a fermentation broth using dibutyl phthalate (Frank and Sirkar, 1985). Preliminary performance details of a hydrophobic hollow-fiber extractor without the complications of fermentation are available elsewhere (Prasad and Sirkar, 1987).

To explore the versatility of the phenomenon of dispersion-free solvent extraction with microporous membranes, the above technique has been extended to microporous hydrophilic and microporous hydrophobic-hydrophilic composite membranes. In the case of a hydrophilic membrane, the aqueous-organic interface is immobilized in the pore mouths by having the organic phase at a pressure higher than that of the aqueous phase, with the pores of the membrane filled with the aqueous phase preferentially wetting the hydrophilic membrane.

Dispersion-free solvent extraction has also been studied with composite hydrophilic-hydrophobic membranes where neither the organic nor the aqueous phase need be at a higher pressure. The hydrophobic section of the composite membrane is wetted by the organic phase, while the hydrophilic section is preferentially wetted by the aqueous phase; the hydrophilic and hydrophobic natures of the membrane (which therefore has asymmetric wetting properties) are sufficient to prevent breakthroughs of the organic phase through the hydrophilic membrane and of the aqueous phase through the hydrophobic membrane unless the differences between phase pressures exceed some critical values characteristic of the solute-solvent-membrane system.

Such a technique without dispersion or coalescence has been studied here with the following solvent-water-solute systems: xylene-water-acetic acid, methyl isobutyl ketone (MIBK)-water-acetic acid, *n*-butanol–water–succinic acid. A variety of flat hydrophilic and stacked composite hydrophilic-hydrophobic membranes with a wide variation in porosity, pore size, thick-

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ness, and material have been used. The concentration boundary layer resistances and the membrane resistance to solute transport have been characterized for the above systems. The previous investigations (Kiani et al., 1984; Prasad et al., 1986) had interpreted the hydrophobic membrane resistance using the notion of unhindered diffusion of solute through tortuous solvent-filled pores of the membrane. We have therefore investigated here the applicability of similar notions to explain the measured membrane transfer resistance values. The role of the excess phase pressure of one immiscible phase over the other on the rate of extraction, if any, has also been explored. Finally, a perspective on the comparative utility of dispersion-free solvent extraction with three kinds of membranes—i.e., hydrophobic, hydrophilic, and hydrophilic-hydrophobic—has been provided.

Theory

Figure 1 shows the solute concentration profiles for a flat hydrophilic membrane as well as for a composite hydrophobic-hydrophilic membrane. Following an approach similar to that of Kiani et al. (1984), an overall mass transfer coefficient based on the organic phase, K_o, can be defined as:

Hydrophilic

$$1/K_o = 1/k_o + m_i/k_{mw} + m_i/k_w \tag{1}$$

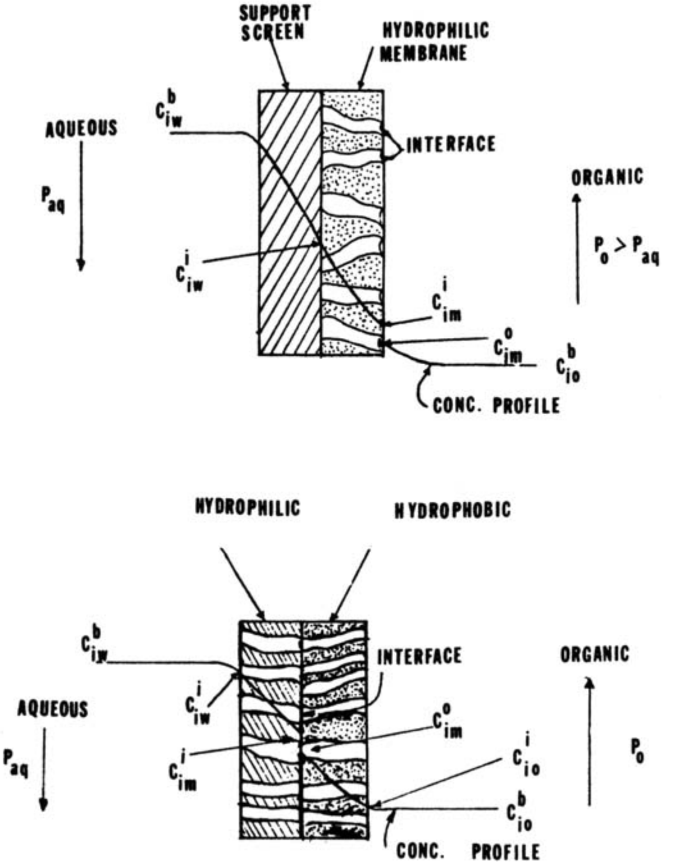

Figure 1. Solute concentration profiles for hydrophilic and composite hydrophilic-hydrophobic membranes.

Composite

$$1/K_o = 1/k_o + 1/k_{mo} + m_i/k_{mw} + m_i/k_w \tag{2}$$

where

$$m_i = C_{im}^o/C_{im}^i \tag{3}$$

Some of the major assumptions in the above analysis are:

a. The distribution coefficient m_i is constant in the concentration range under consideration.

b. For a stacked composite membrane, there is no interfacial resistance between the two membranes due to a liquid film or any tortuosity effects arising at the hydrophilic-hydrophobic interface inside the composite membrane.

c. Each membrane is wetted by one phase only in composite systems, either aqueous or organic as the case may be; further, the aqueous-organic interface is at the interface of the hydrophilic and hydrophobic sections of the composite membrane.

In the following we consider some special cases for the above relations, Eqs. 1 and 2.

Case 1, $m_i \ll 1$

Hydrophilic Membrane. If all the mass transfer coefficients are of the same order of magnitude, then Eq. 1 reduces to

$$1/K_o \simeq 1/k_o \tag{4}$$

The variation of K_o with the organic phase flow rate Q_{or} will then be the same as that of k_o with Q_{or}. A constant K_o is not achieved at high Q_{or}, unlike that in the flat hydrophobic membrane system (Kiani et al., 1984; Prasad et al., 1986) except at very high Q_{or} values. This condition can then be used to determine k_o for a particular solute as a function of the organic flow rate. This case can also be used to study the effect (if any) of the flat membrane thickness or the number of flat membranes in the flow type test cell on k_o.

