Removal of Trace VOCs from Water Through PDMS Membranes and Analysis of Their Permeation Behaviors

C. K. YEOM,¹ H. K. KIM,² J. W. RHIM³

¹ Chemical Process and Engineering Center, Applied and Engineering Chemistry Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejon 305-606, South Korea

² Energy and Environment Research Team, Research and Development Center, Korea Heavy Industries and Construction Co., Changwon P.O. Box 77, Kyongnam 641-792, South Korea

³ Department of Chemical Engineering, Hannam University 133 Ojung-Dong, Daedeog-Ku, Taejon 300-791

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ABSTRACT: The removal of trace chlorinated hydrocarbons from water has been performed through poly(dimethylsiloxane), which had been fabricated by addition crosslinking reaction. The membrane had a more hydrophobic characteristic than that fabricated by a condensation reaction because it has no polar groups in the polymeric chain, such as hydroxyl and chlorine groups. This study concentrated on the comparison of the permeation behaviors of homologous series of chloromethanes aqueous solutions with that of a chloroethane solution. It was suggested that when the hydrophobic characteristics of a membrane system is greater, water molecules in the membrane tend to exist in the form of clusters; thereby, the permeating size of water component increases, resulting in suppressing water permeation and increasing the enrichment factor for the organic component. The permeation behaviors at various temperatures and membrane thicknesses were indirectly interpreted in terms of the effect of concentration polarization and the effect of interactions of organic–membrane, and water–organic-absorbing membrane. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 601–611, 1999

Key words: volatile organic components; chlorinated hydrocarbon; poly(dimethylsiloxane); pervaporation; water clustering

INTRODUCTION

Pervaporation is very attractive in that polluting compounds or volatile organic compounds (VOCs) are selectively removed from the feed; furthermore, this membrane process can be integrated into existing other process to enhance a separation efficiency. Also, the membrane separation process offers significant opportunities of energy saving and reuse of VOCs, compared to conventional VOC control processes. Baker and coworkers¹ has succinctly delineated the merits of a pervaporation process for organic contaminant removal. However, an adverse limitation on the pervaporation process is that an additional resistance to membrane resistance caused by the socalled "concentration polarization of organic permeant"²⁻⁴ originates from the liquid boundary layer at the membrane interface and contributes negatively to the pervaporation performance in the removal of trace VOCs from aqueous solutions.

Membranes showing high organic permeabilities and low air and water permeabilities are required in the membrane process for the VOC

 $Correspondence \ to:$ C. K. Yeom (E-mail: ckyeom@pado. krict.re.kr).

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permeation. Elastomeric organophilic membranes that preferentially permeate organic compounds but retain water are widely used to remove organic compounds from water. Nijhuis et al.⁵ have prepared a wide range of homogeneous elastomeric membranes, such as nitrilbutadiene rubber (NBR), ethylene-propylene terpolymer (EPDM), and poly(dimethylsiloxane) (PDMS), which showed extremely high pervaporation. In selecting membrane material according to the solution diffusion mechanism by which the pervaporation process is most expressed, physicalchemical interactions with permeating molecules should be taken into account in terms of their solubilities and diffusivities in the membrane material. From this point of view, PDMS or silicone rubbers, which have high permeabilities as well as organophilic characteristics, can be suitable for membrane materials for the removal of VOCs. In addition, PDMS membranes offer a good compromise of high permeabilities and moderate selectivities in most cases and are widely used.

Watson et al.⁶ suggested that enhancing the hydrophobic nature of the PDMS membrane is more effective for the improvement of its separation performance rather than enhancing the organophilic nature of the material, which might cause a membrane mobility to decrease due to both the strong interchain interactions and permeant-polymer interactions. Such an approach to membrane improvement led to a significant reduction in the water permeation and, hence, to a significant improvement in the separation factor in favor of the organic component. In fact, PMDS is a notable hydrophobic material that has a tendency to discourage the passage of water molecules while at the same time allowing the passage of a wide range of larger organic molecules. To this extent, a PDMS membrane tends to behave as a true chemical separator that functions according to the chemical nature of the permeating molecules rather than as a sieve that separates according to size. For this reason, it is an interesting subject for investigation and detailed understanding.

