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Perstraction of Phenolic Compounds from Aqueous Solution Using a Nonporous Membrane

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ABSTRACT

An exploratory study of nondispersive extraction of various phenolic solutes using a nonporous membrane has been carried out. Sorption and permeation data for these solutes have been obtained using a silicone rubber membrane. The effects of hydrodynamic factors, concentration of phenols, and temperature on the transmembrane flux are discussed. A film model is used to determine the intrinsic mass transfer characteristics of the membrane. Comparison of sorption of phenolic solutes from the membrane into the organic solvent indicates that methyl isobutyl ketone is a better solvent than butyl acetate.

Key Words. Nonporous membrane; Perstraction; Phenols

INTRODUCTION

Conventional extraction which involves the dispersion of one liquid phase into another poses a number of problems in some situations. For instance, in systems with emulsifying tendencies (low interfacial tension and low density difference), the dispersion is difficult to break, and carryover or loss of the solvent occurs. Previous work (1, 2) has shown that nondispersive solvent extraction (NDSE) can overcome these problems.

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Kiani et al. (2) studied the extraction of acetic acid in butyl acetate using a porous membrane. Uramoto et al. (3) studied the extraction of phenol in butyl acetate using a porous membrane. Netke and Pangarkar (4) used both porous and nonporous membranes for the extraction of naphthenic acids in aqueous sodium hydroxide. Porous membranes, such as those used by Kiani et al. (2), have the drawback that a breakthrough of the phase filling the pores can occur unless an interface immobilizing pressure is maintained (5), Netke and Pangarkar (4) showed that although the porous membranes yield higher solute fluxes than nonporous membranes, the latter do not have the drawback of solvent breakthrough. The present work is a continuation of the work reported by Netke and Pangarkar (4).

Phenolic compounds pose severe pollution problems in industrial processes because of their toxicity. Typical concentrations of these compounds found in industrial liquid effluents make such streams amenable to solvent extraction processes for their removal. The present work deals with the NDSE of some phenolic compounds using a nonporous membrane. A silicone rubber (polydimethyl siloxane, PDMS) membrane was used in this work because of its high sorption selectivity for organics and higher solute diffusion coefficients. The former arises out of the hydrophobic/organophillic nature of PDMS while the latter is a result of the flexibility of the Si—O linkages in PDMS.

THEORETICAL

Netke and Pangarkar (4) discussed the relevant theory of extraction using a dense membrane. In the absence of external film resistances on the feed and extract sides the flux for the solute across the membrane can be written as (Fig. 1)

$$J = k_m(C^*_{mw} - C^*_{mo}) \tag{1}$$

where C^*_{mw} is the membrane phase concentration of the solute on the aqueous side in equilibrium with the solute concentration in the aqueous phase, and C^*_{mo} is the membrane phase concentration of the solute on the organic side. C^*_{mw} and C^*_{mo} are related to the corresponding bulk aqueous and organic concentrations by the following equations, respectively:

$$S_w = C^*_{mw}/C_{bw} \tag{2}$$

$$S_o = C^*_{mo}/C_{bo} \tag{3}$$

Using Eqs. (2) and (3), Eq. (1) can be rewritten as

$$J = k_m(S_wC_{bw} - S_oC_{bo}) \tag{4}$$

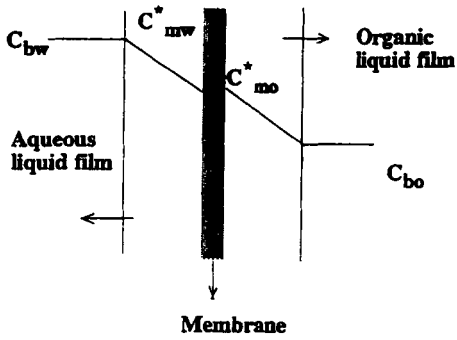

FIG. 1 Concentration profile of diffusing solute in nonporous membrane.

According to Eq. (4), the flux increases with an increase in S_w and a decrease in S_o. Alternatively, we find from Eq. (2) that a membrane which sorbs the solute to a higher extent and from Eq. (3) that a solvent which has a greater ability to extract the solute from the membrane should yield higher fluxes. A differential material balance for a batch system yields the following equation:

$$-V_w\left(\frac{dC_{bw}}{dt}\right) = A_m k_m (S_o C_{bo} - S_w C_{bw}) \tag{5}$$

Integration of Eq. (5) yields the intrinsic membrane mass transfer coefficient, k_m, as follows:

$$k_m = \frac{V_w}{A_m t} \int_{C_{bwi}}^{C_{bwf}} \frac{dC_{bw}}{S_w C_{bw} - S_o C_{bo}} \tag{6}$$

k_m, in turn, is given by

$$k_m = D_m/\delta \tag{7}$$

Thus, by knowing k_m and the membrane thickness δ, the diffusivity, D_m of the solute in the membrane can be calculated.

