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Pervaporation Separation of Trace VOCs from Water Through PDMS Membranes

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Abstract : The removal of trace chlorinated and aromatic hydrocarbons from water by a pervaporation technique has been carried out through poly (dimethylsiloxane) membrane which had been fabricated by the addition crosslinking reaction. This study dealt with the swelling and permeation behaviors of the PDMS membranes with dichloroethane, trichloroethane, and toluene aqueous solutions. The swelling ratio in the toluene aqueous solution was much higher than those in the chloroethane solutions at all of the operating temperatures and concentrations. The solubility parameter theory was introduced to interpret the affinity between permeates and a membrane material and in all cases this approach seemed to be proper. It was suggested that the existence of water clusters in the membrane due to the hydrophobic characteristics of the membrane made the size of the permeating water larger, resulting in suppressing water permeation and increasing enrichment of the organic components. The permeation behaviors at different membrane thicknesses were indirectly interpreted in terms of the effect of concentration polarization.

1. Introduction

Pervaporation is a very attractive membrane process since organic polluting compounds in water could be removed selectively. Furthermore, this process could be integrated with other conventional processes, such as distillation, adsorption, and absorption processes to enhance the separation efficiency. And also it is well-known that this process is energy-saving and provides the opportunity of re-use of organic compounds. Baker et al. [1] illustrated the merits of a pervaporation process for organic contaminant removal. In this case, several authors [2-4] reported that there could exist the limitation due to an additional resistance to membrane resistance caused by the so-called 'concentration polarization of organic permeates' which originates from the liquid boundary layer at the membrane interface and contributes to the negatively to the membrane performance.

In the case of volatile organic compounds(VOC's) removal, highly organic selective membranes are required. Elastomeric organophilic membranes have been widely used to remove organic compounds dissolved in water. Nijhuis et al. [5] prepared several homogeneous elastomeric membranes, such as nitrile butadiene rubber (NBR), ethylene-propylene terpolymer (EPDM) and poly (dimethysiloxane) (PDMS). In pervaporation, the membrane material selection could be considered by understanding the solution-diffusion mechanism which provides the informations of solubilities and diffusivities in the membrane material. From this point of view, PDMS or other silicone rubbers which have already been proved to show organophilic characteristics as well as high permeabilities could be suitable for the removal of VOC's. In addition, the PDMS membranes offer a good compromise be-

tween high permeabilities and moderate selectivities in most cases.

Watson et al. [6] suggested that enhancing the hydrophobic nature of PDMS membrane is more effective for the improvement of the separation performance rather than enhancing the organophilic nature of the material which might cause to decrease a membrane mobility due to both the strong interchain interactions and permeant-polymer interactions. This approach would give a significant decrease in water permeation and result in increase of the organoselectivity. In fact, PDMS is a notable hydrophobic material that has a tendency to discourage the passage of water molecules whilst at the same time allowing the passage of a wide range of larger organic molecules. Therefore, PDMS membranes tend to behave as a true chemical separator that functions according to the chemical nature of the permeant molecules rather than as a sieve that separates according to size. For this reason, it would seem to be an interesting subject to give more detailed understanding in the transport phenomena.

In this study, the chlorinated hydrocarbons and toluene in their permeation and sorption behavior were examined through PDMS membranes which has been fabricated by the addition crosslinking reaction. Since there are no polar groups in the polymeric chain, such as hydroxyl and chlorine groups which could be found in the PDMS membranes prepared by condensation reaction, the membranes prepared by the addition recation had more hydrophobic characteristics. This study will focus on the comparison of the separation and sorption characteristics of the chlorinated hydrocarbons having different chlorine numbers and also hydrocarbon, toluene. The permeation behaviors of the PDMS membrane at various temperatures, different concentrations of organics in water, and different membrane thicknesses will be investigated.

2. Experimental

2.1. Materials

Poly (dimethylsiloxane) which is composed of RTV655A and RTV655B was generously provided by Dongyang Silicone (Seoul, Korea). RTV655A is mainly PDMS oligomers terminated with vinyl groups and RTV655B a mixture of Pt catalyst and PDMS oligomer with active carbons. Hexane, toluene, dichloroethane, and 1,1,2-trichloroethane purchased from Junsei Chemical Co. (Tokyo, Japan) were used without further purification. Ultra pure water produced from the SK Chemical System was used.