In this study, a series of chlorinated hydrocarbons in their permeation and sorption behavior has been examined through PDMS membranes, which had been fabricated by an addition reaction. The membrane had a more hydrophobic characteristic than that fabricated by a condensation reaction because it had no polar groups in the polymeric chain, such as hydroxyl and chlorine groups, which could be found in the PDMS membranes prepared by the condensation reaction. This study will concentrate on the comparison of the permeation behaviors of a homologous series of chloromethanes and a chloroethane in aqueous solutions. The permeation behaviors at various temperatures and membrane thicknesses will be interpreted by using the effect of concentration polarization and the effect of interactions of organic-membrane and water-organic-sorbed membrane.

EXPERIMENTAL

Materials

n-Hexane (guaranteed reagent) were purchased from Junsei Chemical Co. (Tokyo, Japan). Poly-(dimethylsiloxane) (RTV6166) was generously provided by Dongyang Silicone (Seoul, Korea). It was composed of the following two parts: part A is mainly PDMS oligomers terminated with vinyl groups, and part B is a mixture of Pt catalyst and PDMS oligomer with active hydrogens. Ultrapure, deionized water was used. As model organics, a series of chlorinated hydrocarbons were selected on the basis of their industrial relevance. All the organics were of analytical grade and used without further purification.

Membrane Preparation

In the fabrication of PDMS membrane, a casting solution was prepared by dissolving part A and part B with a ratio of 9 to 1 in *n*-hexane. The casting solution was poured into a glass petri dish and then allowed to dry in a fume hood. Subsequently, it reacted at 100°C for 2 h. The crosslinking reaction took place by addition reaction in which the active hydrogens attack the vinyl groups under Pt catalyst, as depicted in Figure 1. In the membrane fabrication, membrane thickness was controlled by the concentration and amount of the coating solution introduced on known coating area. Scanning electron microscopy (SEM) confirmed that this method could provide a good control of membrane coating thickness.

Swelling Measurements

Swelling measurements⁷ of the crosslinked membranes were performed to determine the amount of an organic solvent absorbed in the membranes. Dry membrane strips were immersed in the organic solvent thermostated at 40°C for 48 h to allow the strips to reach equilibrium sorption.



Figure 1 A crosslinking reaction mechanism of PDMS.

The dimension of a strip was 7×1.5 cm. After measuring the swollen length l of a strip at equilibrium sorption, the strip were dried for 30 h at room temperature under vacuum and then the dry length l_0 was measured. The swelling ratio Rfor an isotropic material is defined as

$$R = \frac{l - l_0}{l_0} \tag{1}$$

The volume fraction v_m of the organic in the swollen membrane can be expressed in the following form:

$$v_m = \frac{R^3 - 1}{R^3} \tag{2}$$

The volume fraction was used as the solubility of a permeant in the membrane. All measurements were repeated four or five times, and the resulting data had standard deviation of $\pm 6\%$.

Pervaporation

A schematic pervaporation apparatus used in this study is illustrated elsewhere.⁸ The membrane cell is made of stainless steel. A feed mixture enters the cell through the center opening, flows radially through the thin channel, and leaves the cell through the side opening, which allows relatively high fluid velocity parallel to a membrane surface. The cell structure is depicted in Figure 2.

The effective membrane area was 19.6 cm^2 . The feed mixture was circulated from the feed tank having a capacity of 2.5 L through the membrane cell. The feed tank was wrapped with the heating tape to heat the feed mixture. The feed mixture temperature was controlled by the temperature controller. The permeate pressure was controlled by the PID controller. The composition of permeate vapor was determined by online gas chromatography (GC) analysis. The permeate vapor was injected directly into one of the columns by the injector for the online measurement of permeate composition. The permeate vapor was collected in the cold trap by liquid nitrogen with a given time interval, heated up to room temperature, and weighed to determine the flux. The enrichment factor of organic was calculated by the following equation:

$$\beta = \frac{Y_{\text{organic}}}{X_{\text{organic}}} \tag{3}$$

where X and Y are the weight fractions of organic in feed and permeate, respectively.

