Pervaporation Separation of Binary and Ternary Mixtures with Polydimethylsiloxane Membranes

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ABSTRACT: This study dealt with the separation of binary water–phenol and water–methanol mixtures and ternary water–phenol–methanol mixtures by pervaporation (PV) with polydimethylsiloxane (PDMS) membranes. The effects of the operating conditions (feed temperature, feed concentration, and feed flow rate) on the separation performance for binary mixtures were investigated. An increase in temperature or concentration increased the total permeation flux and decreased the organic separation factor. In other words, an increase in the temperature or feed organic concentration increased the water flux more significantly than the organic compound flux, which resulted in a separation factor reduction. Also, an increase in the feed flow rate increased the total flux and separation factor because the boundary layer effects diminished. The vapor–liquid equilibrium separation factor (α_{VLE}) and pervaporation separation factor (α_{PV}) values for the PDMS membrane were calculated, and this showed that α_{PV} for the water–phenol mixture was greater than α_{VLE}. This means that the membrane was highly efficient for the PV separation of phenol from dilute aqueous solutions relative to the separation of methanol. This was due to the fact that phenol has a higher solubility parameter than methanol in silicone membranes. To study the effect of a third component on membrane performance, PV experiments were also carried out with water–phenol–methanol mixtures. The results for total permeation flux and the phenol separation factor for PDMS membranes in contact with water–phenol–methanol ternary mixtures are similar to those in contact with water–phenol binary mixtures. The phenol separation factor of the membrane in contact with the ternary mixture was slightly lower than that in contact with the binary mixture. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1777–1782, 2008

Key words: waste; diffusion; solution properties; pervaporation

INTRODUCTION

Phenolic resins are polymeric compounds of phenols and aldehydes characterized by their high shear and heat resistance. They are mostly used in molding compounds, coated abrasives, brake linings, clutch facings, laminates, plywood adhesives, glass-wool thermal insulation, bonded organic-fiber padding, foundry-sand bonding, and other miscellaneous applications.[1]

The manufacture of phenolic resins consists of a condensation reaction between phenol and formaldehyde with NaOH. However, this process is also a source of wastewater. The transparent and slightly suspended wastewater contains 5% phenol, 3.4% methanol, 2.8% formaldehyde, and 1% nonvolatile compounds at pH 4.4.[2]

Because of the high toxicity and hazardous character of phenol, the importance of the decontamination of these effluents before discharge into sewage system and the environment is obvious. Phenol is lethal to fish and brings objectionable tastes to drinking water.[3]

Therefore, the removal of phenol from wastewater is essential. This removal, which is difficult to do by conventional biological water-treatment processes, is usually achieved by liquid extraction. In this method, the use of an extraction solvent, that is, methylisobutylketone, might be undesirable with respect to environmental pollution, energy conservation, running costs, and so on.[2]

Pervaporation (PV) as a membrane separation process is one effective physicochemical method. Compared with other traditional processes, PV appears far more effective because of its simplicity and high selectivity.[4] PV is a separation technique based on a selective transport through a dense layer (generally composed of polymers) associated with the evaporation of the permeate.[5]

Silicone-containing polymers have generally been found to exhibit good organophilicity, and silicone rubber [mainly polydimethylsiloxane (PDMS)] based membranes have been the most investigated for the

separation of organic aqueous mixtures such as alcohols, phenols, and chlorohydrocarbons.[6]

The permeation of molecules through a dense non-porous polymeric membrane is generally governed by the sorption–diffusion mechanism. The relative sorption of permeates in the membrane depends on their relative solubility in the membrane. The extents of solubility or miscibility of a component in or with polymeric membranes can be explained by the solubility parameter theory. The solubility parameter was defined by Hildebraned and Scott[7] with cohesive energy density, which is a measure of the cohesive force that holds molecules together in the liquid phase.