Composite Membrane. Assuming the various mass transfer resistances to be of the same order of magnitude, Eq. 2 is simplified to

$$1/K_o \simeq 1/k_o + 1/k_{mo} \tag{5}$$

A plot of K_o against Q_{or} will therefore exhibit characteristics obtained with only a hydrophobic membrane; k_o will gradually reach a plateau when k_o becomes substantially larger than k_{mo}. This plateau value of K_o in a composite hydrophilic-hydrophobic membrane run will yield the hydrophobic membrane transfer coefficient k_{mo} only.

Case 2, $m_i \simeq 1$

Hydrophilic Membrane. The membrane and the aqueous-side resistances cannot be neglected now and the complete relation in Eq. 1 is necessary. A plot of K_o against Q_{or} will exhibit a plateau, as observed in the case of flat hydrophobic membrane systems (Kiani et al., 1984; Prasad et al., 1986). Such a plateau value of K_o may be used to determine the hydrophilic membrane mass transfer coefficient k_{mw} by the following method.

A plot of K_o against Q_{or} is obtained for a system having an m_i of the order of one. This is first carried out with only one membrane in the test cell. The experiment is then repeated with two membranes stacked together. The difference between the two K_o values obtained at any given Q_{or} is related, from Eq. 1, to the membrane resistance $(1/k_{mw})$ by the following relation:

$$1/k_{mw} = (1/K_o|_{2\text{membranes}} - 1/K_o|_{1\text{membrane}})/m_i \tag{6}$$

Note that the aqueous phase flow rate should also be the same for both cases.

The above procedure relies on the assumption that the extraction cell boundary layer resistances remain the same when two membranes are used as they are when only one membrane is used. This assumption can be verified using case 1 outlined earlier (with $m_i \ll 1$) by utilizing succcessively one and two hydrophilic membranes in the test cell.

Composite Membranes. If m_i is of the order of one, the complete Eq. 2 has to be used to determine K_o. The plot of K_o against Q_{or} will also exhibit a plateau at a high Q_{or}. This latter K_o can be used to determine the hydrophilic membrane resistance $1/k_{mw}$ by the methods described below.

Method 1: For a stacked composite system, a plot of K_o against Q_{or} is developed for the hydrophobic membrane only with an $m_i \simeq 1$ system. The overall mass transfer coefficient is then given by

$$1/K_o = 1/k_o + 1/k_{mo} + m_i/k_w \tag{7}$$

The experiment is now repeated with a composite hydrophilic-hydrophobic membrane under otherwise identical conditions. The plot of K_o against Q_{or} follows the relationship defined by Eq. 2 where k_o is a function of Q_{or}. Now, the difference in overall mass transfer resistances for the two cases is related to the hydrophilic membrane resistance by

$$1/k_{mw} = (1/K_o|_{\text{composite}} - 1/K_o|_{\text{hydrophobic}})/m_i \tag{8}$$

when the aqueous and organic phase flow rate are the same for the two cases.

Method 2: For a stacked composite system, a plot of K_o against Q_{or} is obtained with a composite of one hydrophobic and one hydrophilic membrane. The experiment is repeated with a composite of one hydrophobic and two hydrophilic membranes. The plot thus obtained is K_{o2} against Q_{or}, while the first plot is K_{o1} against Q_{or}. The hydrophilic membrane resistance is now obtained as

$$1/k_{mw} = [(1/K_{o2}) - (1/K_{o1})]/m_i \tag{9}$$

The hydrophilic membrane resistance obtained by the various procedures described above will be different if different extraction systems are used to study them. One way of comparing the results obtained by the above methods is given below.

The pores of the microporous membranes under consideration can be viewed as tortuous capillaries with pore sizes very much larger than solute molecules. In this case the membrane resistance to solute diffusion can be related to the diffusion coefficient D_{iM} of the solute in the liquid wetting the membrane as (Kiani et al., 1984; Prasad et al., 1986)

$$1/k_m = t_M \tau_M / D_{iM} \epsilon_M \tag{10}$$

For a composite membrane with asymmetric wetting properties, Eq. 10 can be rewritten for the individual membrane sections as

Hydrophilic

$$1/k_{mw} = t_{Mw} \tau_{Mw} / D_{iw} \epsilon_{Mw} \tag{10a}$$

Hydrophobic

$$1/k_{mo} = t_{Mo} \tau_{Mo} / D_{io} \epsilon_{Mo} \tag{10b}$$

Relation 10a or 10b is obviously utilized when a single hydrophobic or a single hydrophilic membrane is under consideration.

To compare the results from various techniques, the tortuosity of the membrane is found for each membrane resistance using the above relations. The various methods should yield the same value of the tortuosity factor τ_M, τ_{Mo}, τ_{Mw} as long as the membrane swelling conditions are similar.

The above assumption of unhindered diffusion through tortuous pores holds only if the membrane pore size is at least two orders of magnitude higher than the solute molecular dimensions. With smaller pores encountered in Cuprophan films, the membrane tortuosity thus obtained will include the effect of hindered diffusion (Farrell and Babb, 1973; Colton et al., 1971). The extent of hindrance can be estimated by the ratio of the tortuosity for the hindered case over that for the unhindered diffusion.

A major assumption implicit in the above analysis is that no two-dimensional effects (due to the pores of the two membranes not being aligned) are present if two or more membranes are stacked on top of each other, i.e., the resistance of such stacked membrane system is the sum of the individual membrane resistances. Keller and Stein (1967) and Malone and Anderson (1977) have shown that for membranes of over 7% porosity, the membrane can be considered to be essentially homogeneous with respect to surroundings. Since the membranes used in this study have porosities between 0.38 and 0.65, the phenomenon of mass transfer between these stacked membranes may also be considered to be one-dimensional in nature. Hence, the total membrane resistance for stacked membrane systems is very likely to be a sum of the individual membrane mass transfer resistances only. One way to verify this assumption is to compare the tortuosity of the membrane determined on such a basis with that determined by using a single membrane with liquid immobilized in the pores and gas permeation through such a liquid (Bhave and Sirkar, 1986).