Determination of the Diffusion Coefficients of Organics

The following equations describe the relationship between the diffusion coefficient of a permeant and its flux:

$$J = \frac{1}{l} \int_{C_2}^{C_1} D \ dC = D_{\text{avg}} (C_1 - C_2) / l$$
$$D_{\text{avg}} = \frac{\int_{C_2}^{C_1} D \ dC}{C_1 - C_2} = \frac{J l}{C_1 - C_2}$$
(4)



Figure 2 Schematical representation of the membrane cell.



Figure 3 Aperture restrictor to reduce the membrane area.

where J is the flux of the permeant, l is the membrane thickness, C_1 and C_2 are the concentrations of the permeant in the membrane interfaces at feed side and permeate side, respectively, D is the concentration-dependent diffusion coefficient, and D_{avg} is the average diffusion coefficient of the permeant across the membrane. When permeate pressure is kept low well below the saturated vapor pressure of the permeant, the permeant concentration at permeate side membrane surface C_2 is equal to zero. The average diffusion coefficient of a permeant can be calculated from eq. (4) when J and C_1 are determined experimen-

tally. Usually, the flux of pure organic through the PDMS membrane is very large, and then the permeate pressure increases correspondingly. Therefore, it is not possible to maintain low permeate pressure. In order to maintain the permeate pressure low enough to produce zero C_2 , the aperture restrictor, as depicted in Figure 3, was embedded between the porous metal plate and the membrane in the membrane cell to reduce membrane area from 19.6 to 0.95 cm^2 and, thereby, to decrease the flux. Thus, the permeate pressure could be kept below 5 mmHg. It should be stressed that it is not our intention to derive a generalized possibility to calculate diffusivities from sorption and diffusion experiments. The method mentioned above was able to determine the diffusivities of pure components directly in a relatively easy way. The calculation is done only as we believe that it helps to explain the strange permeation behavior found for the chlorinated hydrocarbon aqueous solutions.

RESULTS AND DISCUSSION

Sorptional and Diffusional Properties of Chlorinated Hydrocarbons in PDMS Membrane

Table I shows the physical properties of the chlorinated hydrocarbons. Some peculiarity can be seen among the chloromethanes. The molar volume of organic increases, and the saturated vapor pressure decreases with increasing the number of chlorine in its moiety. Also, for an organic with a larger number of chlorine, both the solubilities of the organic in water and of water in the organic are smaller. It reveals that the chloromethane becomes more hydrophobic, as going from methylene chloride to carbontetrachloride. Dichloroethane has lower saturated vapor pressure than any chloromethane, although its molar volume and solubility are between those of methylene chloride and chloroform.

Organics	Molar Volume (×10 ⁶ m ³ /mol)	Saturated Vapor Pressure at 25°C (Torr)	Solubility at 25°C (g/L)		
			Organic in Water	Water in Organic	
CH_2Cl_2	64.5	430	13.0	2.0	
CHCl ₃	81.1	199	8.2	0.7	
CCl ₄	96.5	115	0.8	0.1	
$\mathrm{C_2H_4Cl_2}$	78.8	81	8.1	1.5	

 Table I
 Physical Properties of Chlorinated Hydrocarbons¹⁹





Figure 4 Solubilities and diffusivities of chlorinated hydrocarbon in PDMS membrane measured at 35°C.