In PV, the feed temperature and concentration affect the total flux (J) through the membrane and the phenol separation factor. The presence of methanol in wastewater may also be expected to affect the membrane performance for phenol separation. This could be due to the fact that the solubility and molecular size of methanol are different, and this affects J and the phenol separation factor.[8]

In this study, the PV of binary water–phenol and water–methanol and ternary water–phenol–methanol mixtures by PDMS membranes was studied. The effects of feed composition, temperature, and flow rate on membrane performance were investigated.

EXPERIMENTAL

Phenol and methanol (99.5%) were supplied by Merck Co., Ltd. (Darmstadt, Germany) Deionized laboratory water was used to make aqueous mixtures. The apparatus used for the PV experiments is shown schematically in Figure 1. The membrane was housed in a PV cell that consisted of two detachable stainless steel parts. The experiments were carried out with PDMS film membranes (GKSS Research
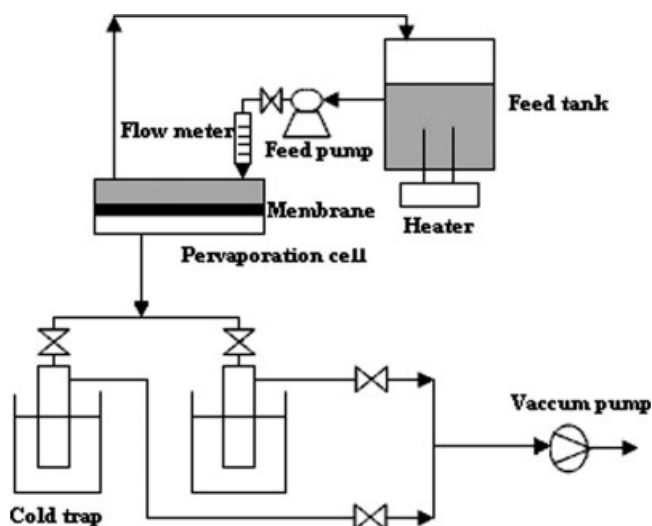

Figure 1 Sketch of the experimental setup.

Institute, Geesthacht, Germany). They had a thickness of 128 μm (a cellulose acetate support layer of 120 μm with an average pore size of 0.5 μm and a dense silicone rubber skin layer of 8 μm) with an effective area of approximately 0.0024 m². Rubber O-rings were used to provide a pressure-tight seal between the membrane and the PV cell. A pump was used to recirculate the feed solution, and the feed temperature was controlled to within 3°C with a thermostat. The volume of the feed tank was 7 L, which was very big compared with permeation volume; therefore, the variation of feed concentration during a period of 1 h could be neglected. In all experiments, feed was kept at atmospheric pressure, whereas permeate pressure was maintained in the range 8–10 mbar by an oil-sealed vacuum pump (MOTO GEN 80-48 with R.P.M. 1380, Tehran, Iran).

Permeate samples were condensed and collected in a Pyrex glass condenser kept inside a cryogenic trap at −35°C. An accurate refractometer (DR-A1) was used to analyze the methanol concentration in the permeate samples. Some samples were also analyzed with a Varian gas chromatograph (model STAR 3400 CX) equipped with a flame ionization detector for confirmation. Phenol concentration in the permeate samples was determined with a spectrophotometer (UV-1650 PC Shimadzu ultraviolet–visible spectrophotometers, Japan).

Permeation flux was calculated with the following equation:

$$J = \frac{M}{At} \qquad (1)$$

where J is the total flux (kg m^{-2} h^{-1}), M is the weight of the permeate (kg), A is the effective membrane surface area (m²), and t is the pervaporation time (h). The separation factor was also calculated with the following equation:

$$\alpha_{PV} = \frac{Y(1 - X)}{X(1 - Y)} \qquad (2)$$

where α_{PV} is the separation factor (dimensionless), X is the weight fraction of the organic component in the feed, and Y is the weight fraction of the organic component in the permeate.