The active interfacial areas for mass transfer will differ from one membrane type to another in a composite film due to the differences in membrane porosity. This difference does not show up in the calculations since the porosity effect is incorporated in the membrane resistance.

Experimental Method

Chemicals and materials

Microporous hydrophilic cellulose acetate (CA) films used in this study were obtained from Millipore Corp. (Bedford, MA) and Micro-Filtration Systems (Dublin, CA). Microporous hydrophilic regenerated cellulose films were also supplied by Micro-Filtration Systems. Additional regenerated cellulose films, Cuprophan 150PM, were obtained from Enka (West Germany). Hydrophobic Celgard 2400 flat films of polypropylene was obtained from Celanese Corp. (Summit, NJ). Goretex 1 Teflon membrane was obtained from W.L. Gore Assoc. Inc., Elkton, MD. The chemicals and solvents used were:

a. Glacial acetic acid (reagent ACS grade, Fisher Scientific, Fairlawn, NJ)
b. Succinic acid (purified crystals, Merck, Rahway, NJ)
c. Xylene (reagent grade, Fisher)
d. Methyl isobutyl ketone (MIBK; reagent grade, Fisher)
e. *n*-Butanol (analytical reagent, Mallinckrodt, Paris, KY).

For titration purposes, NaOH (certified ACS grade, Fisher) was used and anhydrous analytical grade oxalic acid was obtained from Coleman and Bell, Norwood, OH. The indicator for titration was prepared by dissolving 0.1 g bromothymol blue in 100 mL 20% aqueous alcohol solution.

Apparatus and procedure

The flow-type flat membrane extraction test cell used in this study is shown in Figure 2. The membrane area available for mass transfer is 13.37 cm^2. Further details of the cell are given by Kiani et al. (1984) and Prasad et al. (1986).

The experimental setup for extraction is also shown in Figure 2. This is similar to the setup used by Kiani et al. The essential difference is that for a hydrophilic membrane, the top half of the cell is now connected to the solvent reservoir while the bottom half is connected to the aqueous reservoir. The support screen (Rigimesh, grade z, Pall Trinity Corp., Cortland, NY) is between the membrane and the bottom half of the cell. The details of the experimental procedure and distribution coefficient measurements are similar to those in Kiani et al. and Prasad et al.

To obtain a composite hydrophobic-hydrophilic film, a hydrophilic membrane (cellulose acetate, regenerated cellulose, or Cuprophan) was stacked over a hydrophobic Celgard 2400 or Goretex 1 film. If necessary, two or more films of one kind were stacked over another kind to determine different membrane resistances. Experiments with excess phase pressures on the hydrophilic section of the composite membrane were done with the aqueous phase flow in the top half of the cell and solvent flow in the bottom half of the cell; experiments with excess phase pressure on the hydrophobic section of the membrane were done by turning over the membrane (hydrophobic top, hydrophilic bottom) and having the solvent flow in the top half of the cell. Experiments were also done with the same pressure ($\Delta P = 0$) in both phases.

Experiments were done by saturating the *n*-butanol with water, and vice versa, by agitating 3 L *n*-butanol with 3 L water for 24 h and separating the phases in a separation funnel. This *n*-butanol–saturated water phase was used to make a stock solution with succinic acid and extraction was carried out with water saturated with *n*-butanol. Extraction results obtained with these saturated phases were found to be identical to those obtained without equilibrating the two phases.

To be noted here is that the MIBK-H$_2$O-HAc system cannot be used for cellulose acetate film since MIBK attacks cellulose acetate. Therefore the *n*-butanol–H$_2$O–succinic acid system is used for characterizing CA films for $m_i \simeq 1$ systems.

The porosities of the Cuprophan and regenerated cellulose membrane are affected by swelling in contact with aqueous solutions. Therefore the porosities of these membranes were determined in the following way. The membranes were soaked in the respective swelling solutions (e.g., $C^b_{iw} = 0.42 \times 10^{-3}$ gmol/cm^3) for 24 h and the swollen thickness of the membrane measured using a micrometer. The surface of the membrane was carefully cleared of the excess solution and drops, and the wet weight of the membrane was found. The membrane was next dried in an oven at ~ 100°C for 24 h and the dry weight of