Liquid sorption and permeation of the selected organics through the PDMS membrane were performed at 40°C to obtain a first overview of their transport behavior. The results were presented in Figure 4. All of the sorptions of the chloromethanes in the membrane increase with increasing number of chlorine atoms or molar volume. This tendency of increasing the solubility with molar volume is commonly known in that solubility increases with the boiling or critical point of the permeant; or to say it in other words, solubility increases with condensability of the permeant.⁹ However, it is found in this study that dichloroethane has a lower solubility in the PDMS membrane than any chloromethane, although it does not have a smaller molar volume or a higher saturated vapor pressure. This observation is not understandable in considering only the effect of the molar volume or saturated vapor pressure of permeant. It could be explained with respect to the thermodynamic characteristic of materials. Basically, an important factor to determine permeant-polymer mutual solubility is the interaction between permeant and membrane material. One of the approaches to describe the interaction between polymer and permeant is the simple solubility parameter theory.¹⁰ The solubility parameters δ_t used in this approach each have the following three components: δ_d , δ_p , and δ_h , separately quantifying the contribution of dispersion forces, polar forces, and hydrogen bondings to the solubility process, respectively. According to this theory, a good solvent for a polymer has a solubility parameter value close to that of the polymer, which is based on the rule of thumb "like

dissolve like." In spite of some restrictions¹¹ on the solubility parameter theory, this approach is popularly used for a first approximation on the affinity between permeant and membrane material. Table II presents the solubility parameter values of the chlorinated hydrocarbons obtained from literature.¹² When the solubility parameter value of a permeant becomes reduced or closer to that of the PDMS membrane, the solubility of the permeant in the membrane has a higher value, as can be seen in Figure 4. Therefore, the reason why dichloroethane has the smallest solubility is that the affinity of the organic towards the PDMS membrane is the lowest in rank, which could be identified by the highest value of its solubility parameter. Similarly, the sorption behaviors of the chloromethanes in the membrane could also be explained by the solubility parameter theory.

REMOVAL OF TRACE VOCs FROM WATER

Usually, the diffusivity of a permeant through a membrane is a strong function of the size and shape of the permeant; the molecules with smaller molecular size permeate faster. Among the series of chloromethanes, the diffusion coefficient of organic permeant is shown in Figure 4 as a function of its molar volume, which was used as a measure of the organic size. Obviously, the diffusion coefficient of the permeant decreases with its molar volume. However, a deviation from this trend was found again for dichloroethane as in the sorption behavior; the diffusion coefficient of dichloroethane is the smallest, even though its molar volume is not largest. It could be explained in terms of the concentration dependence on diffusivity. The following exponential relationship holds for the case where the diffusion coefficient is strongly concentration-dependent:

$$D = D_0 \exp(\gamma C) \tag{5}$$

where D_0 is the diffusion coefficient at zero permeant concentration, C is the permeant concen-

Table II	Solubility	Parameters	of	Chlorinated
Hydrocan	rbons ¹²			

	Solubility Parameter (MPa ^{1/2}) ^a				
Organics	δ_d	δ_{p}	$\delta_{ m h}$	$\delta_{ m t}$	
CH_2Cl_2	18.2	6.3	6.1	20.2	
CHCl ₃	17.8	3.1	5.7	19.0	
CCl_4	17.8	0	0	17.8	
$C_2H_4Cl_2$	19.0	5.3	4.1	20.2	

^a Solubility parameter of PDMS = 15-16 MPa^{1/2}.



Figure 5 Pervaporation performance with operating temperature in the permeations of various organic solutions; the organic concentration in aqueous solution = 100 ppm.

tration in membrane, and γ is the plasticizing coefficient. D_0 is related mainly to the size and shape of permeant molecules. The deviation mentioned above seems to be attributed to the exponential term. The plasticizing coefficient elucidates the plasticizing effect of the permeate on the mobility of the permeant in the membrane and, thus, is undoubtedly related to the affinity between the permeant and polymeric membrane. Based on this principle, it can be predicted from equation (5) that the lowest solubility and affinity of dichloroethane towards the PDMS membrane might consequently yield a smallest value of the diffusion coefficient among the chlorinated hydrocarbons.