EXPERIMENTAL

The solvent used for extraction of the phenols was butyl acetate. Silicone rubber, kindly supplied by Wacker Chemie, Germany, was used as the membrane material. Netke and Pangarkar (4) described the membrane

casting procedure used in this work. Extraction of the following solutes was studied: phenol, *p*-chlorophenol, *o*-cresol, *m*-cresol, and *p*-cresol. All these solutes are industrially relevant in terms of pollution.

Sorption

According to Eq. (6) values of both S_o and S_w are needed for evaluation of k_m. PDMS membranes were equilibrated with aqueous and organic solutions containing a known weight fraction of the solute at a constant temperature for a period of 96 hours. The membrane was wiped with a tissue paper to remove superfluous solution and then weighed. The solution left behind was analyzed by UV spectrophotometry for the solute on a Perkin-Elmer λ 3B UV-Vis spectrophotometer. The sorbed concentration of the solute was calculated from a material balance involving the total increase in the membrane weight and the initial and final concentrations of the solute in the solution used for equilibration. Sorption of phenols in methyl isobutyl ketone was carried out in the same way except that the concentration of phenols was determined based upon the absorbances in the visible range with the aid of 4-aminoantipyrene (6) due to interference of absorbances in the UV region.

Permeation

The equipment used for permeation studies (4) consisted of two glass vessels of 300 cm^3 capacity connected by a bridge in which the membrane was located. These vessels were provided with baffles and stirrers. Both the aqueous and organic phases were sampled periodically and analyzed by UV spectrophotometry. The swollen membrane thickness δ, required for use in Eq. (7), was measured with a thickness gauge.

RESULTS AND DISCUSSION

Sorption

Membrane/Aqueous Phase

Figures 2a, 2b, and 2c show plots of the membrane phase concentration of the solute versus the aqueous phase concentration of the solute. It is evident that all the phenols studied in this work exhibit a linear sorption isotherm typical of Henry's law. Henry's law is generally valid for dilute solutions (7). In the present work the maximum concentration used was 6000 ppm, which is well within the dilute region. However, it is possible that the isotherm may be different at higher concentrations of the phenols. The sorption coefficients of the various phenols are not significantly different (Tables 1a and 1b). In the small range of variation, the following order

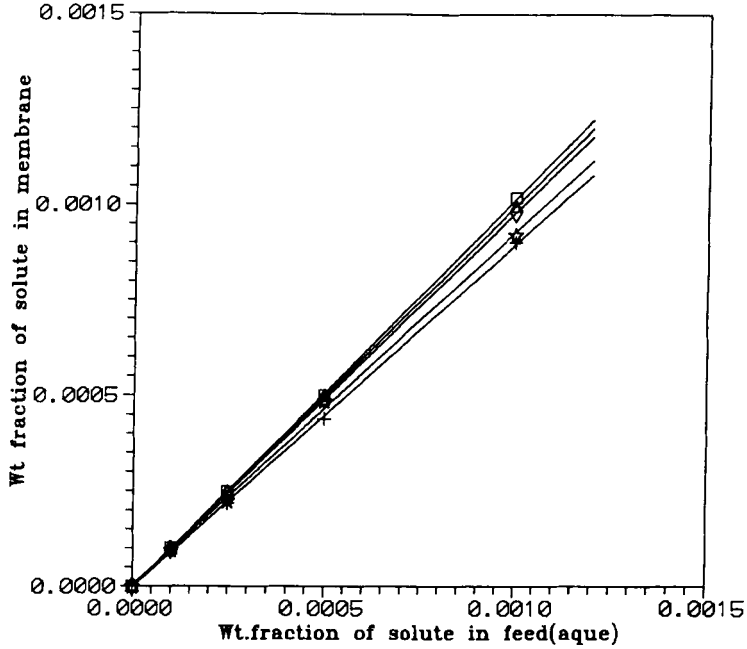

FIG. 2a Sorption in water at 30°C: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

