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Microporous Membrane Solvent Extraction

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Microporous Membrane Solvent Extraction

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ABSTRACT

The versatility of the phenomenon of dispersion-free solvent extraction through immobilized aqueous-organic interface in a microporous hydrophobic membrane is demonstrated here. This technique has been used here for an organic-organic interface to extract aromatics from a hydrocarbon feedstock by a polar organic solvent. The phenomenon has been studied further with microporous hydrophilic and composite hydrophobic-hydrophilic membranes. Operational modes and the influence of the membrane and boundary layer resistances for various solvent-solute-membrane systems have been studied for a CELGARD (hydrophobic) and a CUPROPHAN (hydrophilic) membrane. Limited performance data for microporous hydrophobic CELGARD hollow fibers (X-20) are also presented.

INTRODUCTION

Conventional solvent extraction processes (1,2) require dispersion of one liquid phase in another as drops and subsequent coalescence. A new dispersion-free microporous membrane-based solvent extraction technique (3,4) has been developed. This technique overcomes several other limitations of conventional liquid extraction e.g. flooding, limitations on independent phase flow rate variations, requirement of density difference and inability to handle particulates.

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Consider a microporous hydrophobic membrane in contact with an organic phase which wets the membrane. At the other side of the membrane is a non-wetting aqueous phase at a pressure higher than that of the organic phase but lower than the pressure needed for the aqueous phase to displace the organic phase in the pores of the membrane. The aqueous-organic interface is essentially immobilized at the pore mouth of the membrane. Solute transfer spontaneously takes place through such interfaces. This phenomenon and the characterization of solute extraction rates have been investigated earlier (3, 4). It is to be noted that the membrane does not function here as a species selective transport medium. It merely prevents the dispersion of one phase into the other. In addition, it influences the species extraction rate.

This phenomenon is not limited to an aqueous-organic system. We have presented here dispersion-free extraction of an aromatic (e.g. toluene) from a hydrocarbon feed stock (represented by n-heptane-toluene mixture) using a polar organic solvent (n-methyl pyrrolidone, NMP) which does not displace the hydrocarbon from the pores of hydrophobic CELGARD 2400 membrane.

The phase pressure conditions are completely reversed when microporous hydrophilic membranes are used. We report here the performance of flat CUPROPHAN hydrophilic membrane preferentially wetted by the aqueous phase with the organic phase at a higher pressure. However, it may not be possible to operate dispersion-free with either hydrophobic or hydrophilic membrane if uncontrolled pressure fluctuations are present in the extraction system. We therefore present here a composite hydrophobic-hydrophilic membrane with each section having preferential wetting properties that are different such that no excess pressure is necessary in either phase for dispersion-free operation. Further detailed investigations with hydrophilic and composite membranes are presented elsewhere (5).

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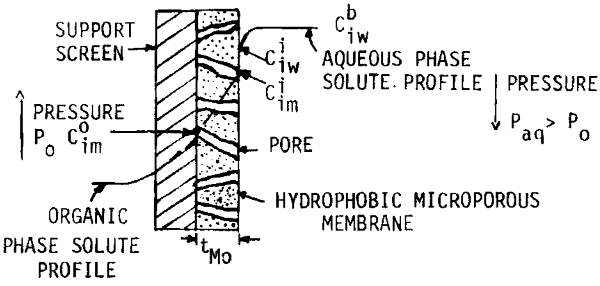
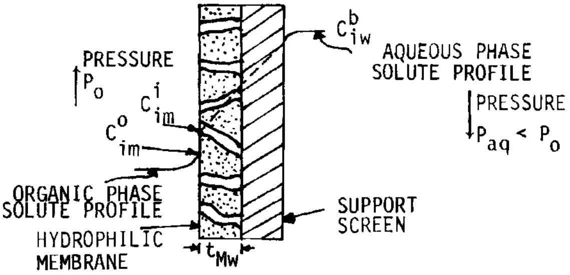
Since large scale industrial application of this technique requires microporous hollow fibers with high surface area per unit volume, we report here some data obtained with CELGARD X-20 hollow fibers for xylene-water-acetic acid and methyl isobutyl ketone (MIBK)-water-acetic acid systems. We note here that the extended use of hydrophobic hollow fibers in a tubular fermentor-extractor for extraction of ethanol as it is being produced by an immobilized yeast system is reported elsewhere (6).

MASS TRANSPORT IN MICROPOROUS MEMBRANE-BASED EXTRACTION AND BASIS OF CHARACTERIZATION

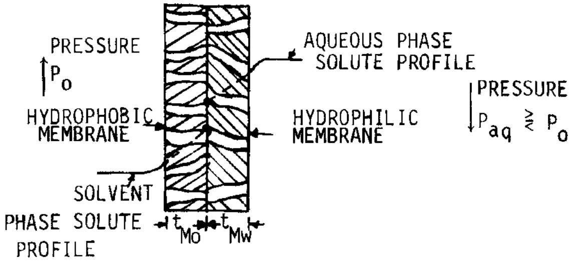
The solute concentration profiles in a microporous membrane-based dispersion-free solvent extraction using a hydrophobic, a hydrophilic and a composite hydrophobic-hydrophilic membrane are shown respectively in Fig. 1a, 1b and 1c. We assume now simple film-type mass transfer coefficients without bulk flow correction for the boundary layers and neglect any solute association or dissociation



1a: HYDROPHOBIC MEMBRANE



1b: HYDROPHILIC MEMBRANE



1c: HYDROPHOBIC-HYDROPHILIC MEMBRANE

Fig. 1. Schematic of solute concentration profiles in solvent extraction with interfaces immobilized in a microporous membrane.

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in either phase. The overall solvent-phase-based mass transfer coefficient K_o may be related to the membrane transfer coefficient k_{mo}, the aqueous and the solvent phase boundary layer coefficients k_w and k_o and a constant solute distribution coefficient m_i for a flat hydrophobic microporous membrane by (3)

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

Note that m_i is defined as the ratio of the organic phase concentration C_{io} to the aqueous phase concentration C_{iw} at equilibrium.

