Novel Liquid-in-Pore Configurations in Membrane Solvent Extraction

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Dispersion-free solvent extraction has been investigated recently using microporous membranes in different forms and wetting characteristics (Kiani et al., 1984; Prasad et al., 1986; D'Elia et al., 1986; Prasad and Sirkar, 1987a,b, 1988; Dahuron and Cussler, 1988; Basu et al., 1990). In hydrophobic microporous membranes, the organic phase wetted the pores; and the aqueous phase, excluded from pores, was maintained at a higher pressure to immobilize aqueous-organic interfaces at pore mouths. For hydrophilic membranes, the pores were filled with the aqueous phase, and the organic phase was at a higher pressure. In aromatics extraction by a polar organic phase, the hydrophobic film pores were filled by the hydrocarbon phase; and the polar organic phase was maintained at a higher pressure.

Prasad and Sirkar (1987b, 1988) have shown that, under comparable conditions, hydrophobic membranes provide a higher mass transfer coefficient K than hydrophilic membranes if $m_i > 1$; conversely, hydrophilic membranes yield a higher K when $m_i < 1$. Although a higher K is always desirable, there are other factors of considerable importance including: chemical/pH stability of membrane (hydrophobic membranes have much higher stability); coupling requirement for enzyme immobilization in extractive membrane reactors (hydrophilic membranes needed); pore size of membrane (lower pore size of available hydrophilic membranes leads to hindered pore diffusion and lower K but higher breakthrough pressure); fouling from the process stream; and precipitation in the pore liquid causing pore plugging.

In using such a technique, the following questions arise:

1. For a given system, could one use the hydrophilic membrane as a hydrophobic membrane with organic in the pore since hydrophobic membranes have other deficiencies and organics wet hydrophilic membranes spontaneously?
2. Could one use a hydrophobic membrane as a hydrophilic membrane with polar organic in pores if it spontaneously wets the hydrophobic membrane since the hydrophilic membrane may be otherwise undesirable? What are the pore-liquid-membrane-wetting-characteristic combinations to successfully accommodate a number of other processes and transport demands?

We report here results for membrane-pore-liquid combinations of hydrophilic-organic, hydrophilic-aqueous, hydrophobic-polar organic, and hydrophobic-nonpolar organic. The systems are: acetic acid extraction by xylene from a 4.2×10^{-4} mol/cm^3 aqueous solution; and toluene extraction from a 50% v/v mixture of toluene with *n*-heptane by *n*-methyl pyrrolidone (NMP). The observed K values have been characterized in terms of individuals *k-s* and membrane characteristics. The phase pressure limits have been identified. The microporous membranes used are: hydrophilic films of nylon and regenerated cellulose, hydrophilic tubes of alumina and glass, and hydrophobic films of polypropylene. Finally, a novel composite membrane of hydrophilic-organic sandwiched with hydrophilic-aqueous has been studied.

Membranes: Preparations and Experimental Procedure

The physical properties of the microporous flat membranes and tubules are listed in Table 1. Cuprophan membrane, shipped with an organic of low volatility in pores, was stirred

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Table 1. Physical Properties of Microporous Membranes Used*

Flat Membrane (Material)	Thickness µm	Porosity	Pore Size µm
Cuprophan 150PM (Regenerated Celluose, ENKA)	22.1	0.59**	—
Celgard 2400 (Polypropylene, Hoechst Celanse)	25.4	0.38	0.02
Nylon (Polyamide, ENKA)	110	0.7	0.2

Tubular Membrane	I.D. µm	Thickness µm	Porosity	Pore Size µm
Ceramic (Alumina, ALCOA)	6,477	1,670	†	40Å (top layer only)
Glass (ASAHI)	2,413	381	(>0.4)	~40Å

*From manufacturer's catalogs or supplied by the manufacturer

**Prasad and Sirkar (1987b)

†Multilayer membrane with differing porosity and pore size in each layer.

gently for 3 hours in isopropyl alcohol (IPA) to leach out the organic. The membrane with IPA in pore was air-dried for 12 hours before using as a hydrophilic substrate with aqueous solution in pores. To use Cuprophan as a hydrophobic support, the film as shipped was put in xylene. The xylene, stirred gently for 12 hours, leached out the organic and replaced it by xylene.

