Separation of Volatile Organic Compounds from Aqueous Solutions by Pervaporation Using S—B—S Block Copolymer Membranes

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Composite membranes of a block copolymer of styrene and butadiene (S-B-S) were cast on highly porous, hydrophobic thin films of PTFE and used for the separation and recovery of volatile organic compounds (VOCs) from aqueous solutions by pervaporation. Trichloroethane, trichloroethylene, and toluene were the VOCs selected for testing the efficacy of these membranes. An analysis of the pervaporation data showed that the liquid film boundary layer offered the main mass transfer resistance to permeation. The separation factor for the VOCs was as high as 5000 at near-ambient temperatures but decreased substantially at higher temperatures. The water flux was practically independent of the solute concentration. But it increased more rapidly with an increase in temperature as compared to the organic flux, thereby reducing the separation factor. Also, the separation of a multicomponent mixture from the aqueous feed could be predicted well from single-component data.

Introduction

The need to remove, separate, and recover volatile organic compounds (VOCs) from contaminated media, such as air or water, has steadily grown in importance because of the potential of these compounds to adversely affect human health and the environment. Chlorinated hydrocarbons, as a group, constitute the greatest concern in this regard. Air stripping (1) or adsorption coupled with such destruction methods as combustion and oxidation technologies are good options when they are the only economic treatment methods available. In these methods, the bulk of the contaminated stream-not just the contaminants-is subjected to the treatment method. For instance, in combusting contaminants in air from an air stripping operation, the entire air is heated to the combustion temperature. In situations where the recovery of the VOCs is economically desirable or a low energy approach is needed, the pervaporation process may be a viable alternative with significant advantages (2). This membrane process is operated at near-ambient temperatures and pressures and offers very large VOC separation factors with respect to water for low VOC concentrations in a liquid stream.

Two principal factors enable a high degree of separation of nonpolar and weakly polar light organics by hydrophobic

membranes from VOC-bearing aqueous solutions: partition coefficients of the VOCs in the membrane and their diffusion coefficients. Successful separation occurs when either the partition coefficients or the diffusion coefficients of the VOCs, or both, are significantly superior to those for water. Typical examples of polymers used in membranes for this purpose are poly(dimethylsiloxane) (PDMS), nitrile-butadiene rubber, polybutadiene, polyurethane, and ethylene-propylene terpolymer (EPDM) (3). PDMS has long been known as a suitable elastomeric material that can be cast in the form of thin films or tubes and used for separating organics from water by pervaporation, particularly for the selective removal of alcohol from an aqueous solution. For instance, Nguyen and Cobe (4) used silicone tubes to explore the removal of halogenated hydrocarbons (e.g., chloroform, bromoform), ethanol, and acetone and found that the halogenated hydrocarbons had higher permeabilities and selectivities than the latter compounds. Psaume et al. (5) also studied the removal of trichloroethylene (TCE) from water using silicone tubes. These authors observed a significant increase in solute flux through the membrane as the feed Reynolds number increased and concluded that the liquid-phase diffusion resistance largely determined the solute flux. Lipski and Cote (6) further studied the above system using two configurations of feed flow-the axial flow mode (lumen-side flow) and the transverse flow (shell-side flow) mode. They developed a resistance-in-series model for both flow configurations. They also reported that the liquid-phase resistance controlled the organic flux. By comparing the economics of the pervaporation process with the conventional technologies of air stripping and carbon adsorption, these authors established that pervaporation is an economically competitive technology. Watson and Pyne (7) analyzed the effects of downstream pressure on solute selectivity and claimed that sorption rather than diffusivity had more influence on the separation. For removing organics from water, Blume et al. (8) tested the efficacy of two spiral-wound membrane modules: a twolayer composite of PDMS coated on a microporous polyester fabric support and a three-layer composite consisting of two coatings, one of PDMS and the other of a polyolefin. Compared to a separation factor of 10 for ethanol removal [(see, for example, Takegami et al. (9)], 50-400-fold enrichment could be achieved for nonpolar organics such as chloroform or trichloroethane. Raghunath and Hwang (10) used a tubular membrane module fabricated from silicone rubber tubing and measured the permeation of benzene, chlorobenzene, and toluene in the laminar regime of feed flow. They calculated the liquid-phase resistance by solving the Greatz problem and found it to contribute significantly toward the total mass transfer resistance. Similar conclusions were also arrived at by the same authors (11) from the results of their work with flat silicone rubber sheets of different thickness. Viswanathan et al. (12) studied the separation of 1,1,1-trichloroethane and its mixture with trichloroethylene in water using a membrane module made of silicone tubing that was operated in the sweeping gas pervaporation mode. They observed that TCE permeated faster than TCA. They also observed some flux coupling. For instance, an increased concentration of one of the components had a negative influence on the flux of the other. Ji et al. (13) studied pervaporation of a mixture of TCA, toluene, and methylene chloride using membranes made of PDMS, polyether block polyimide (PEBA), polyurethane (PUR), and a silicone polycarbonate copolymer (SPC). They found no coupling of the fluxes. A resistance-in-series model was used to interpret the data. They proposed a simple but useful model to account