The membrane resistance $(1/k_{mo})$ for the solute transport through the organic solvent-filled pores has been described (3,4) by the following relation

$$(1/k_{mo}) = (\tau_{Mo}\, t_{Mo}/D_{io}\, \varepsilon_{Mo}) \tag{1a}$$

for unhindered solute diffusion in solvent-filled pores of tortuosity τ_{Mo}. These relations are independent of the direction of solute transport. Further, these relations may also be used for aromatics extraction with an immiscible polar organic hydrocarbon system and a hydrophobic membrane wetted by the hydrocarbon phase. The polar organic phase behaves similar to the aqueous phase in Fig. 1a except that the aromatic constituent is being transferred from the organic hydrocarbon phase to the polar organic phase.

For a hydrophobic microporous hollow fiber with the membrane-wetting organic phase flowing in the fiber lumen and the aqueous phase flowing on the outside at a higher pressure, a relation similar to equation (1) may be developed (6):

$$\frac{1}{K_o d_o} = \frac{1}{k_o d_i} + \frac{1}{k_{mo} d_{\ell m}} + \frac{m_i}{k_w d_o} \tag{2}$$

This relation is valid at any axial location of the hollow fiber of undeformed outside and inside diameters of d_o and d_i respectively. The quantity $d_{\ell m}$ represents the logarithmic mean diameter of the hollow fiber with the membrane resistance being described by

$$(1/k_{mo}) = [\tau_{Mo}(d_o - d_i)/2D_{io}\, \varepsilon_{Mo}] \tag{2a}$$

For a hydrophilic flat film wetted by an aqueous solution and solute transport from the aqueous to the organic solvent phase shown in Fig. 1b, it is possible (5) to develop a relation similar to relation (1)

$$\frac{1}{K_o} = \frac{1}{k_o} + \frac{m_i}{k_{mw}} + \frac{m_i}{k_w} \tag{3}$$

For unhindered solute diffusion in aqueous solution-filled pores, the following relation

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$$(1/k_{mw}) = (\tau_{Mw} t_{Mw}/D_{iw}\varepsilon_{Mw}) \tag{3a}$$

appears to be appropriate (5). In a flat composite hydrophobic-hydrophilic film of the type shown in Fig. 1c, a similar analysis (5) leads to

$$\frac{1}{K_o} = \frac{1}{k_o} + \frac{1}{k_{mo}} + \frac{m_i}{k_{mw}} + \frac{m_i}{k_w} \tag{4}$$

with the solvent wetting the hydrophobic part and the aqueous solution wetting the hydrophilic part of the membrane. The membrane resistance to solute transport through the hydrophobic and hydrophilic sections of the composite membrane may be described for unhindered diffusion by relations (1a) and (3a) respectively. Relation (4) assumes that there is no additional resistance to solute transport at the interface of the hydrophobic and hydrophilic sections of a stacked composite membrane due either to a trapped liquid film or staggered pores. Only the latter assumption is necessary for an integral composite film.

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Although an excess phase pressure is necessary to immobilize the phase interfaces at the pore mouths in the case of a plain hydrophobic or a plain hydrophilic film, it has been shown (3,4) that, pressure plays no role in solute mass transfer from one phase to another with a hydrophobic film. This is found to be valid (4) only as long as the excess phase pressure is much lower than the breakthrough pressure of the nonwetting liquid for that membrane. This breakthrough pressure is a function, amongst others, of interfacial tension and the membrane pore size. Thus, one would expect no pressure dependence on K_o, k_{mw}, k_{mo}, k_o and k_w as long as the excess phase pressure is moderate to low in any of the systems under consideration here.

Various methods have been suggested to obtain experimentally the membrane resistance of a hydrophobic membrane (3,4), a hydrophilic membrane and a composite hydrophobic-hydrophilic membrane (5). Two of these methods are especially suited for determining the resistance of a small flat hydrophobic microporous membrane (3,4). These are:

Approach 1: Use a solvent extraction system with a very low distribution coefficient $m_i (<<1)$ thereby eliminating the aqueous boundary layer resistance (m_i/k_w) in relation (1). A plot of K_o against Q_{or}, the organic solvent phase flow rate, is next obtained for the above system. The plateau value of K_o at high Q_{or} equals the value of k_{mo}: $K_o\big|_{plateau} \simeq k_{mo}$ (5)

Approach 2: Obtain a plot of K_o against Q_{or} first for one microporous flat hydrophobic membrane and then for three (or two) such membranes stacked together. The difference in the plateau values of $(1/K_o)$ thus measured represent the resistance of two (or one) hydrophobic films. For three films stacked together,

$$\frac{2}{k_{mo}} = \left(\frac{1}{K_o}\Bigg|_{3\ \text{membranes}} - \frac{1}{K_o}\Bigg|_{1\ \text{membrane}}\right) \qquad (5a)$$

This relation is valid regardless of the value of m_i and is especially suitable for determining membrane resistances when m_i is not low compared to 1. For aromatics extraction from a hydrocarbon feedstock by a polar organic solvent, we have utilized Approach 2 in this study since m_i is of the order of 1. The two phase flow rates must remain the same for both 3 membranes and 1 membrane.

Approach 1 of the above methods cannot be used to obtain the resistance of a flat hydrophilic microporous membrane since the value of K_o obtained experimentally for a low m_i ($m_i << 1$) system is just k_o from equation (3). In fact, such a result is utilized in our concurrent study (5) to obtain the value of k_o in the extraction test cell. Therefore, Approach 2 of stacking two or more membranes for a solvent extraction system having a $m_i \approx 1$ has been utilized here to characterize the hydrophilic membrane resistance. From equation (3), for a 1-membrane and a 2-membrane systems, we get

$$\frac{1}{k_{mw}} = \left(\frac{1}{K_o}\Bigg|_{2\ \text{membranes}} - \frac{1}{K_o}\Bigg|_{1\ \text{membrane}}\right)/m_i \qquad (6)$$

This assumes that the boundary layer coefficients in the cell are unaffected by adding another membrane, which has been verified in reference (5).

The membrane resistance characterization of a flat stacked composite hydrophobic-hydrophilic membrane is preferably carried out in two steps since both the quantities ($1/k_{mo}$) and (m_i/k_{mw}) contribute to the membrane resistance (5):

Step 1: The resistance ($1/k_{mo}$) of the hydrophobic section of a stacked or integral composite membrane is determined first by utilizing Approach 1 (i.e. plateau K_o value with $m_i << 1$). This may be achieved with either the hydrophobic membrane above or the composite membrane.

