Contribution of Adsorptive or Acid–Base Interaction Between Phenol Molecules and Polyvinylpyridine Membrane to the Large Permeability of Phenol through the Membrane

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SYNOPSIS

Permeability of phenol from aqueous solution to organic solvent through a microporous membrane made of cross-linked poly(4-vinylpyridine) (polyvinylpyridine membrane) was about 12 times larger than that through a microporous membrane made of polyethylene (polyethylene membrane) having similar thickness, porosity, and mean pore diameter with those of polyvinylpyridine membrane. Adsorptive or acid–base interaction between phenol molecules and polyvinylpyridine membrane was shown to play an important role in this unusually rapid permeation of phenol through the membrane. The amount of phenol contained in polyethylene membrane per unit volume of the pores was about six times larger than the phenol concentration in the feed aqueous solution. However, the amount of phenol contained in polyvinylpyridine membrane per unit volume of the pores was 80–260 times larger than the feed phase concentration. The rapid permeation of phenol through polyvinylpyridine membrane was thus explained in terms of the extensive enrichment of phenol in the membrane due to the adsorptive or acid–base interaction between phenol molecules and the membrane. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Highly efficient liquid–liquid extraction through a microporous membrane has been used for transport of organic materials from aqueous solution to organic solvent.[1-4] A recent publication from this laboratory[5] reported unusually rapid permeation of phenol from aqueous solution to butyl acetate through a microporous membrane made of cross-linked poly(4-vinylpyridine) (polyvinylpyridine membrane). The membrane showed a remarkably larger permeability for phenol when compared with commercial membranes made of polyethylene, polypropylene, and polytetrafluoroethylene. The permeability of phenol through the polyvinylpyridine membrane was large and the diffusional resistance through the membrane appeared to be ignored compared to the diffusional resistance in the feed phase.

However, cross-linked poly(4-vinylpyridine) (polyvinylpyridine resin) had been developed in our laboratory as a polymeric adsorbent for removal and recovery of phenol[6] and carboxylic acids[7] from aqueous solution. Acid–base and hydrophobic interactions between the surface of the polyvinylpyridine resin and these acidic organic materials were shown to play important roles in the adsorption.[8] We wonder, therefore, if there is an influence of the adsorption of phenol on the polyvinylpyridine membrane, or that of any acid–base interaction between phenol molecules and the pyridine residue that is a characteristic functional group of the polyvinylpyridine membrane, in the unusually rapid permeation. In this work, we have investigated the contribution of such adsorptive or acid–base interaction between phenol molecules and the polyvinylpyridine membrane to the rapid permeation of phenol through the membrane.

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EXPERIMENTAL

Materials

Reillex X-425 of pigment size (Reilly Corp. Indianapolis, IN) was used as the polyvinylpyridine resin. The resin consisted of 75 mol % of 4-vinylpyridine and 25 mol % of divinylbenzene. The polyvinylpyridine membrane was prepared by kneading and sheeting of a 4 : 1 : 5 (w/w/w) mixture of this polyvinylpyridine resin, crushed polyethylene (Idemitsu PE-640UF, Idemitsu Petroleum Company, Tokyo, Japan), and process oil, followed by removal of the process oil by extraction with hexane according to the procedure reported in the preceding paper.[5] Thickness, porosity, and mean pore diameter of the polyvinylpyridine membrane were 200, 0.50, and 0.08 μm, respectively. For comparison, a commercial product of battery separator Fp-1 made of polyethylene (Asahi Chemical Industry Co., Osaka, Japan) was used as a microporous membrane made of polyethylene (polyethylene membrane). Thickness, porosity, and mean pore diameter of the polyethylene membrane were 250, 0.50, and 0.08 μm, respectively. Commercially available phenol, *p*-cresol, *m*-chlorophenol, *p*-chlorophenol, *m*-nitrophenol, *p*-nitrophenol, butyl acetate, 2-heptanone, toluene, 1-decanol, and 4-aminoantipyrine were used without further purification.