Effect of Operating Temperature

The permeations of the dilute organic aqueous mixtures were carried out at various temperatures ranging from 30 to 45°C, and the results are shown in Figure 5. Usually, the thermal motion of polymer chains in the amorphous region randomly produced free volumes. As the operating temperature increases, the frequency and amplitude of the polymer chain jumping increase, and the resulting free volume becomes larger. In pervaporation, the permeating molecules can diffuse through these free volumes. Thus, the permeation rate is higher at a higher temperature, as shown in Figure 5.

The effect of temperature on enrichment factor is shown in Figure 5. On the whole, the PDMS membrane prepared is observed to have very excellent permselectivity for all the chlorinated hydrocarbons employed in this study. The enrichment factor for dichloroethane changes with temperature differently from those for chloromethanes. The enrichment factor for dichloroethane decreases with increasing temperature, as observed in a common pervaporation process. The same result was also obtained in the previous work¹³ in which the pervaporation of a dilute dichloroethane-water mixture had been carried out through PDMS membranes fabricated by condensation reaction. However, it is very interesting to note that the following opposite result was obtained for all of the chloromethane aqueous solutions: an increasing enrichment factor with increasing temperature. In addition, the enrichment factor shows an increase with increasing the number of chlorine atoms among the chloromethanes. More details on these observations could be obtained through the analysis of individual component permeations.

Figure 6 exhibits the plots of organic component fluxes with operating temperature. All of the fluxes increases monotonously with temperature, which is a normal trend of flux change with temperature in pervaporation process. In the permeations of the chloromethane aqueous mixtures, a steady increase in organic component flux with increasing chlorine content was found for the given temperature range. This can only be explained realizing that the diffusion of the larger permeant has a more retarding influence; and, thus, the diffusion has a more effect on the permeation than the sorption has, leading to a slower permeation, as discussed previously. A distinctive thing from the plots is that the flux of dichloroethane, which has the lowest affinity towards the membrane, changes very slightly with temperature.

Looking at water component fluxes in Figure 7, the permeation behaviors of water component with operating temperature for two groups of the aqueous mixtures are completely different. In the permeation of the chloroethane aqueous mixture,



Figure 6 Organic component flux with operating temperature in the permeations of various organic solutions; the organic concentration in aqueous solution = 100 ppm.

the flux of water component increased with increasing operating temperature, which is common in a normal pervaporation process. However, the water permeation in all the chloromethane aqueous solutions was surprisingly depressed with increasing temperature. Also, the water flux was decreased with an increase in the number of chlorines in the organic, that is, increasing the affinity of the organic towards the membrane material.

These observations might be presumably associated with water clustering developed in the membrane arising from repulsive interaction between water and organic components absorbed. It has been postulated $^{14-16}$ that the permeation of water through polymer membranes can be hindered by the formation of a water cluster. Water itself exists in the form of hydrogen-bonded clusters, depending on its circumstance. Thus, "free" water molecules may diffuse accompanied by clustered molecules. This implies that the diffusing size of water increases and that the diffusion coefficient consequently decreases. The extent and size of clustering also depend on upon the nature of solutes and on the chemical and physical nature of the membrane barrier. Hydrophobic solutes and membranes tend to repel water molecules, forcing them into larger, more icelike, and therefore, less easily permeating clusters. As a result, the presence of hydrophobic solute shifts

the water structure to larger or more ordered clusters at the expense of the unassociated monomeric species. As can be seen in Table I and Figure 4, the chloromethane having higher number of chlorines is more hydrophobic and more absorbed in the PDMS membrane, so that the resulting membrane could have more hydrophobic characteristics. Consequently, water would be less sorbed in the membrane or be more likely to exist in the form of a large size of clusters under such a more hydrophobic circumstance, resulting in permeating less water. With increasing temperature, since the solubility of each chloromethane in the membrane increases, the PDMS membrane would also be more hydrophobic, then the formation of water clusters would be more significant. Thus, the effect of water clustering might become predominant over the enhancement of permeant diffusion or membrane mobility with increasing temperature. Consequently, the permeation of water component could be depressed with increasing temperature. On the other hand, dichloroethane has less hydrophobicity and less solubility in the membrane than any chloromethane to such an extent that the existence of the organic in the membrane could not cause enough water clustering to give rise to the depression of water permeation.