Step 2: A high m_i (say, $m_i \cong 1$) system is used next to carry out two experiments: (a) Determine K_o first with only the hydrophobic film in the test cell and then (b) with the stacked composite membrane in the test cell, the phase flow conditions in both being the same. The difference between the resistances in (b) and (a) above yields the resistance of the hydrophilic section of the membrane:

$$\frac{1}{k_{mw}} = \left(\frac{1}{K_o}\Bigg|_{\text{composite}} - \frac{1}{K_o}\Bigg|_{\text{hydrophobic}}\right)/m_i \qquad (7)$$

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There are a number of assumptions involved here in experiments with a flat membrane test cell. Some of these have been experimentally verified (5). Other methods of characterization of a composite film are available in reference (5) which also considers the characterization of an integral composite film.

For small flat hydrophobic membranes in a flow-through test cell with a system of $m_i \cong 1$, Approach 1 is successful since a highly open screen supporting the membrane on the organic phase side drastically increases k_o and allows the plateau to be achieved in K_o at not too high values of Q_{or}. For an extractor containing hydrophobic microporous hollow fibers with the organic phase flowing through the fiber lumen (so that the aqueous phase with a higher pressure flows on the outside of the hollow fibers), the value of Q_{or} has to be very high before a plateau value of K_o is achieved. An alternate procedure is therefore adopted here based on a method suggested elsewhere (see Approach 4 in reference (3)).

Consider a low m_i ($m_i \ll 1$) system and the mass transfer relation (2) valid at any axial location of the hollow fiber extractor. Since m_i is quite low,

$$\frac{1}{K_o} \cong \frac{d_o}{d_i k_o} + \frac{1}{k_{mo}}\left(\frac{d_o}{d_{\ell m}}\right) \tag{8}$$

Now the dependence of k_o on Q_{or} will be of the form Q_{or}^{ν} where the power ν will depend on the mass transfer regime in the lumen flow. But k_{mo} is independent of Q_{or}. Therefore, if $(1/K_o)$ is plotted against $(1/Q_{or}^{\nu})$, the value of the intercept $(1/K_o)_{\text{intercept}}$ for $(1/Q_{or}^{\nu}) = 0$ will yield $(1/k_{mo}) \times (d_o/d_{\ell m})$. The proper selection of ν is a matter of curve fitting so that $(1/k_{mo})$ can be determined.

Recognize here that the measured $\bar{K}_o$ for a hollow fiber extractor under given conditions is an averaged value over the whole extractor using, say, a logarithmic mean concentration difference driving force. It may be shown that such an averaged $\bar{K}_o$ is essentially equal to the length-averaged value of the K_o in relation (8) provided $m_i (\ll 1)$ is constant over the concentration range and the shell side aqueous stream concentration change along the extractor is very small. Therefore, the measured $\bar{K}_o$ may be plotted against $(1/Q_{or}^{\nu})$ and the hollow fiber membrane resistance determined from the intercept.

Prasad et al. (4) have shown that K_o for a new flat hydrophobic membrane can be predicted quite well by relation (1) provided k_o and k_w are known for the flow geometries and k_{mo} can be independently estimated. A similar predictive effort has been carried out in reference (5) for flat hydrophilic membranes. We are postponing such an effort for hydrophobic hollow fibers to a future manuscript. However, the power ν of Q_{or} in k_o (relation (8)) should correspond to that valid for laminar flow (for example) in a

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tube for the Graetz number range under consideration. Additionally, one can estimate the length-averaged value of k_o by subtracting the membrane resistance contribution from the overall resistance using a length-averaged relation (8) and check how its variation with the Graetz number conforms to the known relationship for tube flow.

To check how realistic the measured value of the membrane resistance is for any of the cases depicted in Fig. 1, determine the value of τ_{Mo} and τ_{Mw} by equations (1a) and (3a) respectively for the particular membrane. There are independent estimates of these tortuosity factors available in literature to find out how close these are to the experimentally determined values. Further, the values of the tortuosity factor for a film determined by different methods or obtained by using different extraction systems should fall in a narrow band if the concept of unhindered diffusion in a tortuous porous medium is valid for transport through the microporous membranes in dispersion-free extraction (3,4).

EXPERIMENTAL

Chemicals and Materials

The solvent extraction systems used in this study are xylene-water-acetic acid, MIBK-water-acetic acid and NMP-n-heptane-toluene. Xylene, MIBK, toluene (all three of certified ACS grade) and n-heptane (HPLC grade) were obtained from Fischer Scientific, Inc., Fair Lawn, N.J. The polar organic NMP (HPLC grade) was obtained from Aldrich Chemicals, Milwaukee, Wisconsin. The membranes used in flat membrane studies were CELGARD 2400 (Celanese Corporation, Summit, N.J.) and CUPROHAN 150 PM (Enka AG, Wuppertal, FRG). The microporous hollow fibers used were the X-20 type supplied by Celanese Corporation, Charlotte, N.C.

Apparatus and Procedure

The basic experimental set up for the dispersion-free extraction is shown in Fig. 2. It was utilized with either a flow type flat membrane test cell or a hollow fiber extraction module. The details of the latter is schematically shown in Fig. 3. Figure 2 indicates a top phase line and a bottom phase line unlike references (3,4). Since the top phase (the phase with an excess pressure for flat membranes) varied with the membrane type, we have separately identified the top phase and the bottom phase for a particular membrane type in Fig. 2. For the hydrophobic hollow fiber module, the organic solvent phase at a lower pressure flowed through the fiber lumen side while the aqueous phase flowed through the shell side.