The nylon film is spontaneously wetted by both xylene and water; it was soaked in the respective liquid before placing it in the test cell. A composite nylon membrane was made by first soaking a nylon film in water, soaking another in xylene, and placing one on top of the other in the cell. The nylon film soaked in water was in contact with aqueous phase and *vice versa*. The Celgard 2400 membrane used is also wetted by both NMP and *n*-heptane. It was soaked in the respective phase before use.

The ceramic tube was supplied in a s. steel module. The glass tube was potted in a glass shell with needed shell-side openings. Both are spontaneously wetted by both xylene and water. Experiments with xylene in the pore were done by starting xylene flow to fill membrane pores with xylene and then starting water flow after 5 minutes. Experiments with water in the pore were done by starting water flow and then xylene flow after 5 minutes. Prior to any experiment, the pores of the tube were dry.

The experimental setup and the flat membrane test cell were used in earlier studies (Prasad and Sirkar, 1987b, 1988). Extraction runs were done by placing the properly wetted film in the flat membrane test cell. The phase wetting the membrane was allowed to flow in the bottom half of the cell, while the other phase at a higher pressure flowed in the top half.

Ceramic tube runs were first done with xylene in the pores and flowing on the shell side. Water flowed on the tube side at a higher pressure pressurizing the tube internally. Experiments were also done by first wetting the ceramic tube with water flowing in the shell side and xylene flowing on the tube side at a higher pressure pressurizing the tube internally. A similar procedure was followed for the glass tube. Acetic acid concentrations were measured by titration against standard NaOH solution using bromothymol blue indicator. Toluene concentrations in both phases of the NMP-*n*-heptane-toluene system were measured using a HP 5890 GC equipped with a FID. The column used was a 6 ft × 1/8 in. (1.8 m × 3.2 mm) 5% SP-2100 (Supelco, Bellefonte, PA) with two programmed temperature gradients.

Mass Transfer Analysis and Results

Aqueous-organic system

The mass transfer coefficient for a membrane-pore-liquid combination is analyzed by considering the total resistance of each of the two liquid phases. The total resistance of the phase present in membrane pores includes the membrane resistance, boundary layer resistance, and a resistance due to two-dimensional effects at the pore bulk transition [the latter neglected here due to high ϵ_m, Keller and Stein (1967)]. The local value of the organic-phase-based overall mass transfer resistance $(1/K_o)$ is then the sum of the resistance R_o of the organic phase and R_w of the aqeuous phase. Table 2 provides such relations.

The relations presented in Table 2 for $m_i \ll 1$ are most relevant since the test system of xylene-water-acetic acid has a low m_i (~ 0.012). In a *hydrophilic* membrane with organic in pore (aqueous phase outside at a higher pressure), $(1/K_o)$ will equal $(1/k_o) + (1/k_{mo})$. By sufficiently increasing v_{or} and therefore k_o, one can make $(1/K_o)$ equal to $(1/k_{mo})$; and then K_o in K_o vs. Q_{or} plot will reach a plateau where $K_o \sim k_{mo}$, the membrane transfer coefficient as was observed for flat hydrophobic membranes with organic in the pore by Kiani et al. (1984). Under identical conditions with an aqueous solution in the pore of a hydrophilic membrane, K_o increases monotonously with Q_{or} since $(1/K_o) \sim (1/k_o)$ (Prasad and Sirkar, 1987b).