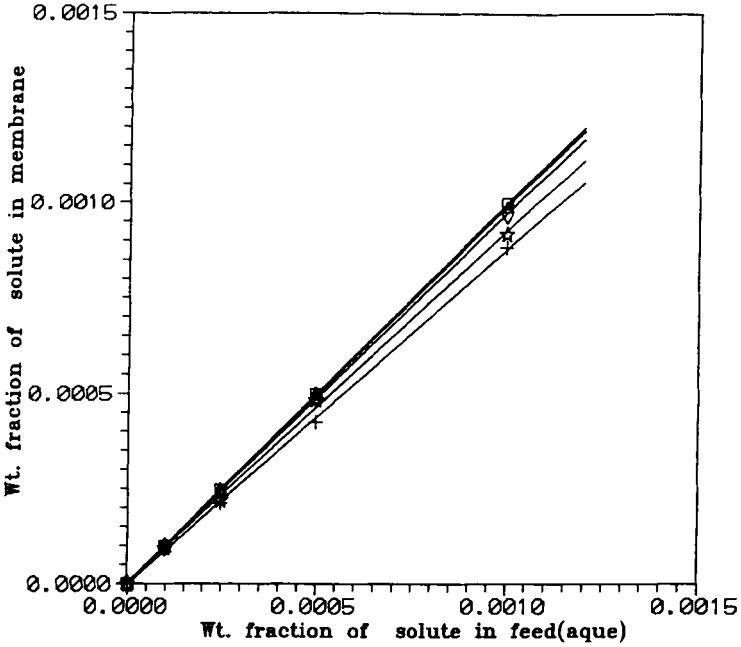

FIG. 2b Sorption in water at 40°C: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

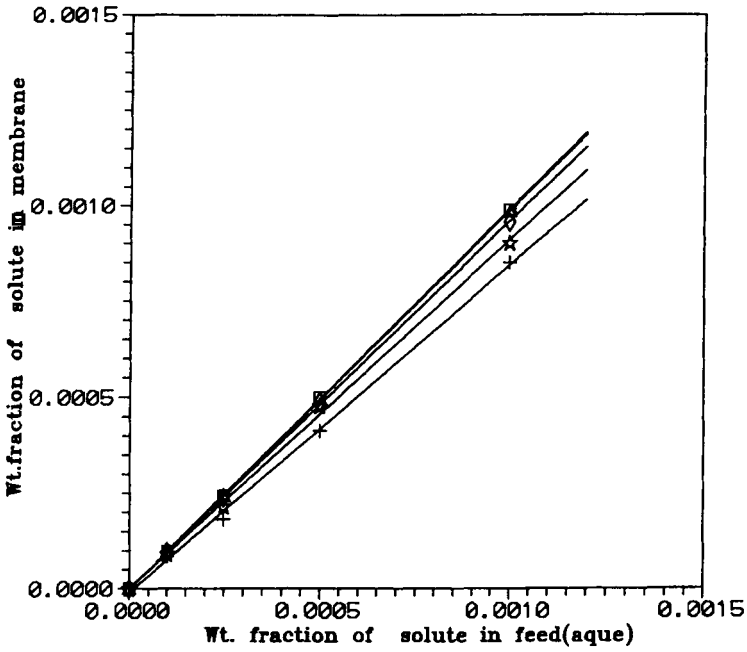

FIG. 2c Sorption in water at 50°C: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

TABLE 1a
Sorption Coefficient and Heat of Sorption of Various Phenols

Type of phenol	Sorption coefficient in aqueous phase, S_w, at 30°C	Sorption coefficient in organic phase (BuAc[a]), S_o at 30°C	Sorption coefficient in organic phase (MIBK[b]), S_o at 30°C	Heat of sorption from aqueous phase, ΔH_{sw}, (kJ/mol)	Heat of sorption from organic phase (BuAc), ΔH_{So}, (kJ/mol)
Phenol	1.02	1.00	0.76	−1.17	−4.33
p-Cresol	1.00	0.98	0.73	−0.50	−2.61
m-Cresol	0.98	0.95	0.68	−0.98	−5.49
o-Cresol	0.93	0.83	0.66	−0.80	−5.08
p-Chlorophenol	0.90	0.83	0.66	−2.14	−6.28

[a] Butyl acetate.
[b] Methyl isobutyl ketone.