Procedure

Transport experiments were performed with the apparatus used in the preceding work,[5] which consisted of a membrane and two glass cells for feed aqueous solution of phenol and receiving organic solvent, respectively. The effective area of the membrane was 20 cm^2, and the volume of each cell was 240 mL. Both phases were stirred by magnetic stirring bars at 300 rpm. The transport experiments were carried out at 30°C. Concentration of phenol in the aqueous solution as well as that in the organic solvent were followed during the transport experiments. The partition coefficient of phenol between aqueous and organic solutions was determined by extraction of phenol from 50 mL aqueous solution by 50 mL organic solvent, which was performed at 30°C using a 300 mL separatory funnel. Experiments of phenol enrichment in polyvinylpyridine and polyethylene membranes were performed at 30°C. An aqueous solution of phenol was placed in the feed cell of the apparatus used for the transport experiments mentioned above, keeping the receiving cell vacant, and the aqueous solution was stirred magnetically at 300 rpm at 30°C. After an equilibrium was obtained, the membrane was taken out of the apparatus, and the phenol contained in the membrane was recovered by extraction from the membrane with ethanol.

Quantitative analysis of phenol and substituted phenols in aqueous and/or organic solutions were performed with a Model UV-150-02 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) with the aid of 4-aminoantipyrine.[9] The concentration was determined based upon the absorptivities.

RESULTS AND DISCUSSION

Rate of Permeation of Phenol through Polyvinylpyridine Membrane

Rate of permeation of phenol from feed aqueous solution to receiving organic solvent through the polyvinylpyridine membrane is expressed by the following equation[5]:

$$-dC_F/dt = PS(C_F - C_S/K)/V_F \qquad (1)$$

Here, C_F and C_S are the concentration of phenol in the feed aqueous phase and in the receiving organic phase, respectively; K, the partition coefficient of phenol between water and the receiving organic solvent; V_F, the volume of the feed aqueous solution; S, the membrane surface area; P, the permeability of phenol through the membrane; and t, the time of the transport experiment.

The partition coefficient, K, is defined as

$$K = (C_S/C_F)_{eq} \qquad (2)$$

and is determined by extraction of phenol from aqueous solution by the organic solvent using a separatory funnel. The permeability, P, is obtained as a constant irrespective of the initial phenol concentration in the feed aqueous phase in the range from 50 to 6000 mg/L. The rate of permeation of phenol through commercial membranes made of polyethylene, polypropylene, and polytetrafluoroethylene is also expressed by eq. (1).

Influence of Phenol Concentration in the Feed Aqueous Phase on the Initial Rate of Permeation

As has been reported in the preceding paper of this work,[5] the polyvinylpyridine membrane shows a remarkably larger permeability for phenol when compared with commercial membranes made of polyethylene, polypropylene, and polytetrafluoroethylene. The unusually rapid permeation of phenol

through the polyvinylpyridine membrane was further demonstrated by some additional experiments.

The rate of permeation of phenol from aqueous solution to organic solvent through polyvinylpyridine and polyethylene membranes is expressed by eq. (1), and permeability, P, is obtained as a constant irrespective of the phenol concentrations. In the case where the initial concentration of phenol in the receiving organic phase, C_S, is zero, the initial permeation rate is proportional to the initial feed phase concentration of phenol, C_{F_0}:

$$-dC_F/dt = PSC_{F_0}/V_F \qquad (3)$$

Transport experiments of phenol through the polyvinylpyridine membrane from aqueous solution to butyl acetate were performed, and the relation between the initial permeation rate and the initial feed phase concentration of phenol is shown in Figure 1. For comparison, transport experiments of phenol through the polyethylene membrane having similar thickness, porosity, and mean pore diameter with those of the polyvinylpyridine membrane were also performed using the same apparatus.