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$$\left(-CH - CH_2 - \right)_m \left(-H_2C \right)_m = C \left(-CH_2 - \right)_m \left(-CH_2 - CH - \right)_m$$

FIGURE 1. Chemical structure of the S-B-S polymer.

for the dependence of flux and selectivity on downstream pressure. Boddeker et al. (14) tested PEBA membranes for pervaporation of a large number of phenolic and substituted benzene compounds. They observed reduced enrichment of the permeate with increased downstream pressure. Canning (15) furnished a list of 33 nonpolar or weakly polar volatile organics, mostly lower halogenated hydrocarbons, that are amenable to separation from groundwater, wastewater, or soil washings by pervaporation. He provided typical performance data of a hollow fiber membrane module coated on the outside surface. A cost analysis of pervaporation visa-vis carbon adsorption and air stripping established the former to be economically competitive and less sensitive to higher contaminant concentrations.

To compete more effectively with the conventional techniques of removal of VOCs from water, pervaporation process has to meet with two major challenges. The first challenge is to significantly reduce the diffusion resistance that results from concentration polarization. Developing membrane materials that can deliver suitable fluxes and separation factors is the other challenge. The crux of the second problem is that higher species selectivity is usually accompanied by lower flux and vice versa. Besides, the ability to withstand harsh environment becomes an important factor in some applications.

In the context of a lack of superior membrane materials for the challenging task at hand, the present investigation was focused on exploring new membrane materials that could provide higher separation factors than are found in the literature, while also ensuring acceptably high pervaporation fluxes. This is the case with a block copolymer of styrene and butadiene (S-B-S). In block copolymers, the homopolymer blocks produce zones of repulsion and association depending on the proximity of similar or dissimilar blocks (16). In the S-B-S polymer, the polystyrene block is the 'hard' phase that has a much higher glass transition temperature (95 °C) than that of the polybutadiene 'soft' block ($\hat{T_{\rm g}} = -90\,^{\circ}{\rm C}$). The latter polymer gives the membrane desirable rubbery properties when the styrene content remains between 20 and 40%. The copolymer tensile strength is 20 MPa at room temperature (17). This excellent tensile property of the material, which is comparable to that of vulcanized rubber, gives the copolymer satisfactory dimensional stability when subjected to stress under pervaporation condition.

As stated earlier, a membrane that offers a high solute separation factor often does not deliver a high flux. We observed that this problem could be largely overcome by casting a thin copolymer film on a porous PTFE support film having the necessary mechanical strength. Furthermore, most of the reported investigation on the separation of VOCs from aqueous streams dealt with simple solutes. In this study we measured the flux and selectivities of solutes (TCA, TCE, and toluene) in mixtures and attempted to relate these quantities with those for single-component data.

Materials Used and Membrane Casting

The block copolymer used in this work was obtained from Aldrich Chemical Co. (Milwaukee, WI). The polymer, which has an average molecular weight of 100 000, consists of an inner soft block of polybutadiene (average molecular weight = 72 000), flanked by two hard blocks of polystyrene (average molecular weight = 14 000) on each side. The chemical structure of the polymer is shown in Figure 1. The overall styrene content of the material is 28%. The membrane

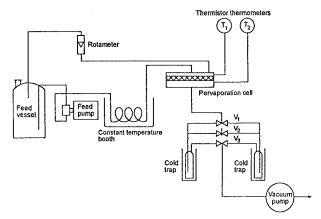


FIGURE 2. Schematic of the experimental setup.

support was a porous polytetra fluoroethylene (PTFE) film having a thickness of 70 μ m and an average pore size of 0.1 μ m. Because of the presence of unsaturation in the soft polybutadiene block, the copolymer tended to undergo slow oxidation that made the polymer rigid. The problem was overcome by using 0.5% of an antioxidant, Naugard 10, in the casting solution.