The flat membrane test cell has been described elsewhere (3,4). The hollow fiber unit contained evenly dispersed 114 fibers of the X-20 type in a 1.27 cm (1/2") stainless steel pipe. The tube sheet for the fibers was prepared by plotting with an epoxy resin (C-4

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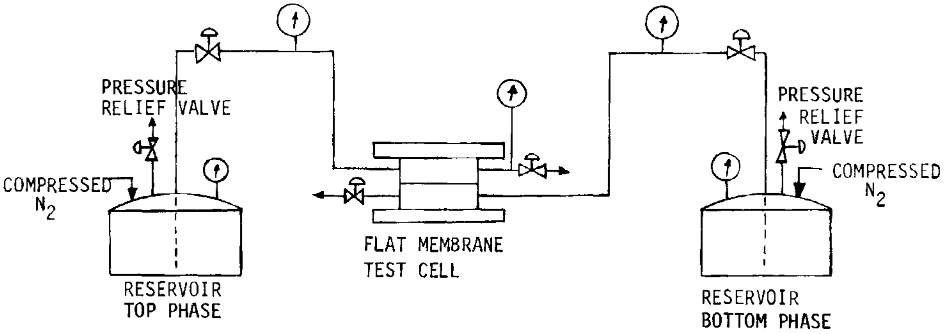

a. HYDROPHOBIC FLAT FILM: TOP PHASE - AQUEOUS
BOTTOM PHASE - ORGANIC

b. HYDROPHILIC FLAT FILM: TOP PHASE - ORGANIC
BOTTOM PHASE - AQUEOUS

c. HOLLOW FIBER MODULE (TEST CELL REPLACED BY HF MODULE): TUBE SIDE - ORGANIC
SHELL SIDE - AQUEOUS

Fig. 2. Schematic of experimental setup

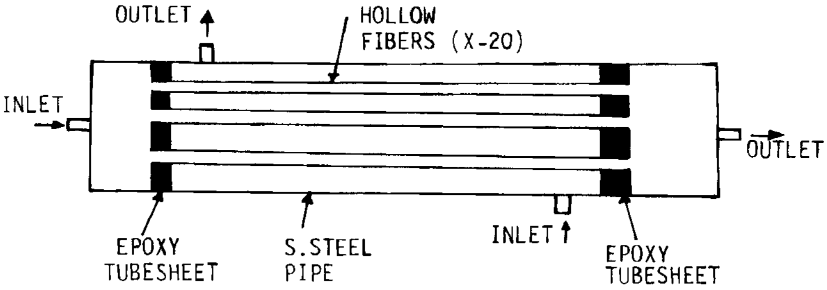

Fig. 3. Hollow fiber module - schematic

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resin with activator D from Armstrong, Warsaw, Indiana). The fiber length exposed for mass transfer was 15.8 cm. The total membrane transfer area available was 164.1 cm^2 compared to an area of 13.37 cm^2 for the flat membrane test cell.

The experimental procedure for testing a flat membrane is described in previous studies (3,4) for hydrophobic membranes. For a hydrophilic flat membrane, since the organic phase is at a higher pressure than the aqueous phase, the organic phase flow was in the top half of the flow type flat membrane cell while the aqueous phase flow was in the bottom half of the cell. Thus, the aqueous phase flow was influenced by the highly open stainless steel screen supporting the hydrophilic membrane. As with hydrophobic membranes, the bottom phase (aqueous) was allowed to flow through the bottom half of the cell containing the hydrophilic membrane first after which the top phase (organic) flow was initiated. For a composite stacked membrane, the procedure corresponded to that of a hydrophobic or a hydrophilic membrane depending on whether the aqueous phase or the organic phase was having an excess pressure. More details are available in reference (5).

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The experimental procedure adopted for extraction studies with the hydrophobic hollow fiber unit was as follows. The aqueous solution flow was started first in the shell side at a low pressure ($\sim 1.36 \times 10^4$ N/m^2). The organic solvent flow was initiated next on the tube side at about 1.36×10^4 N/m^2. After about 5 minutes of organic flow through the tube side to ensure uniform wetting of all the fibers with the organic solvent, the aqueous pressure on the shell side was slowly raised to the desired value. Subsequently some time was allowed to elapse for achieving a steady state (typically, 10 minutes) when samples of exiting aqueous and organic streams were collected for analysis.

The mass transfer rate of toluene in the flat membrane test cell for the NMP-n-heptane-toluene system was determined by measuring the concentration of toluene in NMP flowing out. The change in concentration of toluene in the hydrocarbon feed (50% toluene-50%-n-heptane) was very small. The concentration of toluene in the polar organic extractant NMP was analyzed using a HP 1090 Liquid Chromatograph (Hewlett Packard, Palo Alto, CA) equipped with a filterphotometric detector. The analysis utilized a C-18 reverse phase column while a 70% methanol-water mixture was employed as a mobile phase. The distribution coefficient of toluene between NMP and n-heptane was obtained by contacting 100 cm^3 of a mixture of n-heptane and toluene of known composition with 100 cm^3 of NMP under well-mixed conditions for 24 hours and analyzing both the phases for toluene after separation. Analysis of systems with acetic acid as a solute was done according to procedures described in references (3,4). All measurements were carried out at 25°C.

The porosity of the hydrophilic CUPROHAN 150 PM membrane used in our experiments for acetic acid extraction was determined as follows. The membrane was soaked in approximately 10% aqueous acetic acid solution. The swollen membrane was withdrawn and any surface moisture and drops were carefully removed. The thickness of this membrane in the wet state was measured using a micrometer at three different places on the membrane. The average of the three measurements was used as the wet thickness. The weight of this wet membrane was determined after which the CUPROPHAN membrane was dried in an oven at 100°C for 24 hours. The weight of the dried and shrunk membrane was noted. The difference in the wet and dry weights of the membrane was found. Noting that the density of cellulose is 1.52 gm/cm^3 (7) and that of water is 1 gm/cm^3, the porosity of the membrane was determined.

RESULTS AND DISCUSSION

The relevant physical properties of the hydrophobic CELGARD 2400 membrane, X-20 CELGARD hollow microporous fibers and the hydrophilic CUPROHAN 150 PM regenerated cellulose membrane are given in Table 1. The distribution coefficient of the solute for various extraction systems used here is reported in Table 2. Note that only the data on NMP-n-heptane-toluene in Table 2 are new - others are available from references (3,4).