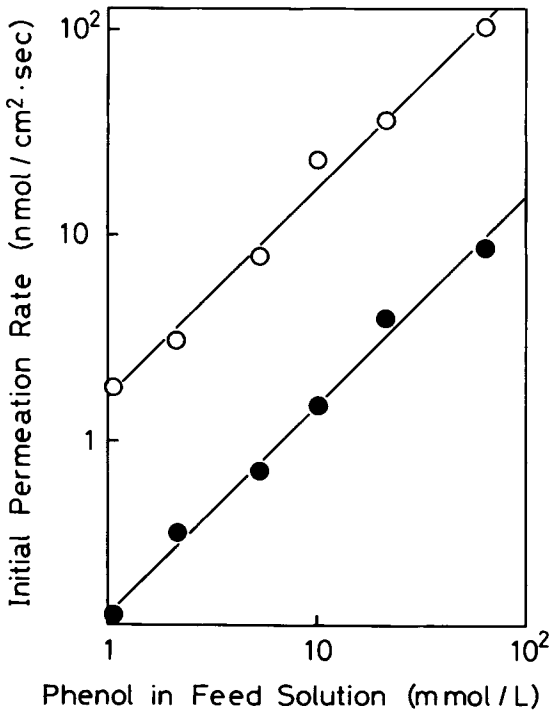

Figure 1 Relation between the initial permeation rate of phenol through polyvinylpyridine membrane (○) and that through polyethylene membrane having a similar thickness, porosity, and mean pore diameter with those of polyvinylpyridine membrane (●) and the initial phenol concentration in the feed aqueous solution. Receiving organic solvent: butyl acetate.

As can be seen in Figure 1, the logarithm of the initial permeation rate through the polyvinylpyridine membrane (open circles) and that through the polyethylene membrane (closed circles) increased with the logarithm of the initial feed phase concentration of phenol, C_{F_0}. However, the permeation rate through the polyvinylpyridine membrane is about 12 times larger than that through the polyethylene membrane. Since the membrane surface area (S) and the volume of the feed aqueous solution (V_F) are the same under the experimental conditions, Figure 1 indicates that permeability of phenol through the polyvinylpyridine membrane is about 12 times larger than that through the polyethylene membrane having similar thickness, porosity, and mean pore diameter as those of the polyvinylpyridine membrane.

Although the porosity and the mean pore diameter are almost equal, the thickness of the polyvinylpyridine membrane (200 μm) is smaller than that of the polyethylene membrane (250 μm), and the permeability should be normalized taking the difference in thickness into consideration. However, the normalized permeability of phenol through the polyvinylpyridine membrane would be still 10 times greater than that through the polyethylene membrane.

Influence of Acidity of Phenol on Its Permeability through the Polyvinylpyridine Membrane

As has been mentioned above, permeability of phenol through the polyvinylpyridine membrane is about 12 times greater than that through the polyethylene membrane having similar thickness, porosity, and mean pore diameter as those of the polyvinylpyridine membrane. A conceivable reason for the large permeability is the adsorptive or acid–base interaction between phenol molecules and the pyridyl group of the membrane during the permeation. To elucidate the contribution of such interaction on the large permeability, we have performed permeation of a series of substituted phenols through polyvinylpyridine membrane and investigated the relation between acidity of phenol and its permeability through the membrane.

In Figure 2, permeability of phenol through the polyvinylpyridine membrane is plotted against Hammett's substituent constant, σ, for the substituent of phenol. Although the permeability depends on the solubility of phenol in the receiving organic solvent, permeability of phenol through the polyvinylpyridine membrane increases with the acidity of phenol. Thus, adsorptive or acid–base interaction between phenol molecules and the pyridyl group of