RESULTS AND DISCUSSION

PV of binary water–phenol mixtures

Three concentration levels were chosen for the removal of phenol from the mixtures: 0.3, 1 and 3 wt % phenol. The feed temperature was varied from 35 to 75°C for each concentration level.

Figure 2 shows that J increased and the phenol separation factor decreased with increasing operating
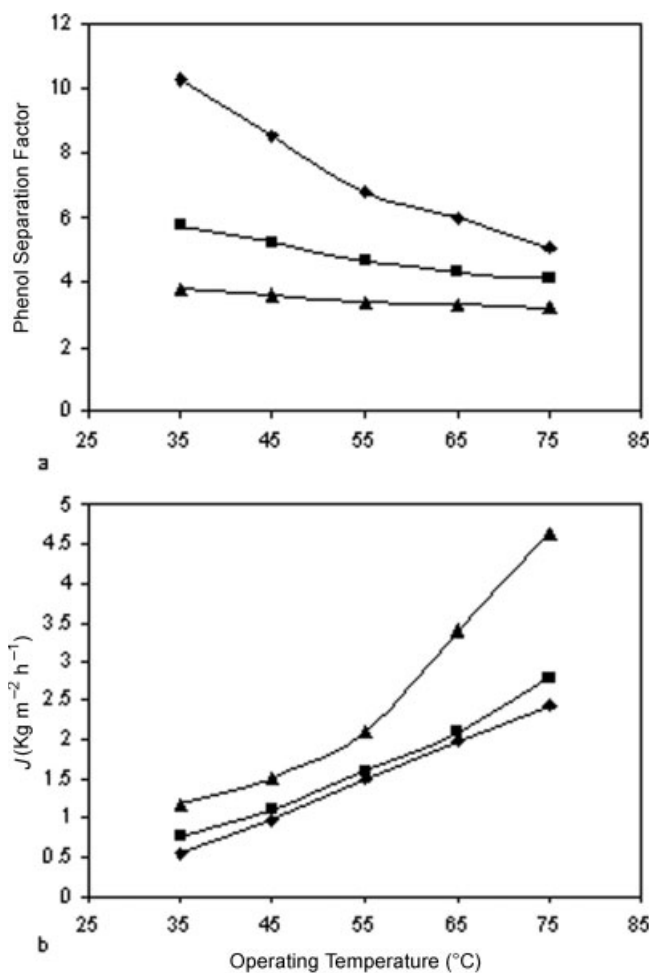
Figure 2 PV performance for the separation of binary water–phenol mixtures at different operating temperatures and phenol concentrations: phenol concentration = (◆) 0.3, (■) 1, and (▲) 3 wt %.

temperature and feed concentration. Also, the phenol concentration in the permeate tended to be higher at lower feed concentrations. For example, at a phenol concentration of 0.3 wt % in the feed, a permeate phenol concentration of greater than 3 wt % was obtained. This corresponded to a separation factor of approximately 10.28, but at a phenol concentration of 3 wt % in the feed, a permeate phenol concentration of greater than 10 wt %, which corresponded to a separation factor of approximately 3.79, was obtained. Over the entire temperature range tested, the phenol separation factor did not vary significantly when the phenol concentration in the feed was low. This implied that the membrane was thermally stable for this separation. The data in Figure 2 also show that at higher temperatures, J was more significantly affected by the phenol concentration in the feed, whereas the phenol separation factor was less affected.

Like many other PV systems, an increase in temperature led to an increase in the permeation flux.[9,10] In other words, the PDMS membrane showed a posi-

tive concentration and temperature dependency on the total permeation flux. This could be explained with a solution–diffusion mechanism. The separation was affected by both sorption and diffusion steps. As the operating temperature increased, the solubility of phenol in water increased. As a result, at a given concentration, the activity of phenol in the mixture decreased, and this resulted in less sorption of phenol in the membrane matrix. However, as the operating temperature increased, the frequency and amplitude of the polymer chain jumping increased. As a result, the free volume of the membrane increased. Thus, the rate of individual permeating molecules increased, which led to a high J. In many cases, such as this case, the diffusion is the rate-controlling step, and the effect of diffusion on J is more significant than that of preferential sorption.