TABLE 1b
Heat of Sorption of Various Phenols in MIBK

Type of phenol	Heat of sorption from organic phase (MIBK), ΔH_{S_o} (kJ/mol)
Phenol	−1.65
p-Cresol	−2.47
m-Cresol	−3.51
o-Cresol	−3.29
p-Chlorophenol	−4.02

of sorption coefficients is independent of the temperature variation: phenol > *p*-cresol > *m*-cresol > *o*-cresol > *p*-chlorophenol.

Membrane/Organic Phase

Figures 3a, 3b, and 3c show plots of the sorption data for the cases using butyl acetate as the solvent. These isotherms also follow Henry's

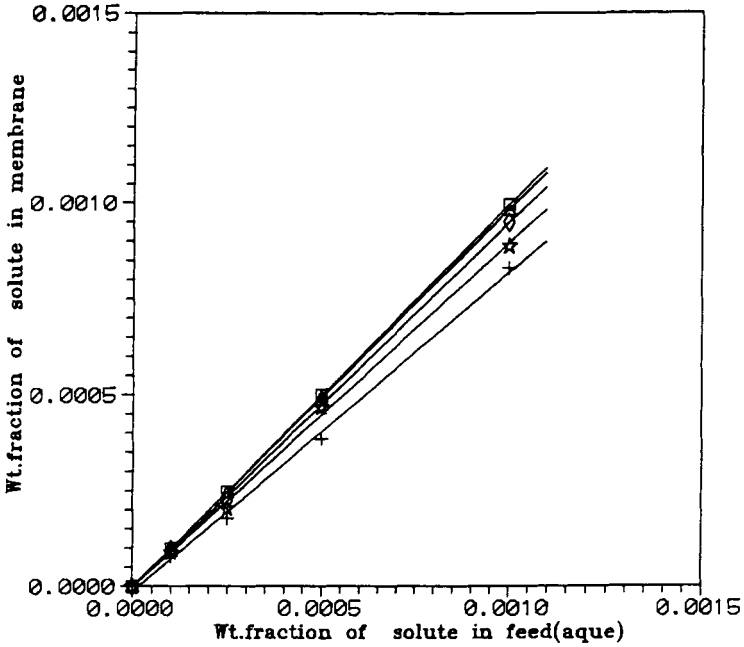

FIG. 3a Sorption in butyl acetate at 30°C: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

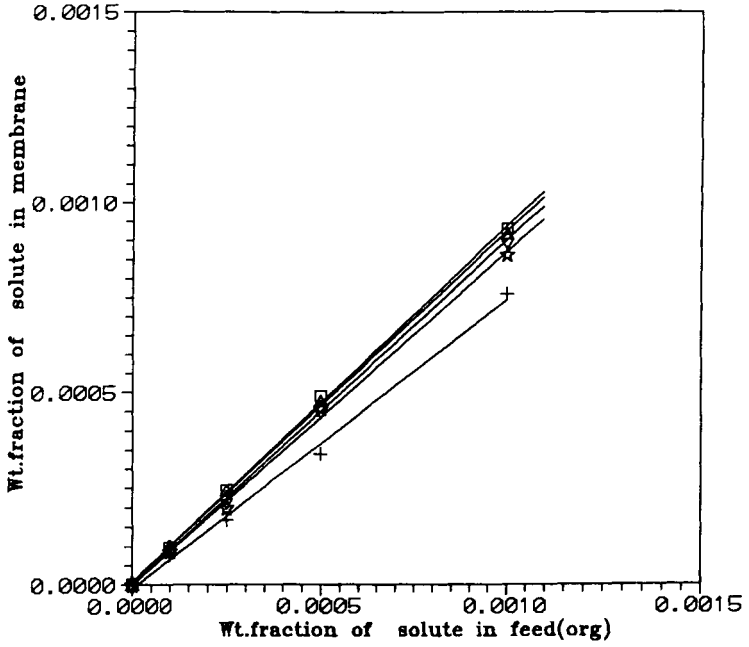

FIG. 3b Sorption in butyl acetate at 40°C: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