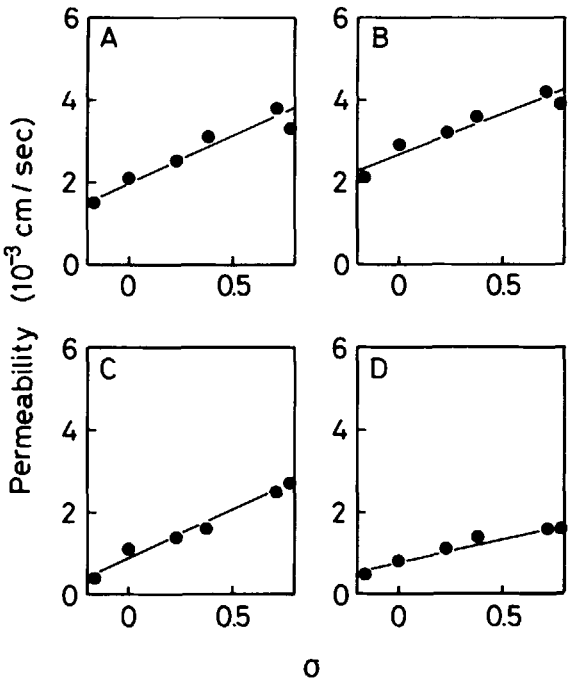

Figure 2 Plots of permeability of a series of substituted phenols from aqueous solution to receiving organic solvent through polyvinylpyridine membrane vs. Hammett's substituent constant, σ, for the substituent of the phenols. Receiving organic solvent: (A) butyl acetate; (B) 2-heptanone; (C) toluene; (D) 1-decanol.

the membrane was shown to play an important role in the large permeability of phenol through the membrane.

Influence of Solubility of Phenol in the Receiving Organic Solvent on Its Permeability through the Polyvinylpyridine Membrane

The difference in solubility of phenol in the receiving organic solvent and that in water would be an important factor that controls the permeability. Solubility of phenol can be evaluated in terms of the partition coefficient of phenol between the organic solvent and water. The partition coefficient is the relative concentration of phenol in the receiving organic phase and that in the feed aqueous phase at the equilibrium measured by extraction experiments using a separatory funnel. Permeability of a series of substituted phenols through the polyvinylpyridine membrane was measured using a variety of organic solvents as the receiving organic phase.

As can be seen in Figure 3, permeability of phenol through the polyvinylpyridine membrane showed a tendency to increase with the partition coefficient, i.e., the permeability tended to increase with the solubility of phenol in the receiving organic solvent. However, it is obvious that the permeability is better correlated with the acidity of phenol (Fig. 2) than with the solubility of phenol in the receiving organic solvent (Fig. 3).

Influence of Phenol Enrichment in the Membrane on the Permeation Rate

As has been mentioned above, permeability of phenol through the polyvinylpyridine membrane was about 12 times greater than that through the polyethylene membrane having similar thickness, porosity, and mean pore diameter as those of the polyvinylpyridine membrane. Adsorptive or acid–base interaction between phenol molecules and the polyvinylpyridine membrane has been shown to play an important role in this unusually rapid permeation of phenol through the membrane. Therefore, enrichment of phenol in the membrane due to such interaction is conceivable. To obtain additional information related to this subject, experiments of phenol enrichment in the membrane were performed.

An aqueous solution of phenol was placed in the feed cell of the apparatus used for the transport experiments mentioned above, keeping the receiving cell vacant. After equilibrium was obtained, the