In Figure 1, K_o for acetic acid is plotted against Q_{or} for a hydrophilic nylon film with xylene in the pore. As Q_{or} increases, K_o has a plateau of 20×10^{-4} cm/s. From previous analysis, the value of k_{mo} should be 20×10^{-4} cm/s. Using $(D_{io}\, \epsilon_m/\tau_m\, \delta_m)$ for k_{mo}, $D_{io} = 2.76 \times 10^{-5}$ cm^2/s, $\delta_m = 110 \times 10^{-4}$ cm and $\epsilon_m = 0.7$, one finds a $\tau_m \sim 0.88$. This nylon film is highly porous with very large pores and appeared significantly compressible. With a slight reduction in δ_m during experiments, τ_m would be around 1.1–1.2, a range observed with highly porous large pore membranes (Prasad et al., 1986).

For extraction with aqueous solution in nylon film pores, observe, via the unfilled circles in Figure 1, a known behavior, namely, $K_o \sim k_o$ with k_o increasing monotonously with Q_{or}. In fact, these K_o values are close to those in Figure 3 of Prasad and Sirkar (1987b) obtained using totally different hydrophilic films. The implication of $K_o \sim k_o$ is precisely this since the system and hydrodynamic conditions are identical.

Table 2. Overall vs. Component Resistances for Different Membrane-Pore-Liquid Combinations

		Value of $(1/K_o)$	
	Aqueous-Organic System	$m_i \ll 1$	$m_i \gg 1$
Hydrophilic Membrane	organic in pore $\frac{1}{K_o}=\overbrace{\frac{1}{k_o}+\frac{1}{k_{mo}}}^{R_o}+\overbrace{\frac{m_i}{k_w}}^{R_w}$	$\frac{1}{k_o}+\frac{1}{k_{mo}}$	$\frac{m_i}{k_w}$
	aqueous in pore $\frac{1}{K_o}=\overbrace{\frac{1}{k_o}}^{R_o}+\overbrace{\frac{m_i}{k_{mw}}+\frac{m_i}{k_w}}^{R_w}$	$\frac{1}{k_o}$	$\frac{m_i}{k_{mw}}+\frac{m_i}{k_w}$
	Polar-Organic, Nonpolar-Organic System		
Hydrophobic Membrane $K_{w'}=m_iK_o$	nonpolar organic in pore $\frac{1}{K_o}=\overbrace{\frac{1}{k_o}+\frac{1}{k_{mo}}}^{R_o}+\overbrace{\frac{m_i}{k_{w'}}}^{R_{w'}}$	$\frac{1}{k_o}+\frac{1}{k_{mo}}$	$\frac{m_i}{k_{w'}}$
	polar organic in pore $\frac{1}{K_o}=\overbrace{\frac{1}{k_o}}^{R_o}+\overbrace{\frac{m_i}{k_{mw'}}+\frac{m_i}{k_{w'}}}^{R_{w'}}$	$\frac{1}{k_o}$	$\frac{m_i}{k_{mw'}}+\frac{m_i}{k_{w'}}$

Figure 1 illustrates also the same phenomena with a totally different hydrophilic membrane, Cuprophan 150 PM with a much smaller pore size and a gellike structure. Variation of K_o with Q_{or} for xylene in the pore and aqueous phase at a higher pressure is shown by filled circles. At higher Q_{or}, K_o reaches a plateau of 29×10^{-4} cm/s. For $\epsilon_m = 0.59$, $\delta_m = 2.21 \times 10^{-3}$ cm (Prasad and Sirkar, 1987b) and $D_{io} = 2.76 \times 10^{-5}$ cm/s, this value of K_o ($\sim k_{mo}$) yields a τ_m of 2.5 as expected from Prasad and Sirkar (1987b). If aqueous solution is in the pores of the same membrane, K_o monotonically increases with Q_{or} as expected since K_o is essentially k_o. Further, values of K_o are close to those for the nylon film as predicted.