2.2. Membrane Preparation

A casting solution was prepared by dissolving RTV655A and B with a ratio of 10 to 1 in n-hexane. The casting solution was poured into a glass petri dish and then allowed to dry at room temperature in a fume hood. Subsequently, it reacted at 60℃ for 6 hrs and then dried again at 150℃ for 2 hrs in a thermostated oven. The crosslinking reaction took place by addition reaction in which the active hydrogens (H in R′) attack the vinyl groups (CH_2=CH-) under Pt catalyst as depicted in Fig. 1. When the membranes were prepared, the membrane thickness was controlled by the concentration of the casting solution and the amount of the polymer solution. The thickness of the resulting PDMS membranes were measured using digital thickness gauge (Mitutoyo Co., Japan). SEM(Scanning Electron Microscopy) confirmed that this method could provide a good control of membrane coating thickness.

2.3. Swelling Measurements (7)

Swelling measurements of PDMS membranes were carried out to determine the amount of organic solvents absorbed in the membranes. Dry membrane strips with the dimension of 10×65 mm were immersed in the aqueous organic solutions in which concentrations are 0, 200, 400, 700, 900 ppm and 100% at 25, 35, and 45℃ until the equilibrium condition reached. After measuring the swollen length, l of a strip, the strip was dried for at least 1 day at room temperature under vacuum and then the dry length, l_0 was measured. The swelling ratio, ϕ, is defined as

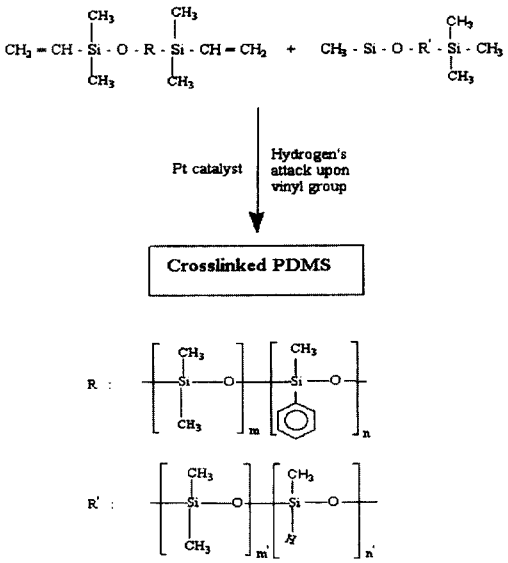

Fig. 1. A crosslinking reaction mechanism of PDMS.

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

All measurements were repeated 10 to 15 times and then averaged. The resulting data had standard deviation of ±5%.

2.4. Pervaporation

A schematic pervaporation cell and apparatus used in this study are illustrated in Figs. 2 and 3, respectively. The membrane cell is made of a stainless steel. A feed mixture enters the cell through the center opening, flows rapidly through the thin channel and leaves the cell through the side opening, which allows relatively high fluid velocity parallel to a membrane surface. The effective membrane area was 17.35 cm^2. The feed mixture was circulated from the feed tank having a capacity of 1 l through the membrane cell. The temperature of the feed mixture was controlled by a temperature controller. The permeate pressure was controlled by a vacuum controller (OKANO WORKS, LTD). The composition of permeate vapour was determined by on-line gas chromatography (DS6200, Donam Instruments Inc.) analysis. The permeate vapour was injected directly into the

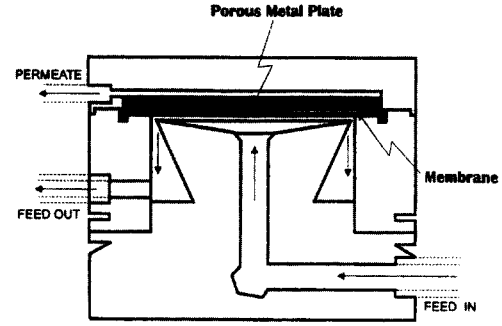

Fig. 2. Schematical representation of the membrane cell.