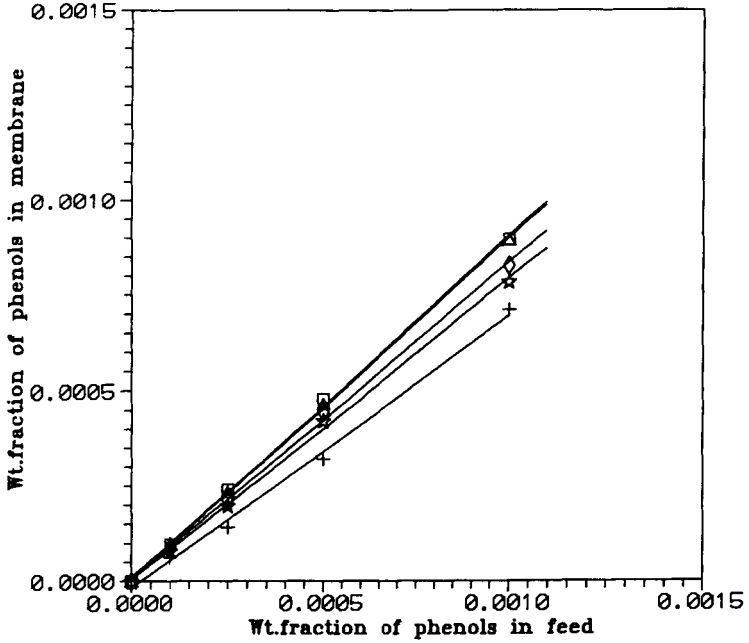

FIG. 3c Sorption in butyl acetate at 50°C: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

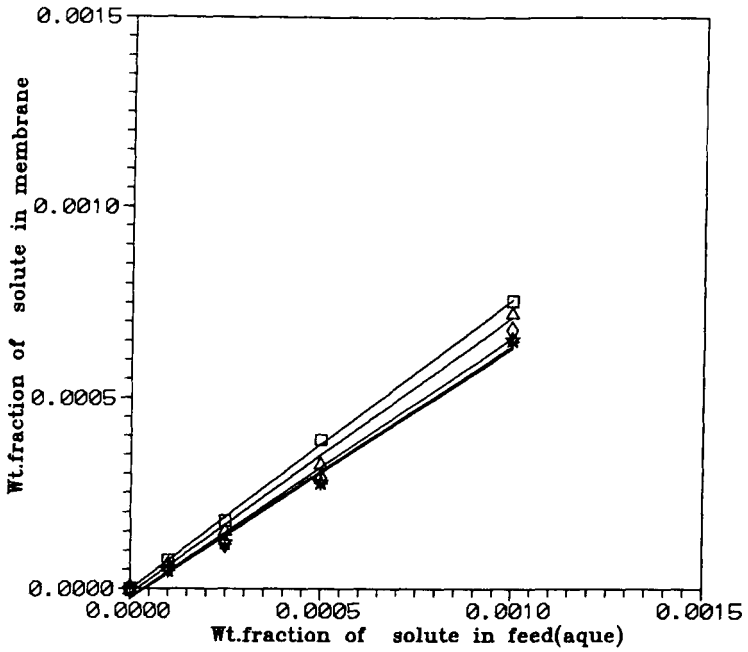

FIG. 3d Sorption in methyl isobutyl ketone at 30°C: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

law, and the order of sorption coefficients is also similar to that for sorption between the membrane/aqueous phase. On the extract side, S_o should be low (as mentioned earlier) when a high flux is desired. The order of the sorption coefficients is practically the same as that given earlier for the aqueous phase. S_w values are approximately 5% higher than S_o values for the various solutes. The heats of sorption of the solutes studied are given in Tables 1a and 1b.

Figure 3d shows plots of the sorption data of all the solutes in methyl isobutyl ketone. The sorption coefficients, S_o, with methyl isobutyl ketone as the extracting solvent are lower than those with butyl acetate, indicating better extraction of phenols with methyl isobutyl ketone.

Permeation

These studies were carried out to obtain the intrinsic mass transfer coefficient (Eq. 6) and from it the diffusion coefficient of solute in the membrane phase (Eq. 7).

Effect of Hydrodynamic Conditions on the Solute Flux

The effect of hydrodynamic conditions needs to be eliminated in order to obtain the intrinsic membrane phase mass transfer coefficient. In the present case the hydrodynamic conditions are defined by the speed of agitation. Since there are two external mass transfer resistances, in the aqueous phase and in the organic phase, the effects have to be separately studied and eliminated.

Aqueous Phase

Figure 4a shows the variation of the solute flux with the speed of agitation for all the solutes studied. For this study the speed of agitation on the organic side was maintained at a relatively high value of 27 rev/s. It is evident from Fig. 4a that the flux is independent of the speed of agitation at and above 20 rev/s, implying that the liquid film resistance on the aqueous side is eliminated at these conditions.