We study now inorganic hydrophilic microporous membranes, a large bore alumina tube and a much smaller bore glass tube. For water in hydrophilic membrane pores and xylene-water-acetic acid system, K_o should equal k_o. Figure 2 shows this with xylene on the tube side. Since tube side k_o in laminar flow varies as $v_{or}^{1/3}$ or as $Q_{or}^{1/3}$, a straight line plot of $1/K_o$ i.e., $1/k_o$ vs. $Q_{or}^{-0.33}$ describes the data quite well for both membranes. The intercept of $1/K_o$ for $Q_{or} \rightarrow \infty$ is zero (Prasad and Sirkar, 1988) since membrane resistance with aqueous phase in pores is negligible for $m_i \ll 1$.

The same membrane tubes with xylene in the pore behave differently. A plot of $1/K_o$ vs. $Q_{or}^{-0.66}$ (Figure 3) with xylene on the shell side shows that the shell-side flow rate dependence of K_o is as expected for both membranes (Prasad and Sirkar, 1988; Basu et al., 1990). Further, both reach finite limiting values when $Q_{or} \rightarrow \infty$ yielding k_{mo} from the intercepts of $(1/K_o)$: the values are $k_{mo} = 1.2 \times 10^{-4}$ cm/s (ceramic) and $k_{mo} = 3 \times 10^{-4}$ cm/s (glass). Using Table 1 and $D_{io} = 2.76 \times 10^{-5}$ cm²/s, we find $(\epsilon_m/\tau_m) = 0.72$ for the ceramic tube and $\tau_m = 1.52$ for the glass tube.

For the glass tube with small pores (~40 Å) and $\epsilon_m > 0.40$, $\tau_m \sim 1.52$ is reasonable. The top layer of the ceramic tube has $\epsilon_m > 0.58$ with 40 Å pores. There are several much thicker layers having pore diameters around 2,000 Å, 7,000 Å and 100,000 Å and ϵ_m up to 0.6–0.7 (Hsieh, 1988; Bhave, 1989). These suggest

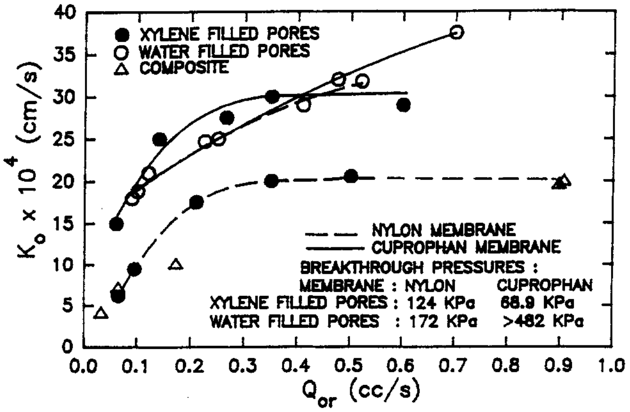

Figure 1. K_o vs. Q_{or} for xylene-water-acetic acid system for xylene in the pore and water in the pore with single or stacked flat nylon film or a single flat Cuprophan membrane.

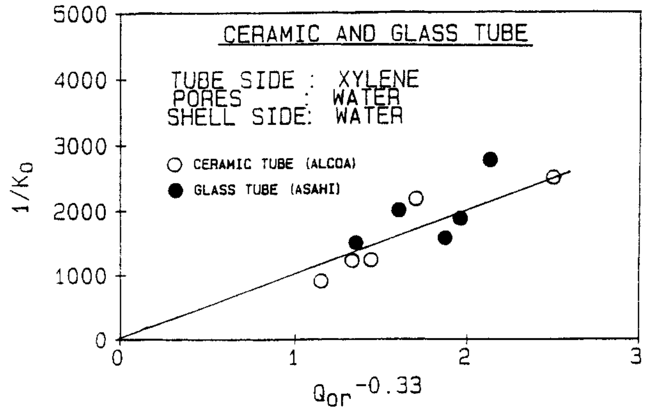

Figure 2. Plot of $1/K_o$ vs. tube-side $Q_{or}^{-0.33}$ for ceramic and glass tubes in xylene-water-acetic acid system with water in the pore.