Aromatic Extraction: Hydrocarbon-Polar Organic System

We first present the results of the NMP-n-heptane-toluene system with a hydrophobic flat CELGARD 2400 membrane in the aromatic extraction mode. Figure 4 shows the values of K_o for toluene extraction from a 50-50 toluene-n-heptane feed into NMP phase as a function of the hydrocarbon feed flow rate, Q_{or}, for a single CELGARD 2400 membrane as well as three CELGARD 2400 membranes. The behavior here is very similar to that of the MIBK-water-acetic acid system studied in reference (4) since m_i was of the order of 1 and the NMP phase (like the water phase in reference(4)) had an excess pressure of 5.44×10^4 N/m^2. It is also obvious that K_o reaches a plateau value at high Q_{or} where K_o is determined by k_w and k_{mo} with k_w here referring to the NMP boundary layer coefficient. Therefore, k_{mo} may be estimated using equation (5a) for any value of high Q_{or} (note, it is not necessary to have a plateau for Approach 2 to be used (reference(4))). The value of k_{mo} thus determined is 17.7×10^{-4} cm/sec which from equation (1a) leads to a value of $\tau_{Mo} = 2.65$ for CELGARD 2400 with a $D_{io} = 3.2 \times 10^{-5}$ cm^2/sec for diffusion of toluene through n-heptane (estimated from Wilke-Chang equation (8)).

This value of τ_{Mo} is quite realistic for the CELGARD 2400 film. Previous solvent extraction studies in aqueous-organic systems (4) yielded a value of τ_{Mo} in the range of 2.3-2.64 for CELGARD 2400. Independent measurement of τ_{Mo} using gas permeation through water immobilized in CELGARD 2400 film yielded $\tau_{Mo} = 2.96$ (9) providing confirmation of the estimate obtained here.

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TABLE 1

Microporous Membrane Properties[†]

Membrane	Thickness x 10^4 cm	Porosity	Internal Diameter X10^4 cm	Pore size μm	Material
CELGARD 2400	25.4	0.38	-	0.02	Polypropylene
X-20 Hollow Fiber	25.4	0.4	240	0.035	Polypropylene
CUPROPHAN 150 PM	22.1*	0.59**	-	-	Regenerated Cellulose

[†] Information supplied by manufacturer unless otherwise indicated

[*] Determined in the wet state with feed aqueous solution in the pores

[**] See experimental procedure for method of determination

TABLE 2

Distribution Coefficients for Various Solvent Extraction Systems[†]

	Extraction System					
	Xylene-water-acetic acid**		MIBK-water-acetic acid		NMP-n-heptane-toluene	
Solute* bulk concentration in feed solution x 10^3 gmol/cm^3	0.42	0.56	4.15	1.8	2.8	9.4
Solute distribution coefficient, m_i	0.012	0.012	0.51	0.53	1.04	1.03

[†] Valid for 25°C

[*] Bulk concentration in aqueous phase for Xylene-water-acetic acid and MIBK-water-acetic acid; bulk concentration in hydrocarbon phase (n-heptane) for NMP-n-heptane-toluene.

[**] From references (3,4).

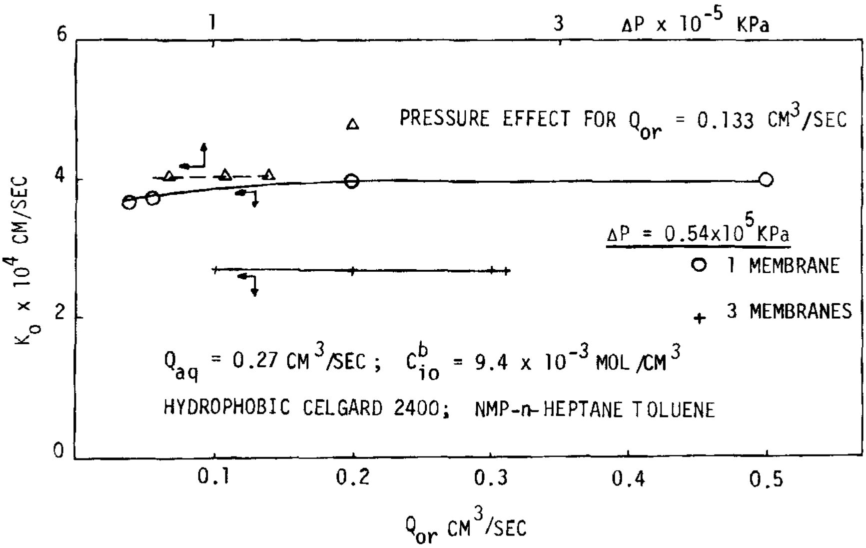

Fig. 4. Effect of hydrocarbon flow rate and ΔP on K_o for NMP-n-heptane-toluene system with CELGARD 2400 flat film.

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Figure 4 also shows the values of K_o for a single CELGARD 2400 membrane with the NMP phase at three other different excess pressures, 6.8 x 10^4, 10.2 x 10^4 and 13.6 x 10^4 N/m^2 (10, 15 and 20 psi) at the indicated NMP and hydrocarbon phase flow rates. We find that the range 5.44 x 10^4 - 13.6 x 10^4 N/m^2 (8-20 psi) does not influence K_o. This was expected in view of our earlier measurements of K_o with aqueous-organic systems as long as the excess ΔP was much smaller than the breakthrough pressure (which is quite high for the very small pore CELGARD 2400 membrane). Thus, dispersion-free solvent extraction behavior of aromatics from a hydrocarbon feed by a polar organic solvent like NMP through a hydrophobic CELGARD 2400 membrane is essentially similar to that with aqueous-organic systems previously studied (3,4).

We have previously indicated that the polar organic NMP does not preferentially wet the hydrophobic CELGARD 2400 membrane in the presence of a hydrocarbon feed stock. Actually, if the dry membrane is kept immersed in NMP, there is a slow imbibation of NMP, the interfacial tension of NMP being only marginally larger than the critical surface tension of CELGARD 2400 material (∿35 dynes/cm). This membrane is however readily and preferentially wetted by the hydrocarbons which cannot be displaced by NMP unless the latter phase has a very large value of excess pressure. This excess pressure of NMP required to displace the hydrocarbon in the pores of CELGARD 2400 film could not be determined as the apparatus could not be operated safely beyond 5.44×10^5 N/m^2. Thus the breakthrough pressure is certainly greater than this value.