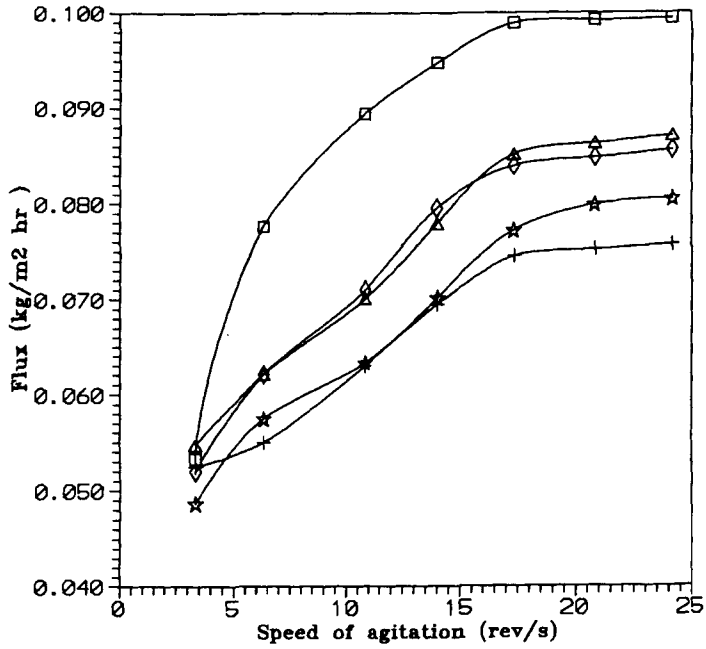

FIG. 4a Variation of flux with speed of agitation in the aqueous phase compartment: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

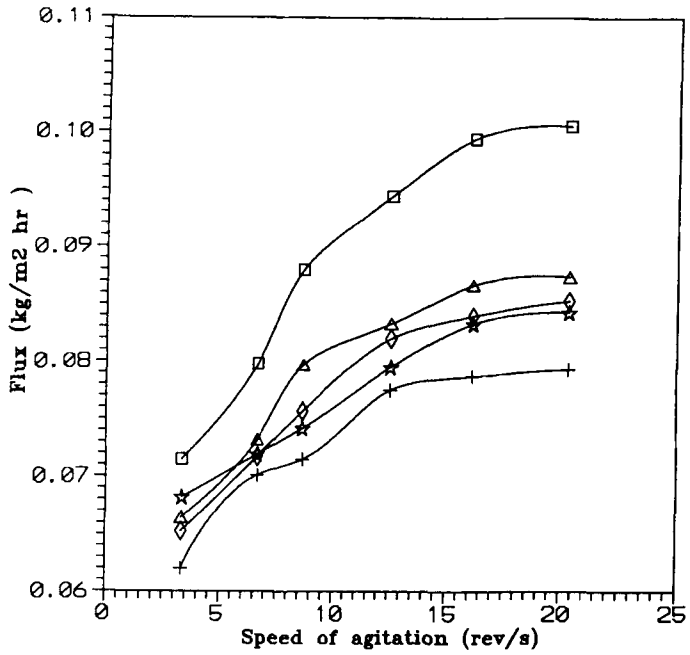

FIG. 4b Variation of flux with speed of agitation in the organic phase compartment: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

Organic Phase

The effect of the speed of agitation in the organic phase was studied by maintaining the speed of agitation in the aqueous phase at 27 rev/s. The plot of flux versus speed of agitation (Fig. 4b) indicates that, similar to the situation for the aqueous phase, the organic phase external mass transfer resistance is eliminated at speeds of agitation of 20 rev/s and above.

In view of the above observations, all further experiments were conducted at a speed of agitation of 27 rev/s in both phases. Under these conditions the extraction of the solute is unambiguously controlled by the membrane phase resistance, and Eq. (6) is valid.

Effect of Solute Concentration on the Flux

Figure 5 shows the variation of the solute flux, J, with the solute concentration in the aqueous phase. It is evident that J is a linear function of the