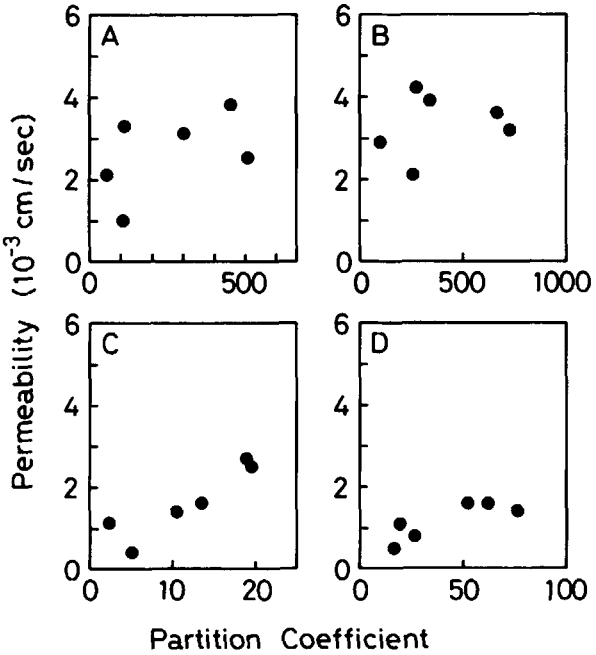

Figure 3 Plots of permeability of a series of substituted phenols from aqueous solution to organic solvent through polyvinylpyridine membrane vs. partition coefficient of the phenols between water and the receiving organic solvent. Receiving organic solvent: (A) butyl acetate; (B) 2-heptanone; (C) toluene; (D) 1-decanol.

Table I Enrichment of Phenol in Polyethylene Membrane and the Permeability of Phenol through the Membrane

C_{F0} [a] (mmol/L)	Contained Phenol (mg)	C_{M0} [b] (mmol/L)	Phenol Enrichment (C_{M0}/C_{F0})	P' [c] (10^{-5} cm/s)
1.06	0.15	6.4	6.0	2.96
2.13	0.30	12.8	6.0	2.94
5.31	0.74	31.4	5.9	2.95
10.63	1.50	63.8	6.0	2.98
21.25	2.88	122.4	5.8	3.12
63.76	9.00	382.5	6.0	2.98

[a] Concentration of phenol in the feed aqueous solution.
[b] Amount of phenol contained in polyethylene membrane per unit volume of the pores.
[c] Revised permeability of phenol through polyethylene membrane defined by eq. (4).

amount of phenol contained in the membrane was determined. The extent of phenol enrichment in the membrane was evaluated by comparison of the amount of phenol contained in the membrane per unit volume of the pores with the concentration of phenol in the feed aqueous solution. Results are given in Tables I and II.

The amount of phenol contained in the polyethylene membrane per unit volume of the pores was about six times greater than the concentration of phenol in the feed aqueous solution (Table I). On the other hand, the amount of phenol contained in the polyvinylpyridine membrane per unit volume of the pores was 80–260 times larger than the phenol concentration in the feed aqueous solution (Table II). Phenol enrichment in the polyvinylpyridine membrane was thus demonstrated to be far more extensive than that in the polyethylene membrane. Based on these observations, the larger permeability of phenol through the polyvinylpyridine membrane than that through the polyethylene membrane having similar thickness, porosity, and mean pore diameter could be explained in terms of the far more extensive enrichment of phenol in the polyvinylpyridine membrane.

The most essential driving force of the permeation of phenol from the feed aqueous solution to the receiving organic solvent would be the difference in phenol concentration between the feed aqueous phase and the receiving organic phase. In the case where the initial concentration of phenol in the receiving organic phase, C_S, is zero, the initial permeation rate is proportional to the initial feed phase concentration of phenol, C_{F_0}, as expressed by eq. (3) and supported by Figure 1.

However, in the case where phenol is enriched in the membrane, the amount of phenol contained in the membrane per unit volume of the pores would be more suitable than the feed phase concentration of phenol. In the case where the initial concentration of phenol in the receiving organic phase is zero, the initial permeation rate would be proportional to the amount of phenol contained in the membrane per unit volume of the pores, i.e.:

$$-dC_F/dt = P'SC_{M_0}/V_F \qquad (4)$$

Table II Enrichment of Phenol in Polyvinylpyridine Membrane and the Permeability of Phenol through the Membrane

C_{F0} [a] (mmol/L)	Contained Phenol (mg)	C_{M0} [b] (mmol/L)	Phenol Enrichment (C_{M0}/C_{F0})	P' [c] (10^{-5} cm/s)
1.06	5.1	271	256	0.76
2.13	9.1	483	227	0.82
5.31	19.0	1009	190	1.04
10.63	37.9	2014	189	1.19
21.25	60.1	3193	150	1.54
63.76	98.5	5233	82	2.70

[a] Concentration of phenol in the feed aqueous solution.
[b] Amount of phenol contained in polyvinylpyridine membrane per unit volume of the pores.
[c] Revised permeability of phenol through polyvinylpyridine membrane defined by eq. (4).