Hydrophilic Membrane Extraction: CUPROPHAN Film

We next consider the results of dispersion-free extraction through a flat regenerated cellulose hydrophilic membrane CUPROPHAN widely used in dialysis studies (10) for artificial kidney. The transfer of acetic acid from water to MIBK through the membrane wetted by the aqueous solution was carried out at an excess MIBK phase pressure of 6.8×10^4 N/m^2 ($\sim$10 psi). Figure 5 shows the values of K_o as a function of Q_{or} for a single CUPROPHAN 150 PM film as well as 2 CUPROPHAN 150 PM films stacked together. For such a system ($m_i \cong 0.5$), K_o depends on k_o , k_{mw} , k_w and m_i by equation (3) till the plateau is reached at high Q_{or} where k_o no longer influences K_o . To determine k_{mw} , utilize equation (6) at the same Q_{aq} and Q_{or} . For any high Q_{or} in the plateau region, we find k_{mw} to be 12.3×10^{-4} cm/sec.

To obtain an estimate of τ_{Mw} from this value of k_{mw} , utilize the value of ε_{Mw} for this membrane from Table 1, namely 0.58 for a swollen membrane thickness of 0.0022 cm and obtain $\tau_{Mw} = 2.68$ when $D_{iw} = 1.24 \times 10^{-5}$ cm^2/sec for acetic acid in water (Perry (11)). This value of τ_{Mw} appears to be realistic since Colton et al. (10) had suggested a value of 2.77 for the tortuosity of the swollen film. There then appears to be essentially unhindered diffusion of solute acetic acid through the very narrow aqueous solution filled pores of CUPROPHAN 150 PM. With larger solutes, unhindered diffusion is no longer possible (5).

Figure 5 also shows the values of K_o at several values of excess aqueous phase pressure at a particular value of Q_{or} , Q_{aq} being 10 cm^3/min. We find that K_o is independent of ΔP in the range of 5.44×10^4 - 27.2×10^4 N/m^2 (the pressure for breakthrough of MIBK into the aqueous phase through the CUPROPHAN film was found to be around 4.08×10^5 N/m^2). Thus, the absence of any effect of the excess aqueous phase pressure on K_o through hydrophobic membranes observed earlier (3,4), is also found to be true for the hydrophilic CUPROPHAN membrane subjected to an excess organic phase pressure. Therefore, the description of mass transfer in dispersion-free solvent extraction with hydrophilic membranes requires only the concentration driving forces.

Solvent Extraction with a Composite Hydrophobic-Hydrophilic Membrane

Consider a stacked composite of a hydrophobic CELGARD 2400 flat film and a hydrophilic CUPROPHAN 150 PM regenerated cellulose flat film as shown in Fig. 1c with the organic solvent phase flowing on

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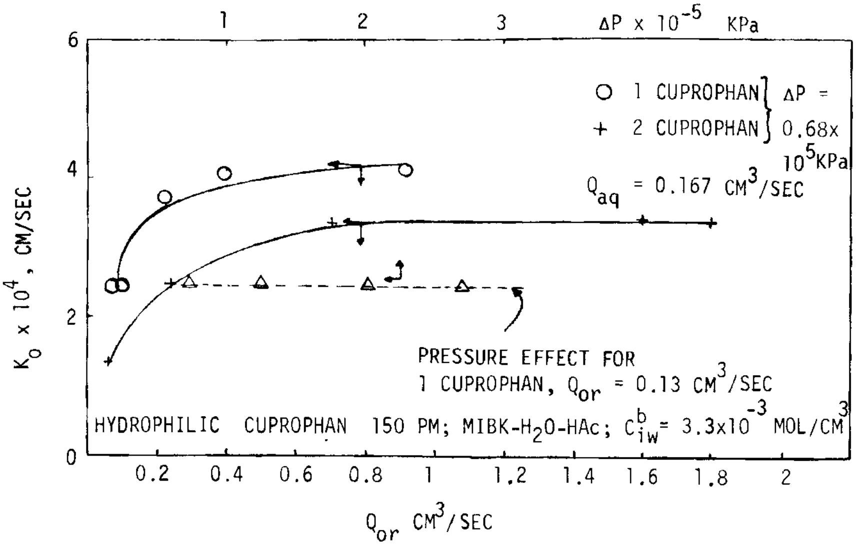

Fig. 5. Effect of organic flow rate and ΔP on K_o for MIBK-water-HAc system with CUPROPHAN 150 PM flat film.

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the hydrophobic side and the aqueous solution flowing on the hydrophilic side. The values of K_o obtained with MIBK-water-acetic acid system as acetic acid was transferred from the aqueous solution to the MIBK phase are shown in Fig. 6 against various values of Q_{or} for a variety of excess phase pressures. These include: o N/m^2 corresponding to the same pressure in both the organic and the aqueous phase, the aqueous phase having an excess pressure of 5.44×10^4 N/m^2 (8 psi) and the MIBK phase having an excess pressure of 5.44×10^4 N/m^2 (8 psi). Dispersion-free extraction was achieved under all three pressure conditions. Thus, a composite hydrophobic-hydrophilic membrane can be operated with or without an excess pressure in either phase to maintain dispersion-free extraction.

Observe further in Fig. 6 that the values of K_o for any Q_{or} are essentially unaffected by the presence or absence of an excess pressure in either phase. Such a behavior was expected since K_o is not affected by an excess phase pressure for either a hydrophobic film (3,4) or a hydrophilic film (see the previous section results). However, it is expected that there may be an effect of the excess phase pressure if the latter is close to the break-through pressure for the particular section of the membrane.

To convey how the extraction rates are influenced by a composite film, we have also plotted in Fig. 6 the values of K_o for various

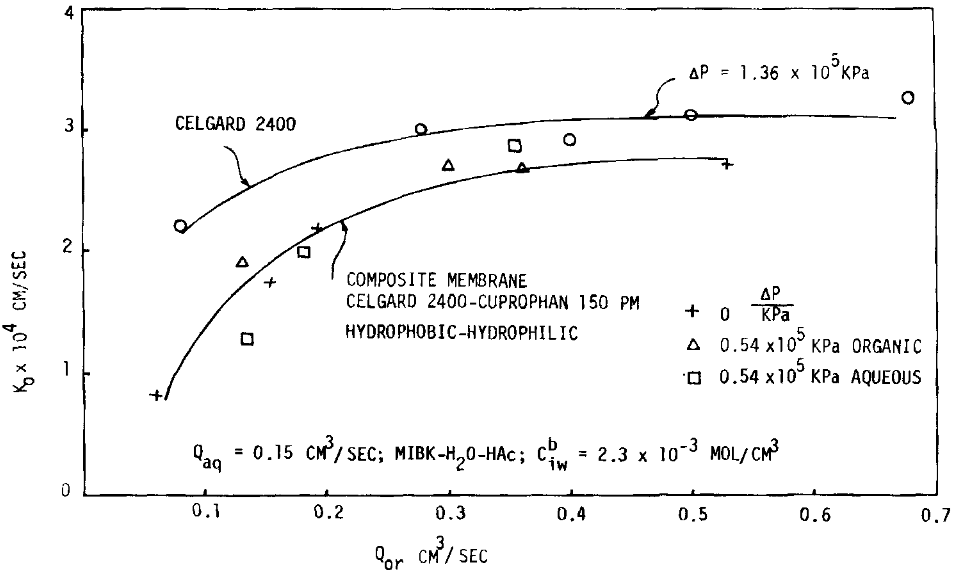

Fig. 6. Effect of organic flow rate on K_o for MIBK-water-HAc system for a composite hydrophobic-hydrophilic membrane.