The membranes were cast on a glass plate lined with a thin PTFE sheet that provided a smooth nonsticky surface. A 20% solution of the polymer in toluene with the antioxidant was prepared, and a thin membrane was cast on the PTFElined plate using an adjustable casting knife (Paul N. Gardener Co.). Membranes of different thickness could be prepared by adjusting the casting knife. After casting, the layer of the polymer solution was allowed to evaporate for about 2 min at 20 °C. The porous membrane support was then laid over the partially dried polymer film. The composite film was allowed to dry for 20 min at 20 °C, then removed from the casting surface, and further dried in an air oven for 1 h to remove the last traces of the solvent toluene. This technique worked better than casting the film directly on the PTFE support, because in the later case the dilute polymer solution entered the pores of the backing and increased the membrane thickness.

All other chemicals (TCA, TCE, toluene, etc.) were obtained from Aldrich Chemical Co. and were used as such.

Experimental Setup and Procedure

Pervaporation experiments were carried out in a Millipore circular membrane cell suitably modified for our purpose. The cell consisted of two compartments each provided with a PTFE O-ring for sealing. The membrane was placed on a perforated, PTFE-coated stainless disk. The membrane and the disk together were sandwiched between the two compartments of the cell. The feed entered into the upper compartment through an inlet located centrally and left through two diametrically opposite outlets placed near the peripherum. The effective area of the membrane exposed to the feed was 45.5 cm². The experimental setup is shown in Figure 2.

The solution of a model organic compound (TCA, TCE, or toluene) was placed in a 20-L feed tank. A diaphragm pump equipped with adjustable delivery pumped the solution. The feed flowed through a helical stainless steel coil immersed in a constant-temperature bath. The feed entered the upper compartment of the cell and was recycled back to the feed tank. The flow rate was measured by a rotameter, and the temperatures of the feed and the permeate sides were measured by thermistor thermometers. Vacuum was applied to the lower compartment by a vacuum pump; the downstream pressure was maintained by a vacuum regulator and was measured by a digital vacuum gauge. A glass trap

was placed in the vacuum line before the vacuum pump on the downstream side. The trap was cooled by liquid nitrogen. Two such traps were placed in parallel connected to the vacuum line by a three-way valve so that any one of the traps could be put on line at any time.

After the feed flow was started, 2 h was allowed for the attainment of steady state before data gathering began. At steady state, the permeate vapor was allowed to pass into the liquid nitrogen trap. A typical experiment continued for 1.5-2 h. The feed concentration remained virtually constant (with a maximum variation of about 2%) over the period of an experiment. At the end of an experiment, the cold trap was removed and 0.5 mL of methanol was added to it and kept loosely stoppered so that loss of the permeate was minimized when the content of the trap warmed to room temperature. The amount of permeate collected was measured by weighing, and the contents were diluted with a measured amount of methanol. A small volume of this methanol solution (5-40 μ L) was further diluted with water (so that the VOCs remained in solution) in a volumetric flask and then analyzed for the VOC content by using purge-andtrap chromatography. A Dynatech purge-and-trap autosampler and a Tremetrics 9001 chromatograph equipped with a flame ionization detector were used for the analyses. The experimental error of the analytical method was within 3%. Feed samples were taken at the beginning and at the end of an experiment. These samples were suitably diluted with water and analyzed by the above procedure. Temperature of the feed was maintained to within 0.1 °C. The downstream pressure was maintained at 1.0-1.4 Torr.

Equilibrium sorption of the model compounds in the S-B-S polymer was measured over a range of concentrations at 30 °C. Pieces of thin sheets of the polymer were equilibrated with solutions of the organics for 48 h. A sheet was removed from the solution; the adhering liquid was wiped off very quickly and weighed in order to determine the uptake. Sorption of pure water was determined separately. Equilibrium sorption of the organic compound was calculated by subtracting the uptake in the solution and that in water.