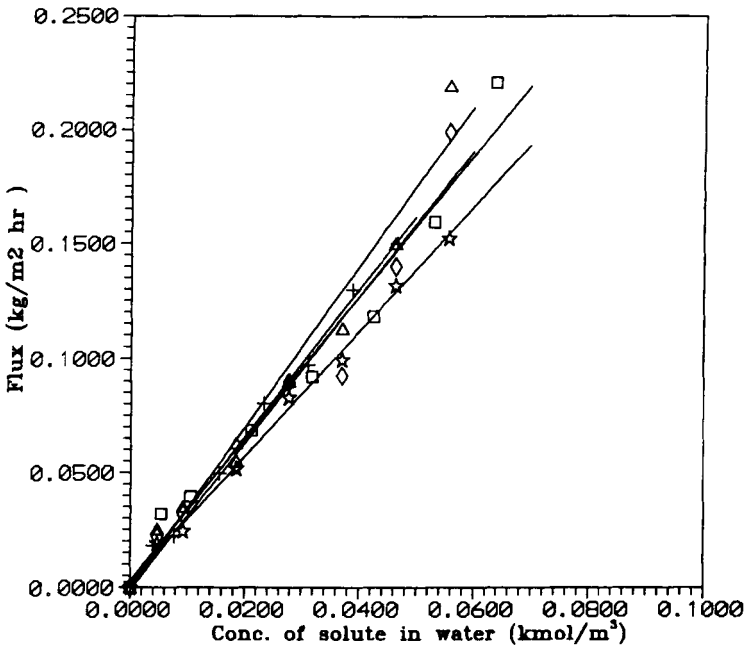

FIG. 5 Variation of flux with feed concentration: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

aqueous phase solute concentration, in conformity with a conventional extraction process without any membrane.

Effect of Temperature on the Flux

The effect of temperature on the flux was studied by varying the temperature from 30 to 50°C for all the solutes. Arrhenius plots for the data obtained are shown in Fig. 6. From these plots the activation energy for permeation, ΔE_p, was calculated for each solute studied. Table 2 gives the ΔE_p values for the various solutes. ΔE_p is a combined effect of the temperature dependence of sorption and diffusion (3) according to the following equation:

$$\Delta E_p = \Delta H_S + \Delta E_D \tag{8}$$

Using the ΔH_S values obtained from sorption data and the ΔE_p values obtained above, ΔE_D was calculated for each solute. These values are also listed in Table 2. The values of the diffusion coefficient, D_m, for all

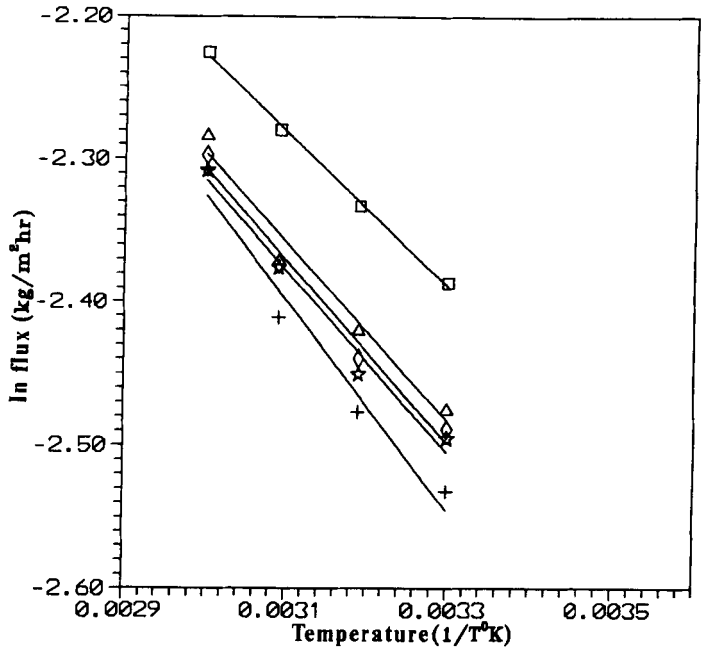

FIG. 6 Variation of flux with temperature: (□) phenol, (△) *p*-cresol, (◇) *m*-cresol, (☆) *o*-cresol, (+) *p*-chlorophenol.

the phenols and their kinetic diameters are also listed in Table 2. The kinetic diameter values of these phenols have been calculated from their bond lengths and bond angles (8). The kinetic diameter is a good indication of the diffusion coefficient, at least for isomers. The diffusion coefficient