The effect of feed flow rate on the separation performance of the PDMS membranes at different feed concentrations is shown in Figure 3. The feed flow rate was varied in the range 0.26–0.53 L/min, which
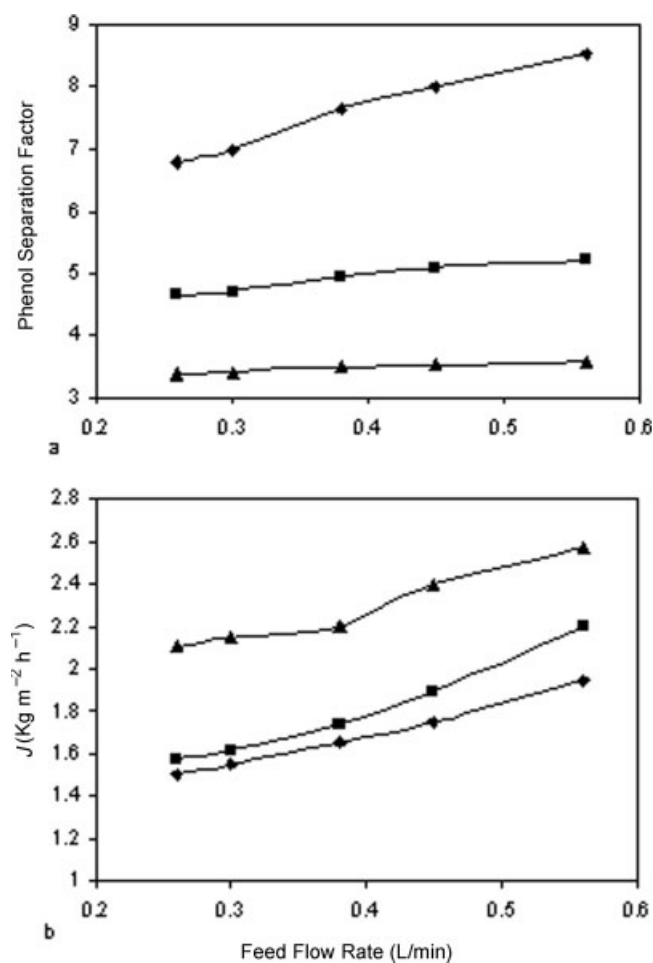

Figure 3 PV performance for the separation of binary water–phenol mixtures at different feed flow rates and phenol concentrations: phenol concentration = (◆) 0.3, (■) 1, and (▲) 3 wt %.
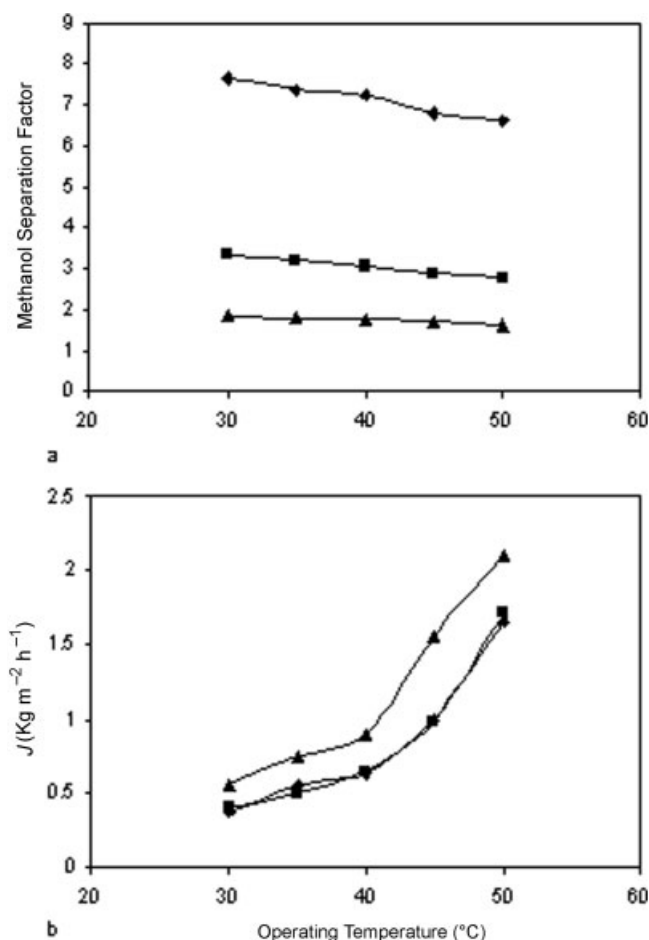
Figure 4 PV performance for the separation of binary water–methanol mixtures at different operating temperatures and methanol concentrations: phenol concentration = (◆) 0.3, (■) 1, and (▲) 3 wt %.