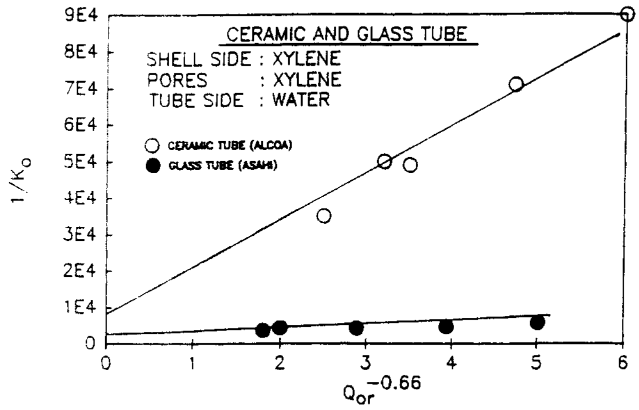

Figure 3. Plot of $1/K_o$ vs. shell-side $Q_{or}^{-0.66}$ for ceramic and glass tubes in xylene-water-acetic acid system with xylene in the pore.

a τ_m around 1 since ϵ_m is around 0.6. Such τ_m values are reasonable. The alumina tube with organic in the pore was run for >85 hours with no performance change (to be reported elsewhere) suggesting high stability in this novel mode since both aqueous and organic phases wet the substrate spontaneously. A run with Celgard 2400 hydrophobic membrane film and aqueous in pore had to be terminated after 1.5 hours since organic phase spontaneously displaced the nonwetting aqueous phase.

Polar-organic, nonpolar-organic system

From Table 2, for a hydrophobic membrane with polar organic in pore,

$$\frac{1}{K_o} = \underbrace{\frac{1}{k_o}}_{R_o} + \underbrace{\frac{m_i}{k_{mw'}} + \frac{m_i}{k_{w'}}}_{R_{w'}} \qquad \frac{1}{K_{w'}} = \underbrace{\frac{1}{k_{w'}} + \frac{1}{k_{mw'}}}_{R_{w'}} + \underbrace{\frac{1}{m_i k_o}}_{R_o} \tag{1}$$

If the hydrophobic membrane had nonpolar organic in the pore, then

$$\frac{1}{K_o} = \underbrace{\frac{1}{k_o} + \frac{1}{k_{mo}}}_{R_o} + \underbrace{\frac{m_i}{k_{w'}}}_{R_{w'}} \tag{2}$$

Since $m_i \sim 1.03$ in toluene extraction from *n*-heptane to NMP, coefficients, k_o, $k_{mw'}$ and $k_{w'}$, are needed to describe K_o. In nonpolar organic in the pore configuration, relation 2 suggests that as Q_{or} or v_{or} increases, K_o reaches a plateau of $[(1/k_{mo}) + (m_i/k_{w'})]^{-1}$. In another experiment with two flat membranes stacked together, the plateau K_o would be $[(2/k_{mo}) + (m_i/k_{w'})]^{-1}$. From these two, k_{mo} is found (Prasad and Sirkar, 1987a). For polar organic in pore using relation 1 for $K_{w'}$ and increasing $Q_{w'}$, $k_{mw'}$ may be obtained also by one- and two-membrane experiments.

Figure 4 illustrates the K_o vs. Q_{or} with *n*-heptane in the pore and $K_{w'}$ vs. $Q_{w'}$ for NMP in the pore for a Celgard 2400 hydrophobic membrane. Both data sets reach a plateau at high values Q_{or} and $Q_{w'}$. Figure 4 shows also the data for NMP in the pore with two Celgard membranes. The value of $k_{mw'}$ obtained is 3.58×10^{-4} cm/s. Since $D_{iw'} = 0.7 \times 10^{-5}$ cm²/s, we obtain a reasonable τ_m value 2.97 for the Celgard 2400 film (Prasad et al., 1986; Prasad and Sirkar, 1987a). Similar experiments with *n*-heptane in the pore reproduce results of Prasad and Sirkar (1987a).