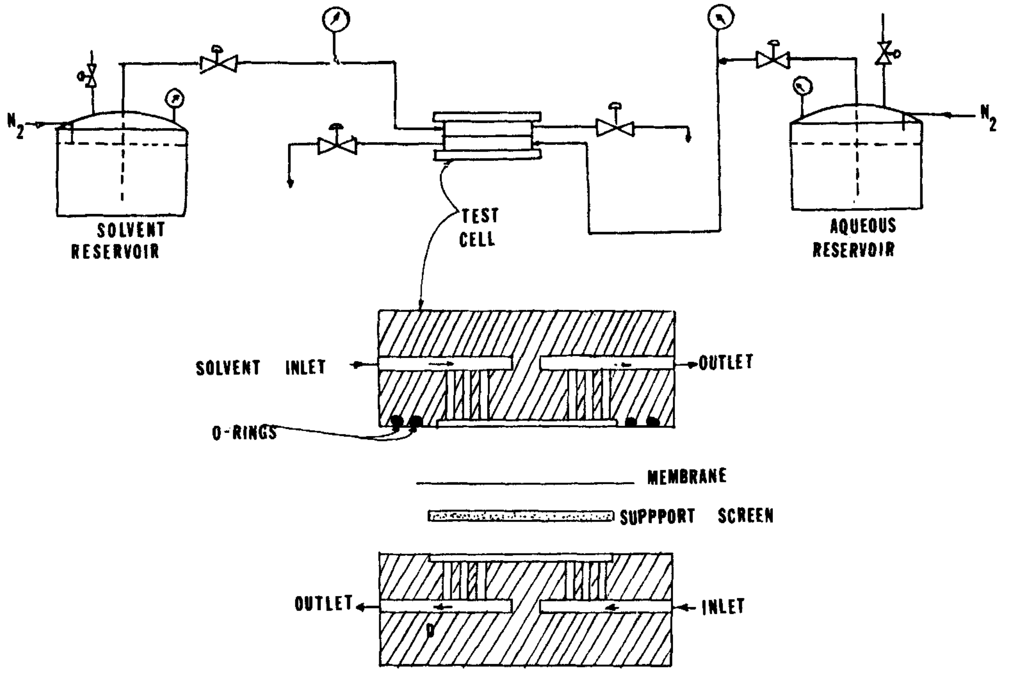

Figure 2. Test loop and flat membrane test cell for typical hydrophilic membrane.

the membrane was found. The porosity of the membrane was found using the following relation:

$$\text{Porosity} = \frac{\text{vol. of pores}}{\text{vol. of pores} + \text{vol. of cellulose}} \tag{11}$$

where

$$\text{vol. of pores} = \frac{\text{wt. of wet membrane} - \text{wt. of dry membrane}}{\text{density of solution}} \tag{11a}$$

$$\text{vol. of cellulose} = \text{wt. of dry membrane/density} \tag{11b}$$

and the density of cellulose was taken as 1.52 g/cm^3 (Malm et al., 1947).

The values of the toruosity factor of these membranes wetted with the respective wetting solutions were also independently determined by gas permeation measurements. The method followed is same as the one used by Bhave and Sirkar (1986) except that hydrophilic support membranes were used as in Suchdeo and Schultz (1974). The technique essentially consists of measuring permeation rates of each gaseous species in a humidified gas mixture of N_2 and CO_2 across an immobilized liquid membrane inside the pores of these hydrophilic support films by measuring their concentrations in a humidified sweep helium stream. Thus the complexities of any boundary layer effects are absent here. Knowing the diffusion coefficient and the solubilities of N_2 in the aqueous solution filling the pores of the hydrophilic film, the tortuosity of these membranes can be determined by the following relation:

$$\tau_M = \frac{D_{N_2} \times S_{N_2} \times \epsilon_M \times \Delta P_{N_2} \times A}{R_{N_2} \times t_M} \tag{12}$$

where ΔP_{N_2} is the N_2 partial pressure driving force across the membrane, A is the area available for permeation (13.19 cm^2), R_{N_2} is the permeation rate of N_2 species through the immobilized liquid membrane, and D_{N_2} and S_{N_2} are respectively the diffusion coefficient and solubility of N_2 through water. It can be shown that using aqueous solutions of 2.5 and 10% acetic acid, the changes in D_{N_2} and S_{N_2} from that of pure water are minimal: <2% in diffusion coefficient (Perry and Chilton, 1973) and <8% in solubility of N_2 (Linke and Seidell, 1965). Further details of the experimental procedure are available elsewhere (Bhave and Sirkar, 1986).

Results and Discussion

The relevant physical properties of the membranes used in this study are shown in Table 1. Table 2 shows the results of distribution coefficient measurements for xylene-water-HAc, MIBK-water-HAc and n-butanol–water–succinic acid systems. The values of m_i for the first two systems for a large number of other concentrations are available in Prasad et al. (1986). For mass transfer studies, the first system is generally not preferred due to association of acetic acid in the xylene phase and its dissociation in the water phase. These complications can lead to concentration-dependent m_i values of acetic acid in xylene-water systems. However, at the low concentration level used in the present studies, the value of m_i is fairly constant (Prasad et al., 1986). The MIBK-water-HAc system possesses many fewer complications since solute association in MIBK is absent. The m_i value still varies a bit with concentration, and the European Federation of Chemical Engineering (1978) urges caution with the above system. The Federation recommends the n-butanol–water–succinic acid system for liquid extraction mass transfer studies.

We now present the results for dispersion-free solvent extraction with different hydrophilic films. In all such experiments the organic phase was at an excess pressure and the pores of the membrane or stacked membranes contained the aqueous solution.

Hydrophilic membranes, $m_i \ll 1$

Figure 3 shows the effect of organic flow rate on the overall mass transfer coefficient K_o for various hydrophilic flat membranes at different excess organic phase pressures. The figure also shows the K_o variation with Q_{or} for two CA films stacked in the test cell. We observe a monotonic increase in K_o with Q_{or} since the K_o obtained with hydrophilic membranes for a system of $m_i \ll 1$ is merely the organic phase film transfer coefficient.

The figure shows no effect on K_o of either excess phase pressure or changing the number of membranes in the cell. The absence of any pressure effect is to be expected as these pressures are significantly below the breakthrough pressures. Changing the number of membranes in the test cell does not affect k_o (K_o in this case) as the flow channel depth is determined by the milled depression in the top half of the cell and the membrane top.

Hydrophilic membranes, $m_i \simeq 1$

Figure 4 shows the K_o vs. Q_{or} characteristics for one regenerated cellulose and one Cuprophan 150 PM film as well as two

Table 1. Physical Properties of Flat Microporous Membranes*

Membrane	Material	Thickness × 10^3 cm	Porosity	Pore Size μm
Celgard 2400 (hydrophobic)	Polypropylene	2.54	0.38	0.02
Goretex 1 (hydrophobic)	Teflon (unbacked)	5.08**	0.5	0.02
Cuprophan 150 PM (ENKA)	Regenerated cellulose	2.21**	0.59**	—
Regenerated cellulose (MFS)	Regenerated cellulose	12.5 –15.0**	0.65**	0.45
Millipore EG series	Cellulose acetate	12.5	0.71	0.2
Cellulose acetate (MFS)	Cellulose acetate	12.5	0.75	0.2