Theoretical Considerations

Enrichment of one or more components of a solution by pervaporation involves the following steps: (i) transport of the diffusing species from the bulk of the solution to the membrane-liquid interface, (ii) sorption of the solute in the membrane at the membrane surface, (iii) diffusion of the species through the membrane, (iv) desorption from the membrane at the vapor or the downstream side, and (v) transport through the vapor or gas film on the downstream side of the pervaporation device. If interfacial equilibrium prevails at the membrane-liquid interface, which is reasonably expected if the membrane surface is clean, step ii does not involve any transport resistance. This was especially true under the conditions of the present study because the experiments were conducted at steady state. Similarly, steps iv and v would not offer any mass transfer resistance because of the very low pressure maintained in the downstream compartment and because the vapor was removed by the vacuum pump as soon as it was desorbed from the membrane. In fact, the diffusion resistance on the downstream can be easily neglected in the case of vacuum pervaporation (18).

The rate of transport of a solute A across the diffusion boundary layer adjacent to the membrane on the upstream side may be expressed as

$$J^{A} = k_{L}^{A} (C_{L,b}^{A} - C_{L,i}^{A}) = k_{L}^{A} \rho_{L} (x_{L,b}^{A} - x_{L,i}^{A})$$
 (1)

where \mathcal{F}^{A} is the flux of the solute, k_{L}^{A} is the liquid-phase mass transfer coefficient, C^{A} is the solute concentration, and x^{A} is

the solute mole fraction. The liquid density, ρ_L , may be taken as that of water because the solute is present in very low concentration.

There is more than one way of expressing the rate of membrane transport. It can be done by using membrane permeability, as is commonly done in analyzing gas transport through a membrane or a film. Alternatively, it can be expressed in terms of the interfacial concentration gradient and diffusivity in the membrane phase. Under steady-state operating condition, the diffusion equation can be written as

$$\frac{\mathrm{d}}{\mathrm{d}z} \left[D(C_{\mathrm{m}}^{\mathrm{A}}) \frac{\mathrm{d}C_{\mathrm{m}}^{\mathrm{A}}}{\mathrm{d}z} \right] = 0 \tag{2}$$

with boundary conditions

$$z = 0, C_{\rm m}^{\rm A} = C_{\rm m,i}^{\rm A}; z = \delta, C_{\rm m}^{\rm A} = C_{\rm m,\delta}^{\rm A}$$
 (3)

where $D(C_{\rm m}^{\rm A})$ is the concentration-dependent diffusion coefficient of the solute in the membrane, z is the distance across the membrane from the interface, and $C_{m,i}^A$ and $C_{m,\delta}^A$ are the interfacial solute concentrations in the membrane at the upstream and the downstream side of the membrane, respectively. Diffusivity of a solute in the membrane may depend on the local concentration of the solute if the membrane undergoes considerable swelling because of a high degree of sorption of the solute (19). Although the oraganics used in this work are practically nonpolar and have a high affinity for the S-B-S polymer, the equilibrium sorption, as revealed by the sorption data, remained low in the range of feed concentrations used. Under this condition, it is reasonable to consider that the solute diffusivities are approximately independent of the membrane-phase concentration. Integration of eq 2 leads to the following expression for the flux through the membrane

$$J^{A} = \frac{D_{\mathrm{m}}^{A}}{\delta} (C_{\mathrm{m,i}}^{A} - C_{\mathrm{m,\delta}}^{A}) \tag{4}$$

If the equilibrium sorption in the membrane is linear in the liquid-phase concentration of the solute

$$C_{\mathrm{L,i}}^{\mathrm{A}} = H_{\mathrm{m}}^{\mathrm{A}} C_{\mathrm{m,i}}^{\mathrm{A}} \tag{5}$$

At low downstream pressures, we can assume that $C_{\mathrm{m},\delta}^{\mathrm{A}}=0$. Equations 1 and 4 can be combined to express the permeation flux in terms of an overall mass transfer coefficient

$$J^{A} = K_{I}^{A} C_{I b}^{A}$$

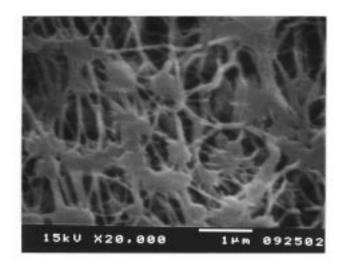
where

$$\frac{1}{K_{\rm I}^{\rm A}} = \frac{1}{k_{\rm L}} + \frac{\delta H_{\rm m}^{\rm A}}{D_{\rm m}^{\rm A}} \tag{6}$$