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Q_{or}-s when a single CELGARD 2400 hydrophobic film is utilized. At high values of Q_{or}, we observe that K_o achieves a plateau in both cases. This is expected from equation (4) as well as equation (1). Since the aqueous boundary layer resistance in both cases is the same for a given Q_{aq}, equation (7) may be used to determine k_{mw}. We find thereby the value of k_{mw} to be 14.1×10^{-4} cm/sec. This value for the CUPROPHAN film in the CELGARD-CUPROPHAN composite is only slightly higher than the value determined earlier in the section on hydrophilic membrane extraction. The corresponding estimate of τ_{Mw} is 2.33.

Thus, except for extraction systems with $m_i << 1$, the resistance of a composite hydrophobic-hydrophilic microporous solvent extraction membrane will always be larger than that of either a hydrophobic or a hydrophilic membrane. The differences can be minimized by drastically reducing the thickness of one of the two layers of the composite film. However, the composite membrane system has the advantage of being able to operate dispersion-free regardless of the pressure of either phase as long as immiscible displacement through any one of the membranes is not initiated.

Solvent Extraction with a Hydrophobic Hollow Fiber Module

The average value $\bar{K}_o$ over the whole module of the overall organic-phase-based mass transfer coefficient for acetic acid extraction into xylene is plotted in Fig. 7 as $(1/\bar{K}_o)$ against $(1/Q_{or}^{\nu})$ with $\nu = 0.34$. The value of K_o was determined using the following overall solute mass balance for N hollow fibers of length L with an interfacial area based on the outside diameter of the fiber since the interface was at d_o with the organic phase in the lumen and the pores:

$$Q_{or}\, C^b_{io}\Big|_{exit} = \bar{K}_o\, (\pi\, d_o NL)\, \Delta\, C^b_{io}\Big|_{\ell m} \tag{9}$$

Note that pure organic phase entered the module. The data displayed the best fit with the value of ν indicated above.

Consider a length-averaged version of equation (8), valid for a $m_i << 1$ system:

$$\frac{1}{\bar{K}_o} \simeq \frac{1}{\bar{k}_o}\,\frac{d_o}{d_i} + \frac{1}{k_{mo}}\left(\frac{d_o}{d_{\ell m}}\right) \tag{10}$$

The intercept of the plot of $(1/\bar{K}_o)$ against $Q_{or}^{-0.34}$ for the very low m_i system, xylene-water-acetic acid, yields $(1/k_{mo})\,(d_o/d_{\ell m})$ in Fig. 7 from which we find $k_{mo} = 17.79 \times 10^{-4}$ cm/sec. Using equation (2a), this yields $\tau_{Mo} = 2.47$ with $D_{io} = 2.76 \times 10^{-5}$ cm^2/sec for acetic acid diffusion in xylene (3,8). An independent estimate of τ_{Mo} for the X-20 fibers using N_2 permeation through water immobilized in X-20 fiber pores yielded a value of 2.2. Therefore the estimate of $\tau_{Mo} \cong 2.47$ for X-20 appears to be quite reasonable. Details of this gas permeation technique are given elsewhere (12).

Figure 7 also shows a plot of the data for the MIBK-water-acetic acid system at $\Delta P = 6.8 \times 10^4$ N/m^2 (10 psi). Since the contribution of the length-averaged form of the term $(m_i/k_w d_o)$ in equation (2) is merely an additive constant in a plot of $(1/\bar{K}_o)$ versus $(1/Q_{or}^{\nu})$, we find that a value of $\nu = 0.34$ also provides the best fit of data for this system with m_i of the order of 1. The effect on $\bar{K}_o$ of a variation in ΔP for a particular set of values of Q_{or} and Q_{aq} is indicated in Fig. 7 with different axes. The value of ΔP varied between 3.4×10^4 to 10.2×10^4 N/m^2 (5 to 15 psi). We find no effect of a ΔP variation at these low levels of ΔP, a behavior also observed with flat hydrophobic films (3,4).

A comment about the value of ν, the exponent of Q_{or}, the organic flow rate through fiber lumen is useful here. The value of $\nu = 0.34$ would suggest that k_o may be described by the Leveque solution in the fiber lumen (see Skelland (13) for details). Qi and Cussler (14) have also experimentally obtained a value of $\nu = 1/3$ for the variation of lumen side mass transfer coefficient with liquid velocity for gas absorption using microporous CELGARD hollow fibers. The value of this exponent, however, depends also on the fiber length through Graetz number.

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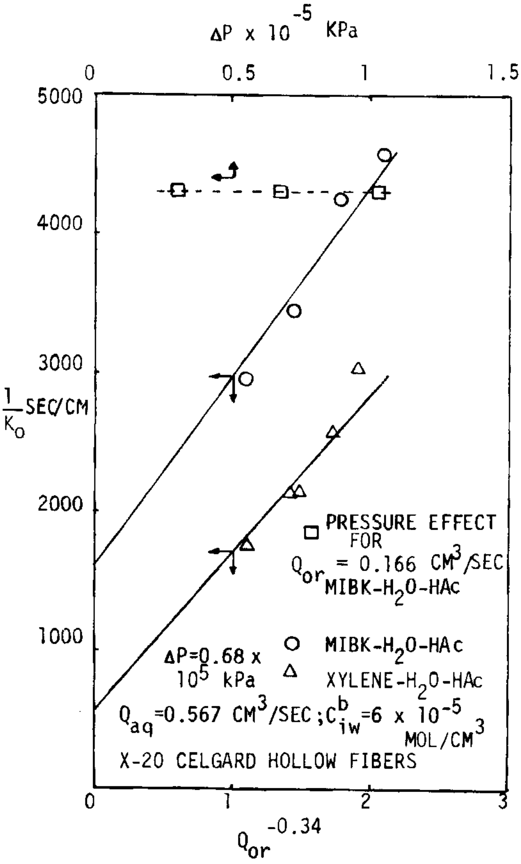

Fig. 7. Extraction behavior of hydrophobic X-20 CELGARD hollow fiber for MIBK-water-HAc and Xylene-water-HAc.