*From Manufacturer's catalogs
**Measured in our laboratory

Table 2. Distribution Coefficients for Solvent Extraction Systems

Test System	Aqueous Phase Conc. $C^b_{iw} \times 10^3$ gmol/cm³	Solute Distrib. Coeff. $m_i \times 10^2$
Xylene-water-HAc	4.75	3.97
	2.33	2.5
	0.96	1.2
	0.42	1.25
	0.274	1.3
MIBK-water-HAc	4.15	51.03
	1.8	53.2
	0.42	52.3
n-Butanol–water–succinic acid	0.92	148
	0.44	150

regenerated cellulose and two Cuprophan 150 PM films stacked together in the test cell, the extraction system being MIBK-water-HAc ($m_i = 0.523$). The K_o values show a plateau according to Eq. 1, a phenomenon observed earlier with hydrophobic membranes (Kiani et al., 1984; Prasad et al., 1986). The relation in Eq. 6 can now be used to calculate the mass transfer coefficient of a single membrane and the relation in Eq. 10a to calculate the tortuosity of the hydrophilic membrane. These are shown in Table 3. The result for τ_{Mw} of Cuprophan 150 PM for acetic acid extraction is close to published values (Colton et al., 1971), suggesting little hindrance to acetic acid diffusion. Note that although the manufacturer had reported thickness values of 100 and 11.2 μm for these regenerated cellulose and Cuprophan membranes, respectively, our measurements indicated that the membranes had swollen to 125 and 22.1 μm, respectively, in contact with aqueous acetic acid solution.

The performance of various stacked composite hydrophobic-hydrophilic membranes are presented next. In all such experiments, the hydrophilic membrane pores had the aqueous solution while the hydrophobic membrane pore had the organic phase. Pressure conditions were varied widely between the limits of an excess organic phase pressure and an excess aqueous phase pressure.

Composite hydrophobic-hydrophilic membranes, $m_i \ll 1$

Figure 5 shows the effect of an excess phase pressure on the performances of different composite hydrophobic-hydrophilic films. The composite films consist of a hydrophilic cellulose acetate or Cuprophan 150 PM film stacked on top of a hydrophobic Celgard 2400 or Goretex 1 film. The performances of these composites are unaffected by an excess phase pressure on either the aqueous or the organic side. More important, there is no phase breakthrough regardless of the phase having an excess pressure. Further, the membrane performance is unaffected when both phases are at the same pressure. It is also seen that the performance of each composite film with a low m_i system, is identical to that of the hydrophobic film (Celgard 2400 or Goretex 1) obtained earlier (Kiani et al., 1984; Prasad et al., 1986). This is to be expected (Eq. 5). This technique can thus be used to characterize the resistance of the hydrophobic section of an integral composite hydrophobic-hydrophilic membrane; the plateau K_o value will yield k_{mo}.

Composite hydrophobic-hydrophilic membranes, $m_i \simeq 1$

Figure 6 displays the performance of a composite membrane consisting of a regenerated cellulose film stacked on top of a Celgard 2400 film with the aqueous phase at an excess pressure of 0.6×10^5 N/m² over the organic-side pressure. The same figure also shows the K_o vs. Q_{or} performance of a single Celgard 2400 film. The difference in the two plateau values is used to calculate the resistance of a hydrophilic regenerated cellulose film by Eq. 8 and hence its tortuosity by Eq. 10a. The k_{mw} and τ_{mw} values thus determined are also shown in Table 3.

Membrane mass transfer resistance and hence the membrane tortuosity have also been found for the same regenerated cellulose membrane using the *n*-butanol–water–succinic acid system. The performance of one Celgard 2400 film, a composite of one Celgard 2400 and one regenerated cellulose film, and a composite of one Celgard 2400 and two regenerated cellulose films are

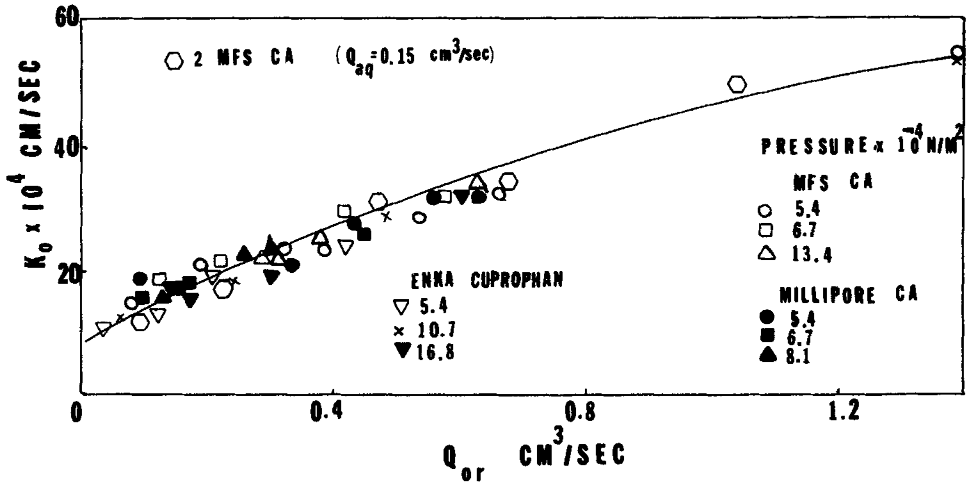

Figure 3. Effect of Q_{or}, ΔP, and number of membranes on K_o for three hydrophilic membranes.
Xylene-water-HAc system
$Q_{aq} = 0.3$ cm³/s; $C^B_{iw} = 4.2 \times 10^{-4}$ mol/cm³