Equation 6 is a simple form of the overall mass transfer coefficient based on the resistance-in-series model. It can be rearranged to

$$\frac{1}{\delta K_{\rm L}^{\rm A}} = \frac{1}{\delta k_{\rm L}^{\rm A}} + \frac{H_{\rm m}^{\rm A}}{D_{\rm m}^{\rm A}} \tag{7}$$

Equation 7 shows that a plot of $1/\delta K_L^A$ against $1/\delta$ should yield a straight line with a slope of $1/k_L^A$ and an intercept of H_m^A/D_m^A . Hence a set of permeation flux data with varying membrane thickness can be used to determine the solute diffusion coefficients as well as the relative magnitudes of



(b) Membrane Membrane 25kU X1,000 10 Pm 092511

FIGURE 3. SEM pictures of (a) the membrane support (surface) and (b) the cross-section of a membrane.

the boundary layer resistance and the membrane resistance. To estimate the diffusivity from the slope of the plot, however, the solute distribution coefficient between the solution and the membrane should be known or determined.

Results and Discussion

(a)

Permeation experiments were done with binary and multicomponent feed solutions of the model compounds-TCA, TCE, and toluene. Relative magnitudes of the resistances offered by the membrane layer, the support, and the liquid boundary layer were measured. The temperature effect and possible flux coupling effects in the case of a multicomponent mixture were investigated. The membrane thickness was calculated using the masses of the composite membrane and the PTFE backing and the density of the membrane polymer. Scanning electron micrographs (with a Joel JSM-5300 and gold coating) of the membrane support and of the composite membrane are shown in Figure 3a,b. The backing had a cobweb structure (Figure 3a). The permselective S-B-S layer on the backing was a defect-free film (Figure 3b) that did not show any polymer penetration into the pores of the backing.

Effect of Feed Concentration. Experimental data on organic flux, water flux, permeate concentration, and separation factor of TCA, TCE, and toluene at 30 °C are presented in Figure 4a-c, respectively. The separation factor is defined as

$$\alpha_{\rm A} = \frac{\left[w_{\rm A}/(1-w_{\rm A})\right]_{\rm permeate}}{\left[w_{\rm A}/(1-w_{\rm A})\right]_{\rm feed}}$$

where w_A is the weight fraction of organic A. In each of the figures, the flux is linear in feed concentration. Global separation factors as high as 5000 were achieved that are considerably larger than the separation factor of the order of 3000 reported by Ji et al. (13) for silicone membranes. Boddeker and Bengtsson (14) used polyether block polyamides and reported separation factors below 1000 for a number of organics including toluene. The permeate concentration increased with the feed concentration, and even at the lowest feed concentration (about 30 ppm) the permeate was rich enough to yield a two-phase liquid product. This is important from a practical viewpoint because the recovered VOCs can be separated from the permeate by decantation,

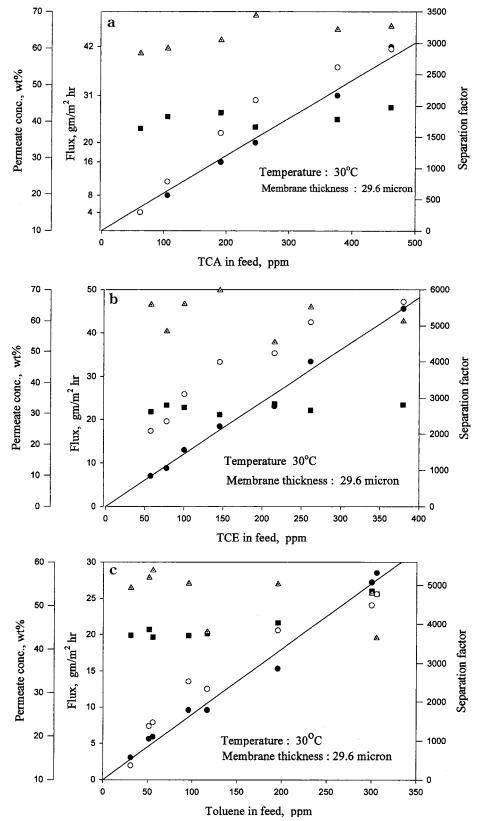


FIGURE 4. (a) Permeation of TCA: () TCA flux; () water flux; () permeate concentrate, wt %; () separation factor. (b) Permeation of TCE: () TCE flux; () water flux; () permeate concentrate wt %; () separation factor. (c) Permeation of toluene: () toluene flux; () water flux; () permeate concentrate, wt %; () separation factor.

and the aqueous layer can be recycled back to the feed. The figures also show that among the three organic compounds selected, TCE exhibited a higher flux than the other two at a given feed concentration. The water flux through the membranes was found to be nearly independent of the

organic concentration in the feed.