The pressure drop along the bulk flow direction in the fiber lumen at the highest flow rate was found to be less than 6.8 x 10^3 N/m^2 (1 psi). Qi and Cussler (14) had observed a pressure drop of less than 1.02 x 10^4 N/m^2 (1.5 psi) for their hollow fiber module at their highest flow rates. Their module was 18 cm long, quite close to that of the present study.

Kim (15) has reported the performance of hydrophobic microporous hollow fiber-based extraction of copper using LIX reagents. The differential pressure conditions at the two ends of his hollow fiber extractor were reversed. Consequently, he could not prevent dispersion and needed an aqueous-organic separator in addition. By maintaining the proper phase pressure conditions, we have avoided dispersion completely. Further, by starting aqueous flow on the shell side at a small positive pressure followed by lumen side organic flow at a similar but lower pressure, the possibility of a small dispersion during start up has also been eliminated (3). We should note that the use of a porous partition for solvent extraction is briefly mentioned in two patents (16,17) dealing exclusively with solvent extraction using solvent-swollen polymeric membranes. However, proper phase pressure conditions and other intrinsic requirements for using a porous partition were not identified.

A Perspective on the Technique

Dispersion-free solvent extraction may be easily carried out using microporous membranes. The technique has numerous advantages over conventional dispersion-based processes for large scale applications. For laboratory studies, the known interfacial area would be a great boon to characterization. The necessity of an independent estimate of, "a", the interfacial area per unit extractor volume to determine k_ℓ from the ubiquitous "$k_\ell a$" is eliminated. The tyranny of the limitations on independent phase flow rate variations, the necessity of an adequate density difference and the vagaries of coalescence endemic in dispersion-based processes are absent in the new technique.

Kiani et al. (3) had compared the value of $K_o a$ in the present technique with that from dispersion-based processes (Treybal (18)) for the MIBK-water-acetic acid system. They had used a $K_o \simeq 4 \times 10^{-4}$ cm/sec from their CELGARD 2400 flat film data and used a realistic estimate of "a" for well packed hollow fiber systems. We note here that, for the same extraction system, the present hydrophobic hollow fiber studies provide easily a $K_o \simeq 3.4 \times 10^{-4}$ cm/sec at very low organic and aqueous phase velocities. Further at these flow velocities, the flow pressure drop in either phase is quite small. In industrial hollow fiber modules that are, say, ten times longer than our laboratory module, the flow pressure drop would still be reasonably low. Thus, energy requirements in the new technique are likely to be relatively modest.

The development of a composite hydrophobic-hydrophilic film with asymmetric wetting properties provides the new technique with extraordinary flexibility vis-a-vis the phase pressure conditions. This is at the expense of an increased membrane resistance. In the same context, we should recognize that, for extraction systems with m_i of the order of 1, the plain hydrophilic system holds no great advantage over a plain hydrophobic system for comparable values of k_{mw} and k_{mo}. For $m_i >> 1$, a hydrophilic system would have a much higher resistance. A more detailed comparison would require a study of a wider variety of membranes under more general conditions (5).

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SYMBOLS

C^{i}_{iM}	concentration of i in membrane at the aqueous-organic phase interface, mol/cm^3
C^{o}_{iM}	concentration of i in hydrophobic membrane at membrane-support interface, mol/cm^3
C^{b}_{io}	bulk concentration of i in organic phase, mol/cm^3
C^{i}_{io}	organic phase concentration of i at organic-hydrophilic membrane interface, mol/cm^3
C_{iw}	concentration of i in aqueous phase, mol/cm^3
C^{b}_{iw}	bulk concentration of i in the aqueous phase, mol/cm^3
C^{i}_{iw}	aqueous phase concentration of i at water-membrane interface, mol/cm^3
d_i,do	inside and outside diameter of microporous hollow fiber, cm
$d_{\ell m}$	logarithmic mean diameter of microporous hollow fiber, $(d_o-d_i)/\ell n(d_o/d_i)$, cm
D_{io}	diffusion coefficient of i in organic solvent, cm^2/sec
D_{iw}	diffusion coefficient of i in aqueous solution, cm^2/sec
k_{mo}	membrane transfer coefficient of species i through organic-wetted membrane, equation (1a), cm/sec
k_{mw}	membrane transfer coefficient of species i through hydrophilic membrane, equation (3a), cm/sec
k_o	organic boundary layer transfer coefficient of species i, cm/sec
k_w	aqueous boundary layer transfer coefficient of species i, cm/sec
K_o	overall organic phase-based transfer coefficient of species i, cm/sec
$\bar{K}_o$	value of K_o for a hollow fiber module, equation (9), cm/sec
L	active length of microporous hollow fiber, cm
m_i	distribution coefficient of species i, organic phase concentration over aqueous phase concentration
N	number of hollow fibers in the module
P_{aq}	pressure of aqueous phase, N/m^2
P_o	pressure of organic phase, N/m^2
ΔP	excess phase pressure; for hydrophobic membranes $P_{aq}-P_o$; for hydrophilic membranes P_o-P_{aq}, N/m^2

Q_{aq}, Q_{or}	flow rate of aqueous and organic phase respectively, cm^3/sec
t_{Mo}, t_{Mw}	thickness of hydrophobic and hydrophilic membranes, respectively, cm

Greek Letters

$\varepsilon_{Mo}, \varepsilon_{Mw}$	porosity of hydrophobic and hydrophilic membranes, respectively
τ_{Mo}, τ_{Mw}	tortuosity factor of hydrophobic and hydrophilic membranes, respectively
ν	power of Q_{or} in the variation of k_o with Q_{or}

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