Here, C_{M_0} is the initial amount of phenol contained in the membrane per unit volume of the pores, and P', the revised permeability of phenol through the membrane.

As can be seen in Figure 4, the initial permeation rate through the polyvinylpyridine membrane (open circles) and that through the polyethylene membrane (closed circles) linearly increase with the amount of phenol contained in the membranes per unit volume of the pores. The averaged value of the revised permeability of phenol through the polyvinylpyridine membrane and that through the polyethylene membrane were 1.34×10^{-5} and 2.99×10^{-5} cm/s, respectively.

As has been reported in the preceding paper of this work,[5] 6–10% of the pores of the polyvinylpyridine membrane were occupied by the aqueous phase and the residual 90–94% were occupied by the organic phase during the transport experiments. On the other hand, experiments of the enrichment of phenol in the membrane were performed by placing an aqueous solution of phenol in the feed cell of the apparatus, keeping the receiving cell vacant. In this work, we assumed that the amount of phenol contained in the membrane per unit volume of the pores obtained by the enrichment experiments mentioned above is nearly equal to the amount of phenol contained in the membrane per unit volume of the aqueous phase of the pores during the transport experiments.

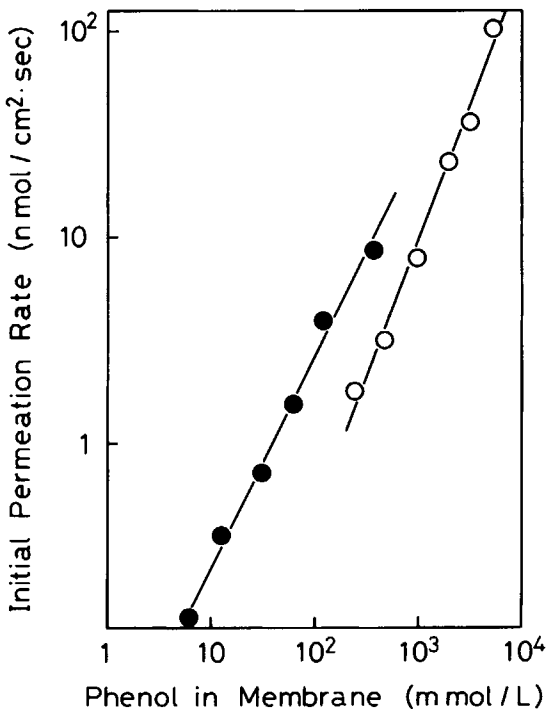

Figure 4 Relation between the initial permeation rate of phenol through polyvinylpyridine membrane (○) and that through polyethylene membrane having similar thickness, porosity, and mean pore diameter with those of polyvinylpyridine membrane (●) and the initial amount of phenol contained in the membranes. Receiving organic solvent: butyl acetate.

The degree of enrichment of phenol in the polyethylene membrane appears to be independent of the concentration of phenol in the feed aqueous solution (Table I). On the contrary, the degree of enrichment of phenol in polyvinylpyridine membrane increased with decrease of the concentration of phenol in the feed aqueous solution (Table II). Enrichment of phenol in the polyvinylpyridine membrane appears to be more extensive at a low concentration of phenol in the feed aqueous solution.