corresponded to Reynolds numbers from 117 to 238. The results show that J and the phenol separation factor increased slightly with increasing feed flow rate. The results could not be attributed solely to the concentration polarization effect in the liquid boundary layer adjacent to the membrane surface because concentration polarization tended to decrease the permeation rate of the more permeable component (phenol) and increase the permeation rate of the less permeable component (water), resulting in a lesser extent of separation. An increase in the feed flow rate reduced the concentration polarization effect, and thus, water flux was more enhanced.

We believe that in addition to concentration polarization, temperature polarization also occurred. Similar to mass transfer in the boundary layer, heat transfer from the feed to the membrane surface was also affected by the boundary layer. Consequently, a temperature drop developed in the boundary layer. As the feed flow rate increased, the heat-transfer coefficient in the boundary layer increased, and the temperature drop decreased. This reduced the tem-

perature polarization effect, and thus, J increased. The results show that J increased up to 40% and the separation factor increased up to 12% as feed flow rate increased from 0.26 to 0.53 L/min at different feed concentrations (0.3–3 wt %).

PV of binary water–methanol mixtures

The results of the PV of water–methanol mixtures with PDMS membranes, which were similar to those of water–phenol mixtures, are presented in Figures 4 and 5. However, J and the organic separation factor for the water–phenol mixtures were higher than those for the water–methanol mixtures.

For PV separation to be enhanced compared to that achieved purely through vapor–liquid equilibrium, α_{PV} must be clearly greater that the vapor–liquid equilibrium separation factor (α_{VLE}).[11] α_{VLE} values can be calculated with the following equation:

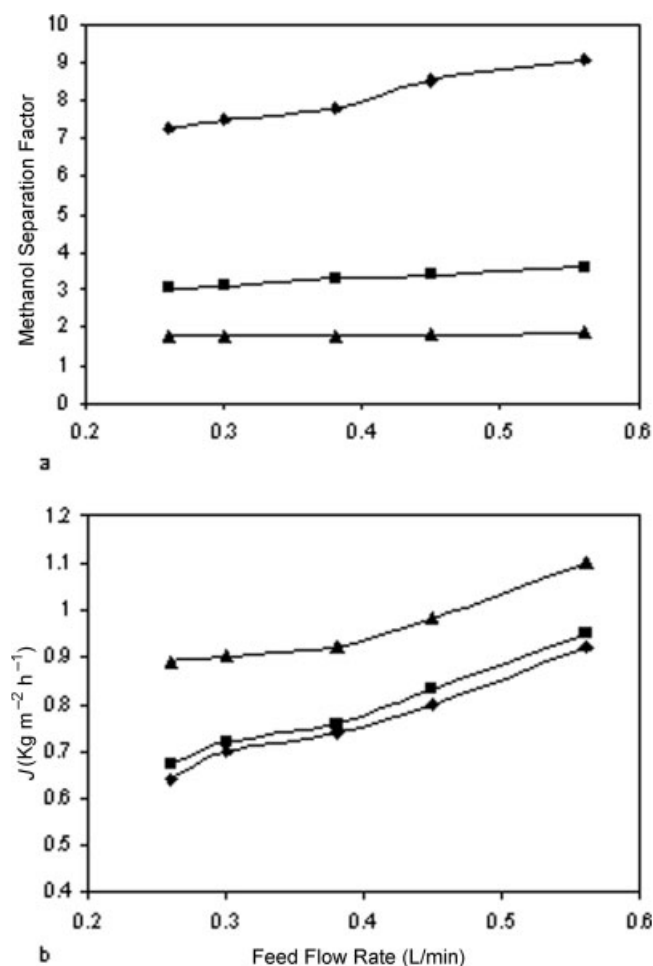$$\alpha_{VLE} = \frac{P_o^{sat}\gamma_o}{P_w^{sat}\gamma_w} \tag{3}$$

Figure 5 PV performance for the separation of binary water–methanol mixtures at different feed flow rates and methanol concentrations: phenol concentration = (◆) 0.3, (■) 1, and (▲) 3 wt %.

where P_o^{sat} and P_w^{sat} are the saturated vapor pressure of the organic and water components, respectively, and γ_o and γ_w are the activity coefficients of these components estimated by the universal functional activity coefficient (UNIFAC) group contribution method, respectively. In all cases, γ_w was assumed to be unity.

α_{VLE} and α_{PV} values for the PDMS membranes are presented in Table I. The results show that α_{PV} values for the water–phenol mixtures were greater than the α_{VLE} values. This means that the PDMS membrane was more highly efficient for the PV separation of phenol from dilute aqueous solutions than of methanol. This could have been due to the fact that the solubility parameter of phenol was higher than that of methanol in silicone membranes [the solubility parameters of phenol and methanol were 24 $(MPa)^{1/2}$ and 29.7 $(MPa)^{1/2}$, respectively[12]].

PV of ternary water–phenol–methanol mixtures

The PDMS membrane was evaluated for the separation of ternary water–phenol–methanol mixtures to study the effect of methanol as a third component on phenol removal. The composition of water in the ternary mixtures was kept at 95 wt %, and the total composition of organic compounds (phenol and methanol) was kept at 5 wt % (Table I).

J and the phenol separation factor for the ternary and binary mixtures at different phenol and methanol concentrations at a temperature of 50°C are presented in Figure 6. The results show that the trend of both the separation factor and J of the membrane that was in contact with the ternary mixture was almost similar to those with the binary mixture. In general, the results show that the phenol separation factor and J for the ternary mixtures were less than those for the binary mixtures. Also, an increase in the phenol concentration in the feed increased J and decreased the phenol separation factor.