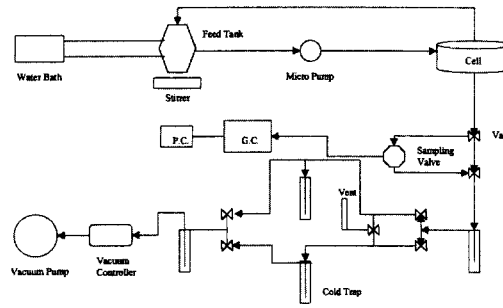

Fig. 3. Schematic diagram of the pervaporation apparatus.

gas chromatography by the auto-sampling valve through the 5 ml sampling loop. The permeate vapour 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 separation factor toward organic (α) was calculated by the following equation

$$\alpha = \frac{Y_{\text{organic}}/Y_{\text{water}}}{X_{\text{organic}}/X_{\text{water}}} \tag{2}$$

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

3. Results and Discussion

3.1. Swelling Measurements

Table 1 shows the physical properties of the toluene, dichloroethane and 1,1,2-trichloroethane.

Table 1. Physical Properties of Organics in Question [8]

organics	molar volume ($\times 10^6$ m^3/mol)	saturated vapor pressure at 25℃ (torr)	boiling temperature (℃)	solubility at 25℃, wt.%	
				organics in water	water in organics
toluene	106.38	27.75	110.8	0.052	0.033
$C_2H_4Cl_2$	78.80	81	82.5	0.81	0.15
$C_2H_3Cl_3$	100.69	120.76	74.1	0.13	0.034

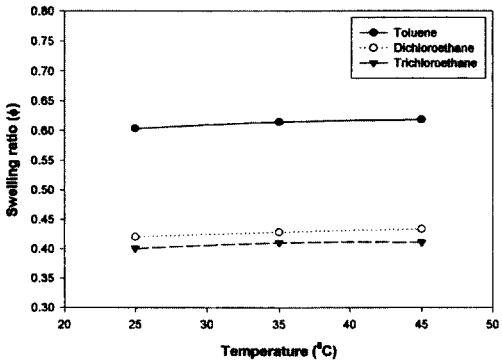

Fig. 4. Swelling ratio of pure organics in PDMS membrane at 25, 35, and 45℃.

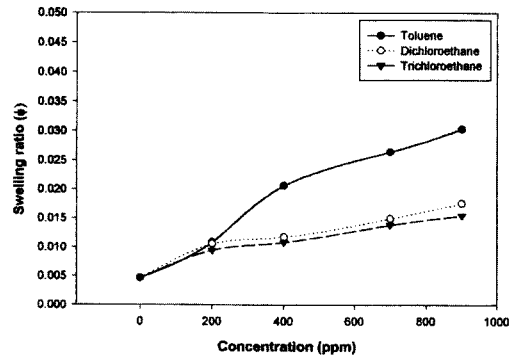

Fig. 5. Swelling ratio of aqueous organic mixtures with varying concentrations at 25℃.

As the number of chlorine increases, the vapor pressure increases and also both the solubilities of the organic in water and of water in organic decrease. It indicates that the trichloroethane is more hydrophobic than the dichloroethane. For the aromatic hydrocarbon of toluene, the solubilities of organics in water is the lowest while the solubility of water in organic lies between the di- and trichloroethane.

In order to investigate mutual interaction between the permeants and the polymer, the solubilities of pure organics and the organic solutions dissolved in water were measured for PDMS membranes at 25, 35 and 45℃. The results were presented in Fig. 4 through Fig. 7. As can be seen in the figures, all of the sorptions in the membrane increase with increasing the boiling temperature. It is reported that this tendency of increasing solubility with boiling points is due to the condensability of permeants [9]. For the chlorinated hydrocarbons, the solubility increases with decreasing number of chlorine atom or molar volume. This observation is understandable with respect to the thermodynamic characteristics of materials based on the solubility parameter theory as shown in Table 2. The solubility parameters, δ_t, used in this approach can be extended into three components, disperse forces (δ_d), dipole forces (δ_p), and hydrogen forces (δ_p). It is well known that a smaller difference in δ_t between a solvent and a polymeric membrane material results in a higher degree of swelling [10]. In spite of some restrictions [11] on this solubility parameter theory, this approach is popularly used for a first approximation on the affinity between permeant and membrane material. Table 2 shows that the smallest difference in the solubility parameters between organic and membrane material is the toluene and PDMS, and the next is the dichloroethane and PDMS and final one is the trichloroethane and PDMS. Therefore, the swelling ratio of toluene in PDMS membrane is the highest and then dichloroethane and trichloroethane as can be seen in Fig. 4. And also the fact that

Table 2. Solubility Parameters of Organics [12]

organics	solubility parameter ($MPa^{1/2}$)			
	δ_d	δ_p	δ_h	δ_t
toluene	16.4	8.0	1.6	18.3
dichloroethane	14.2	11.2	9.1	20.2
trichloroethane	13.9	12.9	7.0	20.9