The revised permeability of phenol through the polyvinylpyridine membrane (Table II) was about half that through the polyethylene membrane (Table I). The adsorptive or acid–base interaction between phenol molecules and the polyethylene membrane is perhaps very weak, and the phenol contained in the polyethylene membrane would easily be eluted from the membrane. However, the adsorptive or acid–base interaction between phenol molecules and polyvinylpyridine membrane is probably very strong, and the elution of the enriched phenol from the polyvinylpyridine membrane would be rather difficult. The low value of the revised permeability of phenol through the polyvinylpyridine membrane when compared with that through the polyethylene membrane can be attributed to this difference in the ease of elution from the membranes.

The revised permeability of phenol through the polyethylene membrane appears to be independent of the amount of phenol contained in the membrane (Table I). On the contrary, the revised permeability of phenol through the polyvinylpyridine membrane decreased with decrease of the amount of phenol contained in the membrane (Table II). This difference in the revised permeability would suggest that elution of phenol from the polyvinylpyridine membrane is relatively more difficult when the amount of phenol contained in the membrane is lower.

Liquid–Liquid Extraction of Organic Materials through a Microporous Membrane Made of Polymeric Adsorbent for the Transporting Organic Materials

In membrane extractions, facilitated permeation is of immense interest in the practical application to separation processes. As has been mentioned above, unusually rapid permeation of phenol from the feed aqueous solution to the receiving organic solvent

through the polyvinylpyridine membrane has been explained in terms of the enrichment of phenol in the pores of polyvinylpyridine membrane due to the adsorptive or acid–base interaction between phenol molecules and the membrane. In other words, adsorptive or acid–base interaction between the transporting organic materials and the membrane considerably facilitated the permeation of the organic materials through the membrane. This type of facilitated permeation appears not to be available in the literature. Thus, the solvent extraction described in this report would be a new field of membrane extraction, i.e., liquid–liquid extraction of organic materials through a microporous membrane made of polymeric adsorbent for the transporting organic materials.

On the other hand, there have been several works available in the literature that bear some resemblance to the present work: for example, transport of chloroacetic acid from an aqueous solution through the poly(4-vinylpyridine-*co*-acrylonitrile) membrane to an aqueous sodium hydroxide solution containing sodium chloroacetate.[10] In this report, however, the permeation was not facilitated by the adsorption of the transporting materials on the membrane. Although the report described the transport of an acidic organic material through a membrane containing 4-vinylpyridine as a component, organic solvent was not used as the extractant in the receiving phase, in sharp contrast to the present work.

CONCLUSION

Adsorptive or acid–base interaction between phenol molecules and polyvinylpyridine membrane has been demonstrated to make an important contribution to the unusually rapid permeation of phenol through the membrane. The facilitated permeation of phenol through the polyvinylpyridine membrane seems to develop a new field of membrane extraction, i.e., liquid–liquid extraction of organic materials through a microporous membrane made of polymeric adsorbent for the transporting organic materials. The point of this work is summarized as follows:

1. As shown in Figure 1, the rate of permeation of phenol through the polyvinylpyridine membrane is about 12 times greater than that through the polyethylene membrane having similar thickness, porosity, and mean pore diameter as those of the polyvinylpyridine membrane.
2. As shown in Figure 2, the permeability of a series of substituted phenols through the polyvinylpyridine membrane increased with acidity of the phenols. The result indicates that adsorptive or acid–base interaction between phenol molecules and the polyvinylpyridine membrane plays an important role in the rapid permeation of phenol through the membrane.
3. As shown in Figure 3, permeability of a series of substituted phenols through the polyvinylpyridine membrane showed a tendency to increase with solubility of the phenols in the receiving organic solvent. However, the contribution is not very distinct when compared with the influence of acidity of phenols shown in Figure 2.
4. Enrichment of phenol in the polyvinylpyridine membrane (Table II) is far more extensive than that in the polyethylene membrane (Table I). The unusually rapid permeation of phenol through the polyvinylpyridine membrane appears to be derived from this extensive enrichment of phenol in the membrane.

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