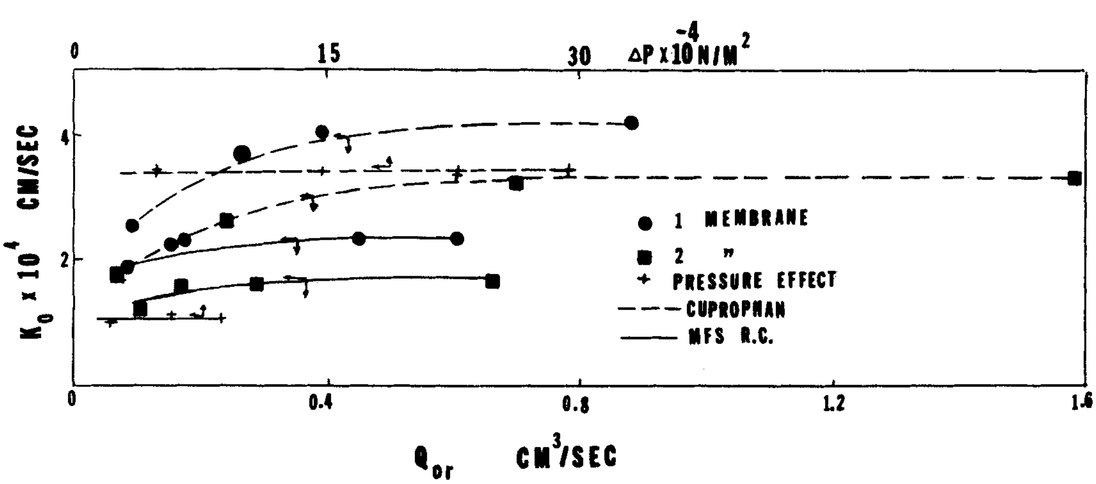

Figure 4. Effect of Q_{or}, ΔP, and number of membranes on K_o for regenerated cellulose (MFS) and Cuprophan 150 PM flat films.
MIBK-water-HAc system, $Q_{aq} = 0.3$ cm^3/s
MFS at $\Delta P = 5.4 \times 10^4$ N/m^2; $C^b_{iw} = 1.7 \times 10^{-3}$ mol/cm^3
Cuprophan at $\Delta P = 6.7 \times 10^4$ N/m^2; $C^b_{iw} = 3.3 \times 10^{-4}$ mol/cm^3

indicated in Figure 7. The plateau values of the above plots are used to calculate the membrane resistance and hence the tortuosity of the regenerated cellulose film. Specifically, Eq. 8 is used to determine k_{mw} from Celgard 2400 and Celgard 2400 plus one regenerated cellulose membrane, and Eq. 9 to determine k_{mw} from Celgard 2400 plus one regenerated cellulose membrane and Celgard 2400 plus two regenerated cellulose membranes. The results are shown in Table 3. It can be seen that the two systems used yield very close values of τ_{Mw}; further, these τ_{Mw} values are quite close to the values obtained from MIBK system, Figure 6, thus generating considerable confidence in the MIBK system.

Figure 7 also shows the performance of a composite of Celgard 2400 and Cuprophan 150 PM with the *n*-butanol–water–succinic acid system. Using method 1 for composite membranes outlined earlier, we can find the Cuprophan membrane resistance for this extraction system. However, at this stage, our assumption of unhindered diffusion in the pores of the membrane breaks down. This is because the pore size of the swollen membrane is not two or more orders of magnitude larger than the solute molecule (succinic acid). Using a value of 4 obtained by gas permeation measurements, Table 3, for the tortuosity of the Cuprophan membrane, we can obtain an estimate of the hindered diffusion of succinic acid in the pores and hence, the ratio of $(D_{io})_{\text{hindered}}/(D_{io})_{\text{free}}$ for succinic acid. This ratio is found to be 0.27, showing the considerable effect of hindered diffusion.

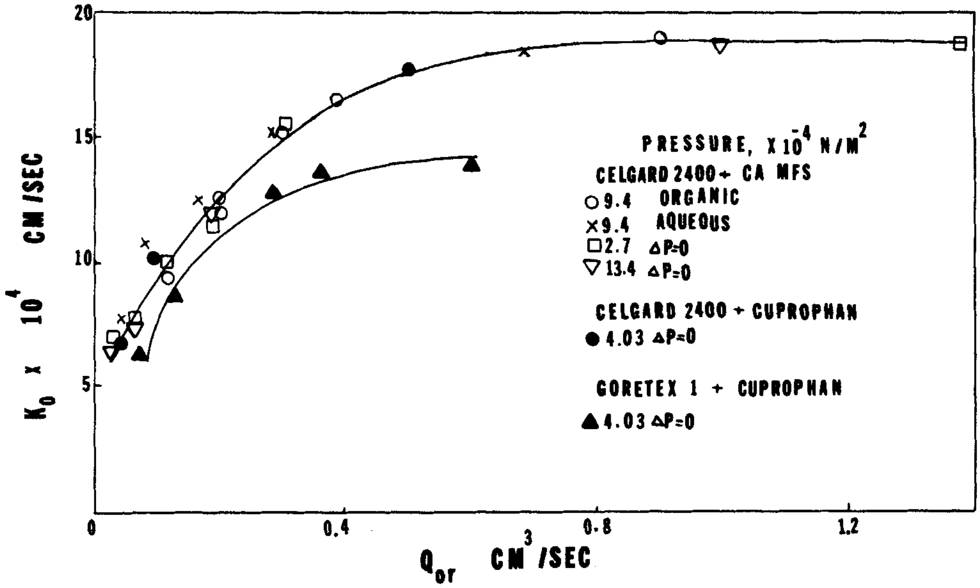

Figure 5. Performance of various composite membranes.
Xylene-water-HAc system
$Q_{aq} = 0.3$ cm^3/s; $C^b_{iw} = 4.2 \times 10^{-4}$ mol/cm^3