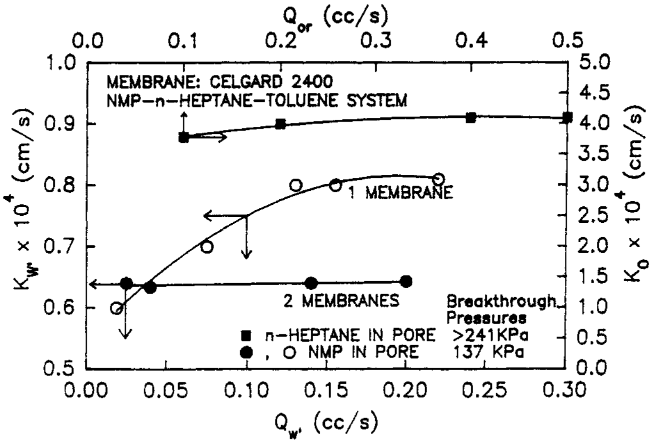

Figure 4. K_o vs. Q_{or} with *n*-heptane filled pores of 1 polypropylene membrane and $K_{w'}$ vs. $Q_{w'}$ with NMP filled pores for 1 and 2 polypropylene membranes in NMP-*n*-heptane-toluene system.

Composite membrane in aqueous-organic system

Prasad and Sirkar (1987b) studied composite membranes using a sandwich of a hydrophobic membrane with organic in the pore and a hydrophilic membrane with aqueous in the pore. We propose novel composites: a sandwich of two hydrophilic membranes or two hydrophobic membranes. The data for a nylon film with water in the pore and another with organic in the pore are shown in Figure 1. Since $m_i \ll 1$, the organic-in-pore section will control K_o. We observe exactly that the composite's performance coincides with that of the nylon film with organic in the pore. However, there is no hydrophobic film.

Breakthrough pressure

Hydrophilic microporous membranes, polymeric or inorganic, are obviously versatile. To maximize mass transfer for high membrane surface area in a module, we recommend organic in the pore for $m_i > 1$ and aqueous in the pore for $m_i < 1$. Are there other limitations to this changeover?

In the nondispersive membrane solvent extraction, the excess pressure of the phase not present in the pores has an upper limit, ΔP_{cr}, the breakthrough pressure. Once it is exceeded, the excluded phase not in the pores displaces the phase in the pores terminating nondispersive processing. The ΔP_{cr} values for hydrophilic membranes with organic in the pore in Figure 1 are significantly lower than those with aqueous in pore. Similarly, ΔP_{cr} for organic in the pore of a hydrophobic membrane in Figure 4 is larger than that for polar organic in the pore.

Conventional operational modes adopted earlier provide a larger window of excess phase pressure and greater operational flexibility. This conclusion, limited to polymeric membranes of this study, needs to be studied for inorganic substrates.

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Notation

$D_{io}, D_{iw}, D_{iw'}$ = diffusivity of i in organic, aqueous and polar organic phase
$k_o, k_w, k_{w'}$ = boundary layer mass transfer coefficient for organic, aqueous and polar organic phase
$k_{mo}, k_{mw}, k_{mw'}$ = membrane transfer coefficient for organic in pore, aqueous in pore, polar organic in pore
$K_o, K_w, K_{w'}$ = overall mass transfer coefficient based on organic, aqueous, polar organic phase
m_i = solute distribution coefficient (= concentration in organic/concentration in aqueous or polar organic phase)
Q_{aq}, Q_{or} = volumetric flow rates of aqueous and organic phase
$R_o, R_w, R_{w'}$ = resistance of organic, aqueous and polar organic phase
$v_{aq}, v_{or}, v_{w'}$ = flow velocity of aqueous, organic and polar organic phase
ΔP_{cr} = value of breakthrough pressure
$\delta_m, \epsilon_m, \tau_m$ = membrane thickness, membrane porosity, membrane tortuosity

Subscripts

o, or = organic phase
w = aqueous phase
w' = polar organic phase

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