Effect of Membrane Thickness

Figure 8 presents the plots of total flux and selec-



Figure 7 Water component flux with operating temperature in the permeations of various organic solutions; the organic concentration in aqueous solution = 100 ppm.



Figure 8 Pervaporation performance with membrane thickness in the permeations of various organic solutions; the organic concentration in aqueous solution = 100 ppm, and the operating temperature = 35° C.

tivity against membrane thickness. Total flux shows an increase with inverse membrane thickness. Usually, flux is inversely proportional to membrane thickness in pervaporation, assuming that diffusion is the rate-determining step. The dot line indicates the approximate variation that would be followed if diffusion is the rate-determining step. More negative deviation of the real flux from the straight line is found with decreasing membrane thickness. This reflects that there must be other significant resistance in addition to the diffusion resistance contributing to total permeation. In the removal of volatile organic compounds (VOCs) from water, Psaume et al.,² Côté and Lipski,³ and Nijhuis et al.⁴ reported that the concentration polarization of organic permeant at the boundary layer adjacent to the upstream membrane interface takes place so seriously that it can provide an additional resistance to permeation. Its effects can be particular severe for compounds that are highly enriched in the permeate. Also, Bode et al.¹⁷ suggested that the interface

resistance at the permeate side becomes significant as membrane thickness decreases. From these facts, it can be postulated that possible resistances causing the negative deviation of flux from the linearity with decreasing membrane thickness in this study could be deduced to be (1) the concentration polarization developed across the boundary layer in feed and (2) the interface resistance at the downstream side interface of the membrane. Details on this postulation will be discussed later through the analysis of component fluxes.

The plots of enrichment factor have somewhat complex shape of curve in this figure, depending on the kind of organic permeant. The aqueous solution containing dichloroethane, which has the lowest solubility in the PDMS membrane, shows a tendency of increasing enrichment factor with increasing membrane thickness, especially in the large range of membrane thickness, while the solution containing carbon tetrachloride with the largest solubility in the membrane presents the following opposing tendency: an increasing enrichment factor with a decreasing membrane thickness, particularly in the small range of membrane thickness. The enrichment factors for the other two aqueous solutions have a parabolic shape of curve with membrane thickness. In removal of VOCs from water by pervaporation, it is commonly reported^{4,18} that the enrichment factor increases with increasing membrane thickness. It is in conformation with the result on the aqueous solution containing dichloroethane, but not with the other results. The reason for that will be explained through the analysis of component permeations.

Figures 9 and 10 present the permeation rates of organic and water components, respectively. All of the organic permeations demonstrate some deviation from a linearity between flux and inverse membrane thickness, showing the depression of organic permeation with decreasing membrane thickness. In fact, as the membrane thickness decreases, the membrane resistance decreases while the resistance originating from the concentration polarization increases.⁴ Thus, overall resistance to organic permeation is dependent on the resistance arising from the concentration polarization as well as membrane resistance. With changing membrane thickness, that these two resistances would change contributes to the organic permeation in the following opposite way: with decreasing membrane thickness, the membrane resistance decreases to enhance the organic permeation, following the linear relationship be-



Figure 9 Organic component flux with membrane thickness in the permeations of various organic solutions; the organic concentration in aqueous solution = 100 ppm, and the operating temperature $= 35^{\circ}$ C.

tween flux and inverse membrane thickness, whereas the resistance arising from the concentration polarization decreases to reduce the organic permeation. Therefore, the resistance arising from the concentration polarization would be



Figure 10 Water component flux with membrane thickness in the permeations of various organic solutions; the organic concentration in aqueous solution = 100 ppm, and the operating temperature $= 35^{\circ}$ C.