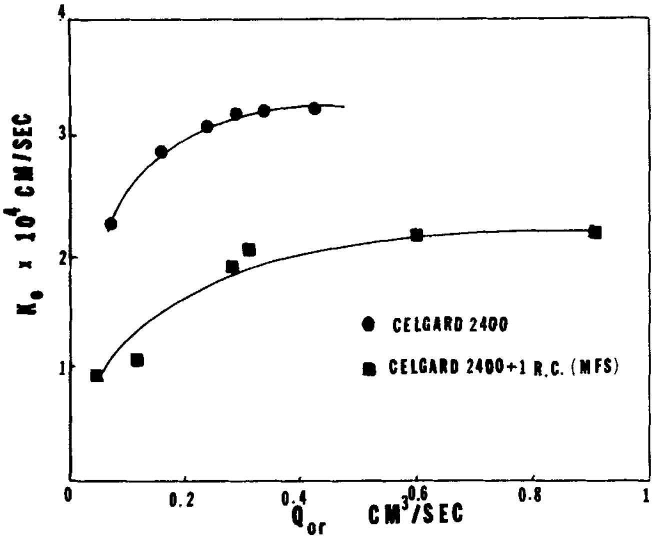

Figure 6. Performance of Celgard 2400 plus regenerated cellulose composite membrane.
MIBK-water-HAc system
$\Delta P = 6.05 \times 10^4$ N/m²; $Q_{aq} = 0.3$ cm³/s; $C^b_{iw} = 1.36 \times 10^{-3}$ mol/cm³

We now try to characterize the resistance and tortuosity of a cellulose acetate (MFS) film. Figure 8 shows the performance of a single Celgard 2400 film, a composite of Celgard 2400 and one CA (MFS) film, and a composite of one Celgard 2400 and two CA films for the *n*-butanol–water–succinic acid system with the aqueous phase at an excess pressure of 6.7×10^4 N/m². Using techniques described earlier, the cellulose acetate membrane transfer coefficient k_{mw} and tortuosity are calculated; they are shown in Table 3. It is obvious that the estimates of τ_{Mw} for CA membrane using either one or two CA membranes are very close to each other.

When one compares the values of τ_{Mw} estimated by different methods for different films with those determined from gas permeation method, Table 3, we find that they are quite close. This suggests that our experimental strategy of stacking films on top of each other did not introduce much error. The observation that the calculated τ_{Mw} is usually slightly larger than the independently estimated τ probably indicates the presence of a small resistance between the stacked films.

Breakthrough pressure

The results presented so far were concerned with characterizing the various resistances to solute transport. We also identified the excess phase pressure conditions (if any) needed for stable dispersion-free operation. We have further observed how the solute transport rate remains unaffected by the magnitude of any excess phase pressure (if required). However, the upper limit of the excess phase pressure beyond which phase breakthrough is initiated by immiscible displacement was not identified.

In Table 4 we indicate the values of the breakthrough pressure for the hydrophilic membranes in this study for particular membrane-solvent-solute systems. It is obvious that the smaller the pore size, the higher is the breakthough pressure. However, we have not related these to the pore size and the interfacial tension of the system (Kim and Harriott, 1987) using well-known relations for a cylindrical capillary. These are currently under investigation.

Comments on Dispersion-free Solvent Extraction Technique

Dispersion-free solvent extraction has been carried out with hydrophilic and composite hydrophobic-hydrophilic films. Phase pressure conditions have been identified for dispersion-free operation. Hydrophilic films are particularly attractive for a low m_i system since the mass transfer resistance of such a system is lower than that for a hydrophobic film (due to negligible contribution of the m_i/k_{mw} term in the expression for K_o). It is to be noted that an attempt has been made earlier (Cooney and Jin, 1985; Kim, 1984) to utilize hydrophilic membrane for solvent extraction. However, Kim (1984) had not maintained

Table 3. Membrane Transfer Coefficient and Tortuosity Factor for Hydrophilic Membranes

Membrane	System	Method	$k_{mw} \times 10^4$ cm/s	τ_M	τ_M*
Cellulose Acetate (MFS)	*n*-Butanol–water–succinic acid	Composite meth. 1	1.64	1.4	1.33
		Composite meth. 2	1.67	1.3	
Regenerated Cellulose (MFS)	MIBK-water-acetic acid	Hydrophilic	3.44	1.5	1.3
		Eq. 6	3.44	1.5	
	n-Butanol–water–succinic acid	Composite meth. 1	1.55	1.52	1.3
		Composite meth. 2	1.65	1.45	
Cuprophan 150PM (ENKA)	MIBK-water-acetic acid	Hydrophilic	12.1	2.7	2.8
	n-Butanol–water–succinic acid	Eq. 6	1.04	13.6	4.0
					2.77**

*From gas permeation studies
**From Colton et al. (1971)

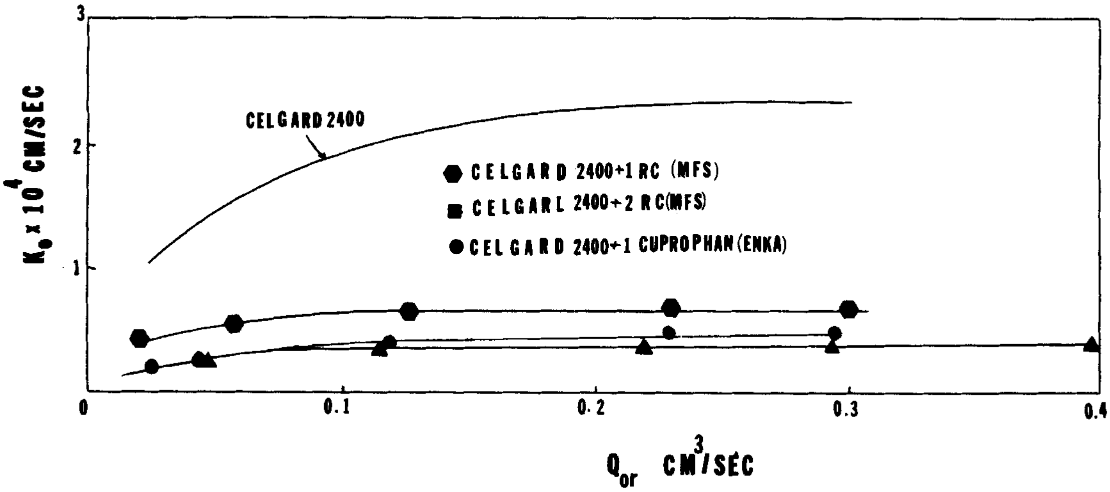

Figure 7. Performance of various stacked composite membranes of Celgard 2400 with regenerated cellulose and Cuprophan 150 PM.

n-Butanol–water–succinic acid system
$Q_{aq} = 0.3$ cm^3/s;
$\Delta P = 6.72 \times 10^4$ N/m^2; $C^b_{iw} = 5.0 \times 10^{-3}$ mol/cm^3

proper pressure conditions (higher pressure on organic phase along the whole length of the hollow fiber) and hence had problems of phase intermixing, necessitating an extra aqueous-organic phase separation drum. Cooney and Jin (1985) had also experimented with hydrophilic saponified cellulose acetate hollow fibers but did not identify the pressure conditions they maintained and could not carry out extraction with fluid flow of the organic phase.