This may have been due to the fact that in the presence of methanol, the solubility of phenol increased. As a result, for a certain concentration, the
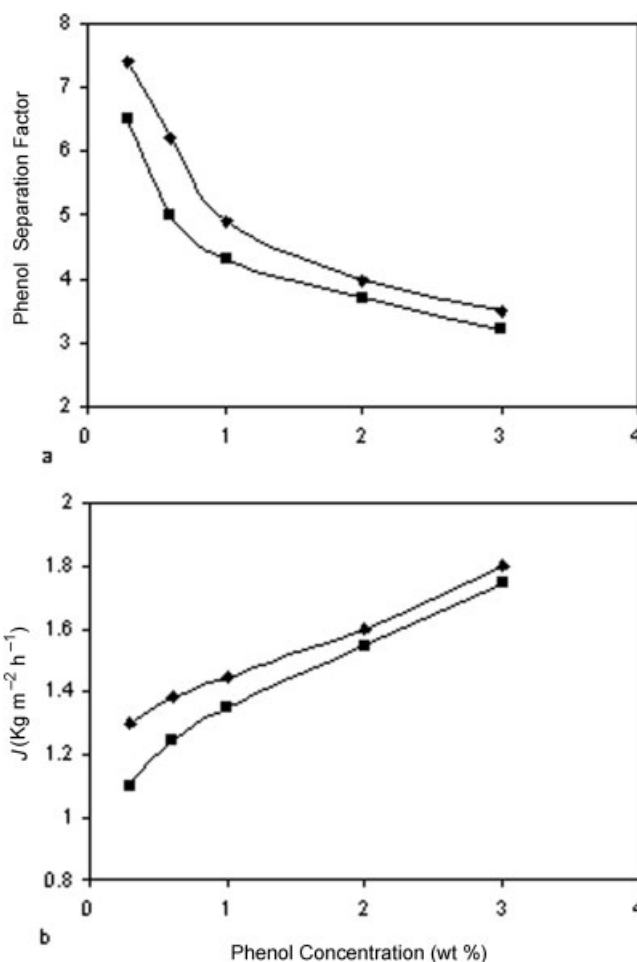
TABLE I
Compositions of the Feed Mixtures

Mixture	Organic concentration (wt %)	$\gamma_{organic}$	α_{VLE}	α_{PV}
Water–phenol	0.3	2.410	0.053	10.280
	0.1	2.359	0.051	5.670
	3	2.260	0.049	3.790
Water–methanol	0.3	2.970	14.290	7.260
	0.1	2.806	13.490	3.060
	3	2.665	12.750	1.750

$\gamma_{organic}$, Activity coefficient of organic (phenol or methanol).

Figure 6 Phenol separation factor and J for the separation of (■) ternary water–phenol–methanol mixtures and (◆) binary water–phenol mixtures.

activity of phenol in the water–phenol–methanol mixture decreased because more phenol could be dissolved in the water–methanol mixture. In other words, the forces that trapped phenol in the mixture became stronger. This resulted in less phenol being sorbed into the membrane matrix, and thereby, the phenol diffusion rate was reduced. This was due to a reduction in the driving force across the membrane.

In addition, the lower sorption of phenol into the membrane matrix due to the presence of methanol also reduced the plasticization of the membrane, and consequently, the membrane displayed a stronger resistance for diffusion of the three components. This hypothesis was in agreement with the experimental observations. As seen, at higher methanol concentrations, J was more affected by the presence of methanol. In other words, at lower methanol concentrations, the activity coefficient of phenol in the feed was higher, and as a result, phenol sorption into the membrane increased, and the membrane became more swollen because of its high affinity to phenol. Consequently, small-sized water and large-sized

methanol molecules could permeate easily through the swollen membrane; however, the number of water molecules in the ternary mixture, which could diffuse through the membrane was lower than that in the binary mixture because of the special prevention of methanol molecules. As a result, we concluded that the diffusion step was a controlling step for such a process.

CONCLUSIONS

The separation of binary water–phenol and water–methanol mixtures by PV with PDMS membranes was studied. The results show that phenol could be effectively removed from the aqueous mixture with the organophilic PDMS membrane. α_{VLE} and α_{PV} values for the membrane were calculated. They revealed that α_{PV} for the water–phenol mixture was greater than α_{VLE}. This means that PDMS membrane was highly efficient for the PV separation of phenol from dilute aqueous solutions. This was due to the fact that the solubility parameter of phenol was higher than that of methanol in the silicone membranes. The influence of impurity in phenolic wastewaters was also studied. PV experiments were carried out with water–phenol–methanol mixtures. PDMS membrane showed interesting phenol separation factor and J values for binary water–phenol and ternary water–phenol–methanol mixtures. However, the presence of methanol caused the phenol separation factor and J to decrease slightly.

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