* solubility parameter of PDMS = 15~16 $MPa^{1/2}$

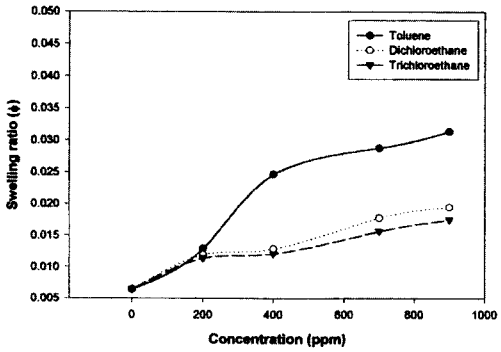

Fig. 6. Swelling ratio of aqueous organic mixtures with varying concentrations at 35℃.

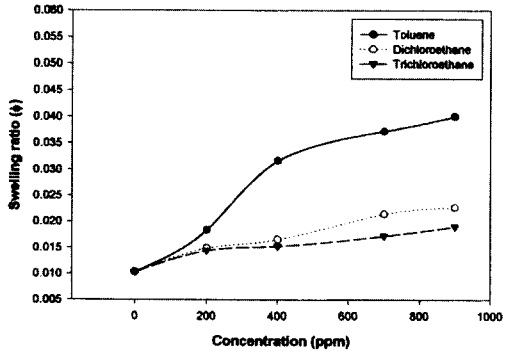

Fig. 7. Swelling ratio of aqueous organic mixtures with varying concentrations at 45℃.

there is not much difference in the solubilities of dichloroethane and trichloroethane coincides with the small gap of the resulting solubilities of this two organics in PDMS membrane. This tendency remains same at different temperatures.

Figs. 5 through 7 illustrate the solubilities with varying concentrations of organics in water at 25, 35, and 45℃. At low concentration of organic in water, below 200 ppm, there are no effects of the concentration on the solubilities of the mixtures. However, the solubilities are getting higher at higher concentrations of organics in water, particularly for toluene mixtures. The chlorinated hydrocarbons show the fairly higher value of hydrogen bonding force component in solubility parameters rather than toluene. Therefore, the chlorinated hydrocarbon molecules in water could form the clusters with water molecules through hydrogen bonding. Since the PDMS material is highly hydrophobic, the material itself may limit the sorption of this clusters into the PDMS membrane. In contrast, toluene molecules could exist freely in water because toluene does not have the strong interaction with water. This free toluene molecules could be sorbed more than chlorinated hydrocarbon molecules. This could be the reason why the solubility of toluene is getting higher than those of the chlorinated hydrocarbons as the organic concentration in water is larger. And the effect of temperatures on solubility as shown in Figs. 5 to 7 typically increase with increasing temperatures. This can be explained in terms of the 'free volume theory'. The description would be found in next section.

3.2. Effects of Temperature and Concentration

The permeations of the dilute organic aqueous mixtures of 0 to 900 ppm were carried out at various temperatures ranging from 25 to 45℃. The results are shown in Figs. 8 to 10. On the whole, the thermal motion of polymer chains in amorphous region randomly produces free volumes. As operating temperature increase, the frequency and amplitude of the polymer chain jumping increase and the resulting free volume becomes larger. In pervaporation, permeating molecules can diffuse through these free volumes. Thus, the permeation rates are higher at higher temperature as shown in Figs. 8, 9, and 10. The effects of temperature on the separation factor are also shown in Figs. 8, 9 and 10. The PDMS membranes are observed to have the excellent permselectivities for all the organics employed in this study.

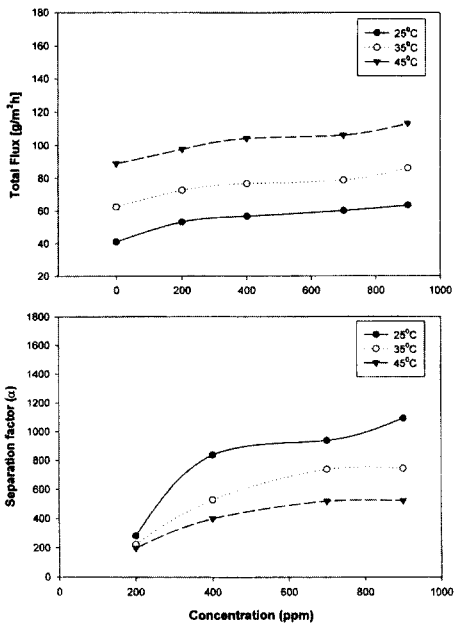

Fig. 8. Pervaporation performance with varying concentrations in the permeations of toluene solutions at 25, 35, and 45℃.