Since composite films with asymmetric wetting characteristics can operate dispersion-free with an excess pressure in either phase, they are ideal for handling accidental process pressure fluctuations. However the overall solute extraction flux will always be lower than that obtained with either a hydrophilic or a hydrophobic membrane.

The notion of unhindered diffusion through tortuous pores containing the wetting aqueous solution describes the hydrophilic membrane transfer coefficient well as long as the solute molecule size is quite small compared to the pore size. It does not hold for Cuprophan membrane and succinic acid, Table 3, since the pore size is small and the solute size is larger. The reduction in membrane transfer coefficient and in the overall mass transfer coefficient can be considerable when hindered diffusion exists. In the absence of hindered diffusion, the very thin Cuprophan 150 PM will show much lower solute transfer resistance. However, for $m_i \simeq 1$ systems boundary layer transport resistances will be quite important so that extraction rate variation from membrane to membrane is reduced as long as unhindered diffusion is operative.

The selection of organic acids, e.g., acetic acid and succinic acid, as solutes in this study is to be considered from the point of view of illustrating the technique with commonly used extraction systems. Stripping of organic acids may be carried out by conventional technique, e.g., distillation, although one could also use membrane solvent extraction to this end.

The industrial utility of the dispersion-free solvent extraction technique most likely lies in its use with microporous hollow-fiber membranes due to the tremendous surface area per volume of a hollow-fiber membrane module. Results for hydrophilic hollow-fiber modules have been reported elsewhere (Prasad and Sirkar, 1986). However, as the histories of reverse

Table 4. Breakthrough Pressure for Some Hydrophilic Membrane Extraction Systems

Membrane	System	$C^b_{iw} \times 10^3$ gmol/cm^3	Excess Organic Breakthrough Pressure N/m^2
Cellulose acetate (MFS)	Xylene-water-HAc	0.42	2.15×10^5
Cellulose acetate (millipore)	Xylene-water-HAc	0.42	1.1×10^5
Cuprophan 150 PM (ENKA)	MIBK-water-HAc	2.33	4.14×10^5
Regenerated cellulose (MFS)	MIBK-water-HAc	2.33	0.83×10^5

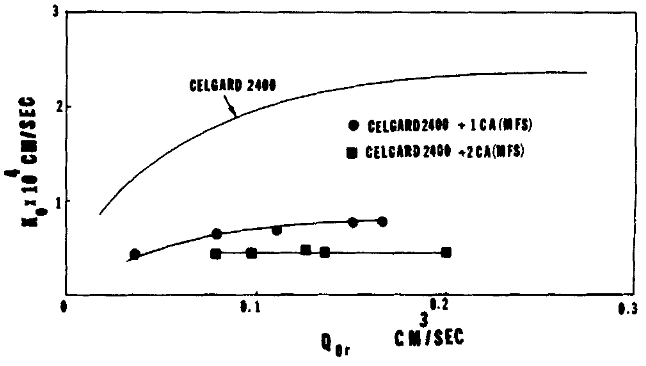

Figure 8. Performance of Celgard 2400 plus CA composite membrane.

n-Butanol–water–succinic acid system.
$\Delta P = 6.72 \times 10^4$ N/m^2; $Q_{aq} = 0.3$ cm^3/s; $C^b_{iw} = 0.5 \times 10^{-3}$ mol/cm^3

osmosis, ultrafiltration, and gas separation processes demonstrate, flat membrane modules are not to be ruled out.

Notation

A – area for gas permeation, cm^2
C^i_{io} – concentration of i in organic phase at membrane-organic interface, mol/cm^3
C^i_{im} – concentration of i in membrane at membrane-water interface, mol/cm^3
C^o_{im} – concentration of i in membrane at membrane-organic interface, mol/cm^3
C^b_{io} – bulk concentration of i in organic phase, mol/cm^3
C^*_{io} – concentration of i in organic phase in equilibrium with C^b_{iw}, mol/cm^3
C^b_{iw} – bulk concentration of i in aqueous phase, mol/cm^3
C^i_{iw} – concentration of i in aqueous phase at membrane-water interface, mol/cm^3
D_{N_2} – diffusion coefficient of N_2 in water, cm^2/s
D_{io}, D_{iw} – diffusion coefficient of i in organic, aqueous phase, cm^2/s
k_{mo}, k_{mw} – membrane transfer coefficient for hydrophobic, hydrophilic membrane, cm/s
k_o, k_w – boundary layer mass transfer coefficient for organic, aqueous phase, cm/s
K_o – overall mass transfer coefficient based on organic phase, cm/s
m_i – solute distribution coefficient, Eq. 2
N_i – flux of species i, mol/cm$^2 \cdot$ s
ΔP – pressure differential across membrane, N/m^2
ΔP_{N_2} – partial pressure difference for N_2 permeation across immobilized liquid membrane, cm Hg
Q_{aq}, Q_{or} – flow rates of aqueous, organic phase, cm^3/s
R_{N_2} – N_2 permeation rate across the immobilized liquid membrane, std cm^3/s
S_{N_2} – solubility of N_2 in water, std cm^3 gas/cm^3 sol/cm Hg
t_M – thickness of membrane
ϵ_M – porosity of membrane
τ_M – tortuosity of membrane

Subscripts

i – solute species
M – membrane phase
o – organic phase
w – aqueous phase

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