Diffusional Resistance of the Backing. We tested the possibility that the backing of the composite membrane offered an additional diffusion resistance. For this purpose, pervaporation experiments were done for several feed

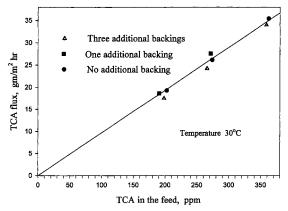


FIGURE 5. Effect of additional membrane supports on TCA flux.

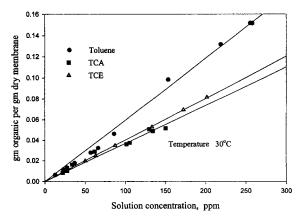


FIGURE 6. Equilibrium sorption in S-B-S films.

concentrations, and the results were plotted in Figure 5. It was inferred from the results that the backing did not offer any measurable resistance to mass transfer.

Sorption Data. Equilibrium sorption data for various concentrations of the organics were collected at 30 °C and were plotted in Figure 6. Sorption for the three organic compounds increased with decreasing polarity. Toluene is the least polar, having a dipole moment of 0.4 D (20). The dipole moments of TCE and TCA are 0.9 and 1.7, respectively. Thus, toluene had the highest sorption in the polymer (S-B-S) followed by TCE and TCA. The equilibrium concentration in the membrane varied linearly with the corresponding organic concentration in the liquid. Sorption of water by the membrane was very small, and the presence of organics in low concentration did not have any detectable effect on water sorption. The sorption equilibrium could, therefore, be described by a linear relationship, as given in eq 5. The sorption equilibrium constants were used to calculate the organic diffusivities in the membrane.

Resistance-in-Series Model. Several previous researchers used the resistance-in-series model to interpret pervaporation data obtained from separating nonpolar or weakly polar organics from water (3, 21, 22). We used eq 7 for testing the resistance-in-series model. Figure 7 presents the plots of $1/\delta K_{\rm L}^{\rm A}$ against $1/\delta$ for TCA, TCE, and toluene. The plots are linear. The liquid-phase mass transfer coefficients, $k_{\rm I}^{\rm A}$ for TCA, TCE, and toluene were obtained from the slopes of the plots. The membrane diffusivities were calculated from the intercepts. The calculated values of the boundary layer mass transfer coefficient and the membrane diffusivity are presented in Table 1. Dotremont et al. (21), who worked on the pervaporation of volatile organics using a silicone membrane, reported k_L values in the same range as obtained in this work. We conducted a set of experiments at different feed flow rates. The corresponding flux and selectivity data from these

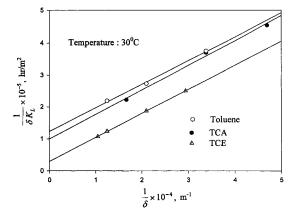


FIGURE 7. Mass transfer resistance plot.

TABLE 1. Equilibrium and Transport Parameters of the Model Organic Compounds^a

parameter	TCA	TCE	toluene
sorption coeff,	2.723×10^{-3}	2.497×10^{-3}	1.690×10^{-3}
k_L (m/s) D_m (m ² /s) solubility in water ^b (%)	$3.660 \times 10^{-5} \\ 8.113 \times 10^{-12} \\ 0.15$	3.646×10^{-5} 2.567×10^{-11} 0.11	$\begin{array}{c} 3.745 \times 10^{-5} \\ 3.774 \times 10^{-12} \\ 0.053 \end{array}$

^a Feed flow rate = 0.108 m³/h; temperature = 30 °C. ^b At 25 °C.

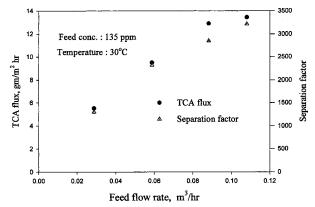


FIGURE 8. Effect of feed flow rate on flux and separation factor (permeation of TCA).

experiments were plotted in Figure 8. Both the flux and the selectivity were reduced remarkably at lower feed flow rates.