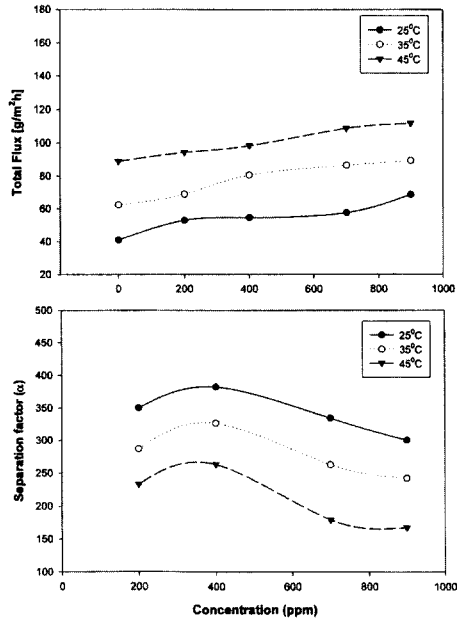

Fig. 10. Pervaporation performance with varying concentrations in the permeations of trichloroethane solutions at 25, 35, and 45℃.

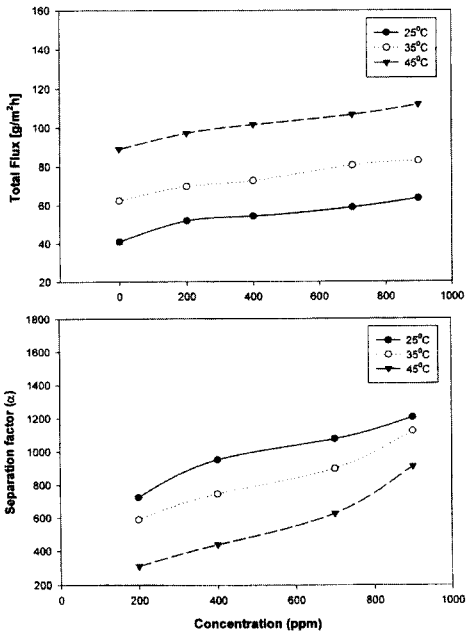

Fig. 9. Pervaporation performance with varying concentrations in the permeations of dichloroethane solutions at 25, 35, and 45℃.

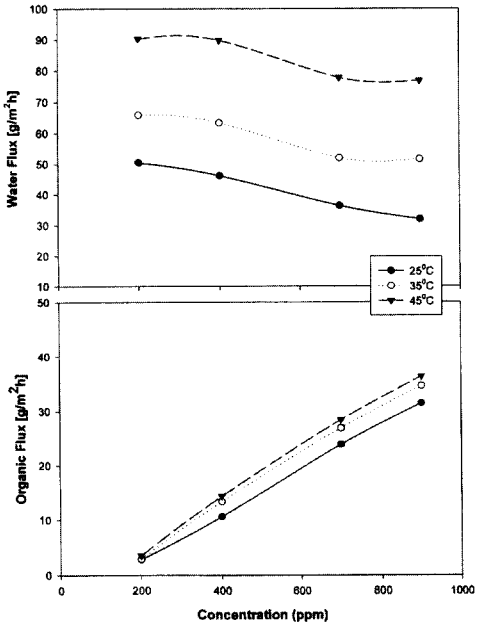

Fig. 11. Individual component flux with varying concentrations in the permeations of toluene solutions at 25, 35, and 45℃.

As the organic concentrations in water increase, the permeation rates increase as illustrated in Figs. 8, 9, and 10. Since PDMS material is highly hydrophobic, the chances of organics in water would be larger with increasing organic concentrations. Therefore, the permeation rates are higher at higher concentration of organics. This observations can be found consistently for all of the organic mixtures.