Figure 11 Schematical representation of the permeant concentration profile developed in a membrane with membrane thickness.

attributed to the negative deviation from the linearity. It is assumed¹⁸ that water permeation is independent of organic permeation in the removal of trace VOCs from water by pervaporation and is governed only by membrane resistance. However, the water flux in this figure does not have a linear relationship with an inverse membrane thickness either. This observation justifies the conclusion that, besides the membrane resistance, other additional resistance contributes to the water permeation in the removal of trace organics from aqueous solutions. The question is what causes the additional resistance in water transport behavior. Looking at the water flux curves, the depression of water permeation is found to be more significant at a small membrane thickness range as it goes from dichloroethane to carbontetrachloride, that is, as increasing the solubility of organic permeant in the membrane. In real pervaporation, it is not possible to maintain a constant permeate pressure at varying flux density. It was investigated⁸ that an increase in permeant flux by decreasing membrane thickness gives rise to an increasing permeate pressure, and, simultaneously, the permeant concentration in the membrane at permeate side increases correspondingly, as depicted in Figure 11. In other words, a broader permeant concentration profile is developed in a thinner membrane, and, thereby, the permeant concentration in the membrane is higher. It was already mentioned that the organic permeant with greater affinity towards the membrane would have a higher concentration in the membrane for a given membrane thickness during pervaporation. Thus, with decreasing membrane thickness, the concentration of organic permeant having more affinity towards the membrane would presumably increase more significantly, and then the resulting membrane would have an increase in hydrophobic characteristics. Considering this principle, it could be predicted that with increasing the affinity of organic permeant and/or decreasing membrane thickness, the water molecules would be more likely to exist in the form of clusters in the membrane during pervaporation, resulting in more depressing water permeation. From the above discussions, it can be rationalized that the concentration polarization causes the suppression of organic component permeation while the water clustering leads to the depression of water component permeation. In addition, these two effects compete to influence the enrichment factor with membrane thickness in an opposite way. When the effect of water clustering is predominant over the effect of the concentration polarization, the water permeation would be more depressed than the organic permeation so that the enrichment factor could increase. When the organic dissolved in aqueous solution has a higher affinity towards the PDMS membrane and the membrane thickness is smaller, the effect of water clustering is of more significance and vice versa. Now the change in the enrichment factor in Figure 8 and the water permeation behavior in Figure 10 can be explained in association with the combined effects of the water clustering and the concentration polarization. which are described as functions of membrane thickness and the affinity of organic dissolved in the aqueous solution. From this study, it is suggested that the relationship between water clustering and the hydrophobicity of the membrane system should be taken into account for the selection or design of membrane materials for a given organic aqueous mixture or could be utilized to establish an optimum process condition for the removal of VOCs from water.

CONCLUSIONS

The removal of trace organic components from water has been performed through poly(dimethylsiloxane), which had been fabricated by an addition reaction. This study concentrated on the pervaporative separation of aqueous solutions dissolving trace chlorinated hydrocarbons. The PDMS membrane prepared yielded very high permselectivity from all the chlorinated hydrocarbons employed because of the high hydrophobicity of the membrane.

In the removal of VOCs from water, water clustering taking place in the membrane as well as the concentration polarization of organic occurring in the boundary layer in feed adjacent to membrane surface was observed to influence the pervaporation performance. It could be rationalized from the analysis of component permeation that the concentration polarization causes the suppression of organic component permeation, while the water clustering leads to the depression of water component permeation. The water clustering could be formed more significantly in the membrane under a more hydrophobic circumstance.

The effect of water clustering became predominant over the enhancement of permeant diffusion with increasing temperature. Consequently, the permeation of water component could be depressed to increase the enrichment factor. With varying membrane thickness, these two effects compete to influence on the enrichment factor in an opposite way. When the organic dissolved in aqueous solution has higher affinity towards the PDMS membrane and the membrane thickness is smaller, the effect of water clustering is of more significance, resulting in an increase in the enrichment factor for VOCs.

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