Separation of Multicomponent Mixtures. To test the resistance-in-series model and to identify possible coupling effects among the organic fluxes, experiments were done on aqueous solutions of TCA, TCE, and toluene at different concentrations. In contrast to the experimental fluxes so obtained, fluxes were also calculated using $k_{\rm L}^{\rm A}$, $D_{\rm m}^{\rm A}$, and the sorption equilibrium constants for the individual components. The experimental and calculated flux data are plotted in Figure 9. The good fit between the experimental and calculated data establishes the validity of the model as well as the absence of any flux coupling effect.

Temperature Effect. Corresponding to TCA pervaporation tests at selected temperatures, several experiments were done on pure water permeation. Fluxes of both TCA and water were found to increase substantially with temperature. To have a quantitative estimate of the temperature effect, a semilog plot of the organic flux against 1/T was prepared (Figure 10a). The overall activation energy of pervaporation was calculated from the slope of the plot and was found to

TABLE 2. Separation of VOCs from Field Soil Washings^a

^a Downstream pressure = 1 Torr

fee	d concn (p	pm)	perm	eate concn	(wt %)		flu	x (g m ⁻² h	⁻¹)		sep	aration fa	ctor
TCA	TCE	PCE	TCA	TCE	PCE	TCA	TCE	PCE	water	total	TCA	TCE	PCE
110 81.4 65.4	696 474.5 394.1	102.4 76.9 59.2	8.38 8.2 7.82	63.23 63.2 58.7	10.57 6.1 6.0	7.37 6.22 5.0	55.96 47.1 37.6	9.35 4.53 3.92	15.8 15.8 17.5	88.5 74.6 64.0	4237 4819 4370	5084 6265 5444	5776 3731 3778
47.1	274.6	45.8	7.47	57.7	6.0	3.7	28.6	3.03	14.7	49.5	5340	7075	4506

Calculated flux 14 TCA -TCE ---12 Toluene 10 gm/m² Flux, TCA flux TCE flux Toluene flux 100 120 140 160 Feed concentration, ppm

FIGURE 9. Experimental and caluculated flux values for mixtures of organics.

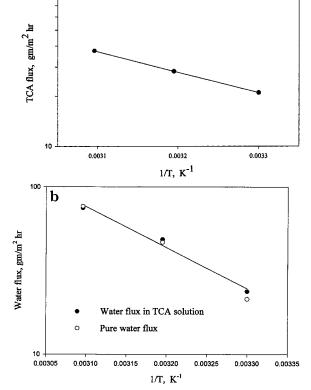


FIGURE 10. (a) Temperature dependence of TCA flux, Arrhenius plot. (b) Temperature dependence of water flux, Arrhenius plot.

be 5.6 kcal/gmol. A similar plot for pure water permeation and that for water flux from solutions of TCA practically coincided (Figure 10b), indicating that there were no coupling effects for water transport either. The activation energy for water permeation is 12.3 kcal/gmol, which is about double that of TCA. This enhanced activation energy for water

permeation as compared to the organic permeation at elevated temperatures resulted in a substantial fall (50%) in the separation factor. Watson and Pyne (7), however, reported a lower activation energy of water transport through a PDMS membrane.

Separation of a Field Sample. A set of experiments was conducted on the removal of TCA, TCE, and perchloroethylene (PCE) from a soil-washing sample from a contaminated site. The sample also contained isopropyl alcohol, a surfactant, emulsified grease, and mineral oil. Four experiments were done using the field sample at four dilutions. The results, presented in Table 2, show that the S-B-S membrane effectively separated these compounds from the surfactant- and oil-laden aqueous emulsions of the organics. However, the fluxes were slightly lower than those for emulsion-free aqueous solutions, although separation factors were higher. It is inferred that the oil and grease in the emulsion formed a coating on the membrane surface, thereby reducing the water flux and affecting the equilibrium distribution of the organic between the solution and the membrane.

Notations

Nota	UONS			
\boldsymbol{C}	solute concentration (kmol/m³)			
D	diffusivity (m ² /s)			
H	distribution coefficient			
J	flux of a solute (kmol $m^{-2} s^{-1}$)			
\boldsymbol{k}	boundary layer mass transfer coefficient (m/s)			
K	overall mass transfer coefficient (m/s)			
X	mole fraction of a solute			
\boldsymbol{z}	transverse coordinate (m)			
α	separation factor			
δ	membrane thickness (m)			
ρ	density (kmol/m³)			
Subscripts and Superscripts				

A	solute A
b	bulk phase
i	interface
L	liquid phase
m	membrane phase

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