Fig. 11 exhibits the typical plots of individual component fluxes with operating temperatures and concentrations for toluene and water mixtures. It shows that the water fluxes decreases with concentrations while the organic fluxes increase with concentrations. The fact that the organic component flux increase with concentrations is a normal trend of flux change in pervaporation process as described previously. But, for water fluxes with concentrations, the flux was depressed with the increasing organic concentrations. This observations might be associated with water clustering developed in the membrane arising from repulsive interaction between water and organic components. It has been postulated [13-15] that the permeation of water through polymer membranes can be hindered by the formation of water clusters. Water itself exists in the form of hydrogen-bonded clusters depending on its circumstance. Thus 'free' water molecules may diffuse followed by clustered molecules. This implies that the diffusing size of water increase and the diffusion coefficient consequently decreases. The extent of size of clustering also depend upon the nature of solutes and on chemical and physical natures 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 discussed previously, the toluene is more absorbed in the PDMS membrane so that the resulting membrane could have more hydrophobic characteristics. As the organic concentration increases in the feed mixture, water would be less sorbed in the membrane or be more hydrophobic circumstance, resulting in less water

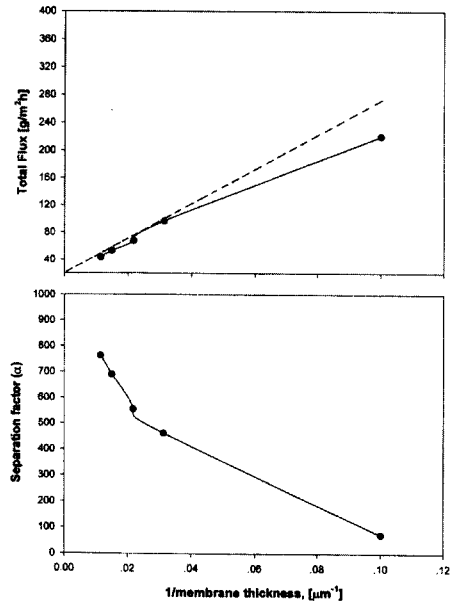

Fig. 12. Pervaporation performance with membrane thicknesses in the permeations of toluene solutions; toluene concentration in water = 400 ppm and the operating temperature = 35℃.

permeation. This phenomena for toluene and water mixture was observed same for aqueous dichloroethane and trichloroethane solutions even if the individual component fluxes of this systems are not shown in this article.

3.3. Effect of Membrane Thickness

Fig. 12 presents the plots of total flux and selectivity against membrane thickness for 400 ppm toluene solution at 35℃. As can be seen, the total flux shows an increase with inverse membrane thickness. In pervaporation, it is well-known that the flux is inversely proportional to membrane thickness. As the membrane thickness decreases, the deviation from the straight line to the real flux line is found. In the removal of volatile organic compounds from water, Psaume et al. [2], Cote and Lipski [3] and Nijhuis et al. [4] reported that the concentration polarization took place at the boundary layer provides an additional resistance to permeation. Its effects could be particularly severe for

compounds that are highly enriched in the permeate. Also, Bode et al. [16] suggested that the interface resistance at permeate side becomes significant as membrane thickness decreases. Therefore, from these facts, it could be postulated that the possible resistances causing the negative deviation of real flux from the straight line are deduced to be (1) the concentration polarization developed across the boundary layer in feed and (2) the interface resistance at the down stream side interface of the membrane.

4. Conclusions

The removal of trace chlorinated and aromatic hydrocarbons from water by pervaporation technique has been carried out through poly (dimethylsiloxane), which had been fabricated by addition crosslinking reaction. This study dealt with the swelling and permeation behaviors of dichloroethane, trichloroethane, and toluene aqueous solutions. The PDMS membrane prepared by addition crosslinking reaction gave more hydrophobic properties so as to yield high permselectivity for all organic aqueous solutions. Toluene showed higher swelling ratio compared with chlorinated hydrocarbon mixtures at all temperatures and concentrations. The solubility parameter theory was well applied to interpret the swelling phenomena of the solutions employed. In pervaporation, it was suggested that both water clustering in the membrane and concentration polarization influenced the separation performance. It could be rationalized from the permeation studies that water clustering leads permeating water molecular size to be larger, resulting in suppressing water permeation and increasing organic flux when the organic concentration increases. As a result, the selectivities and the total flux increase with increasing organic concentrations. With varying membrane thickness, the concentration polarization becomes more severe and, therefore, acts as an another resistance on permeation, causing the negative deviation of real flux from the ideal flux line when the membrane thickness decreases.

Acknowledgment

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