TABLE 2
Values of ΔE_p, ΔE_D, k_m, and D_{30} for Various Phenols

Type of phenol	Activation energy for permeation, ΔE_p (kJ/mol)	Activation energy for diffusion, ΔE_D (kJ/mol)	Membrane phase mass transfer coefficient, k_m (m/s)	Kinetic diameter (Å)	Diffusion coefficient at 30°C, D_{30} (m^2/s)
Phenol	4.50	1.34	3.61×10^{-5}	6.00	19.80×10^{-10}
p-Cresol	5.16	3.05	2.40×10^{-5}	6.00	13.10×10^{-10}
m-Cresol	5.27	0.75	2.07×10^{-5}	6.53	11.40×10^{-10}
o-Cresol	5.29	1.01	1.80×10^{-5}	6.68	9.90×10^{-10}
p-Chlorophenol	6.09	1.95	1.46×10^{-5}	6.00	8.00×10^{-10}

values of cresols in Table 2 increase with a decrease in kinetic diameter for the isomeric cresols studied in this work. However, for the other solutes, phenol and *p*-chlorophenol, other factors such as interactions of the solute with the polymer phase, which can be substantially different, also play a role, and the kinetic diameter alone may not be a good indicator.

NDSE can also be carried out using porous membranes, as mentioned earlier. However, in this latter case an interface immobilizing pressure difference has to be carefully maintained to prevent solvent breakthrough (5). In the event of failure to maintain such a pressure difference, solvent breakthrough can occur and the advantages of NDSE are lost. Nonporous membranes do not require the maintenance of such a pressure difference, and thus the operation is trouble-free. On the other hand, nonporous membranes afford lower (approximately 40%) mass transfer coefficients than do porous membranes, as shown by Netke and Pangarkar (4). The lower mass transfer coefficient can be overcome by providing a higher membrane area, but this increases the capital cost of the equipment. The organic extractant has an influence on flux in the NDSE which is similar to that in conventional liquid extraction. A powerful solvent (low S_o) increases the driving force (Eq. 4) and yields higher fluxes.

CONCLUSION

An exploratory study of the nondispersive extraction of phenolic solutes using a nonporous silicone rubber membrane has been reported. Sorption studies with butyl acetate and methyl isobutyl ketone indicate that the latter is a better solvent for all the solutes studied. The permeation data have been used to calculate the intrinsic membrane phase mass transfer coefficient and consequently the diffusion coefficient of the solute in the membrane.

NOMENCLATURE

A_m	area of membrane (m^2)
C_{bo}	bulk phenols concentration in the organic phase ($kmol/m^3$)
C_{bw}	bulk phenols concentration in the aqueous phase ($kmol/m^3$)
C^*_{mo}	solute concentration in the organic phase at the membrane organic interphase ($kmol/m^3$)
C^*_{mw}	solute concentration in the membrane on the aqueous side in equilibrium with solute concentration in the aqueous phase
D_m	diffusion coefficient of solute (m^2/s)
J	molar flux ($kmol/m^2 \cdot s$)
k_m	membrane phase mass transfer coefficient (m/s)

S_o membrane sorption coefficient for the organic phase (—)
S_w membrane sorption coefficient for the aqueous phase (—)
t duration of experiment (s)
V volume of the aqueous phase in the vessel (m^3)

Greek Symbol

δ thickness of the membrane (m)

Subscripts

b bulk phase
m membrane phase
o organic phase
w aqueous phase
i initial
f final

Superscript

* equilibrium value

REFERENCES

1. L. T. C. Lee, W. S. Ho, and K. J. Liu, "Membrane Solvent Extraction," US Patent 3,956,112 (1976).
2. A. Kiani, R. R. Bhave, and K. K. Sirkar, "Solvent Extraction with Immobilized Interfaces in a Microporous Hydrophobic Membrane," *J. Membr. Sci.*, *20*, 125 (1984).
3. H. Uramoto, N. Kawabata, and M. Teramoto, "Transport of Phenol from Aqueous Solution to Organic Solvent through a Microporous Membrane Made of Crosslinked Poly(4-vinylpyridine)," *Ibid.*, *62*, 219 (1991).
4. S. Netke and V. G. Pangarkar, "Extraction of Naphthenic Acid from Kerosene Using Porous and Nonporous Polymeric Membranes," *Sep. Sci. Technol.*, *31*(1), 63 (1996).
5. K. K. Sirkar, "Immobilized-Interface Solute-Transfer Apparatus," US Patent 4,789,468 (1968).
6. S. Gottlieb and P. B. Mass, "Quantitative Determination of Phenolic Fungicides," *Ind. Eng. Chem., Anal. Ed.*, *18*, 16 (1946).
7. J. M. Prausnitz, *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice-Hall, Englewood Cliff, NJ, 1969.
8. A. Raychoudhuri and V. G. Gaikar, "Adsorptive Separation of 2,6-Xylenol/Cresol Mixture with Zeolites," *Sep. Technol.*, *5*, 91 (1995).

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