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Research Paper

Removal of Dilute Benzene in Water through Ionic Liquid/Poly(Vinyl Chloride) Membranes by Pervaporation

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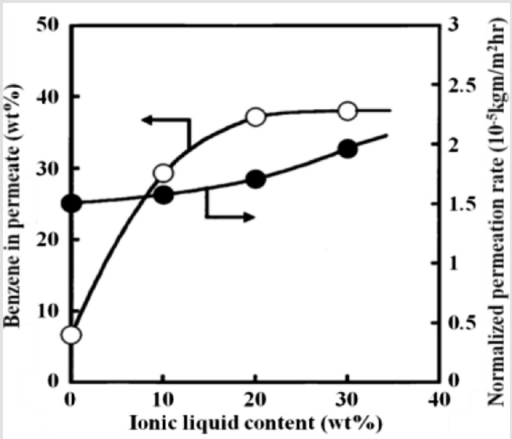
GRAPHICAL ABSTRACT



HIGHLIGHTS

- Membranes contained an ionic liquid which has a high affinity for benzene were prepared for the removal of benzene from aqueous solutions of dilute benzene during pervaporation
- Both the permeation rate and permselectivity of benzene for dilute aqueous benzene solution increased with an increase of the ionic liquid content in the membrane
- The permeation and separation characteristics were discussed from viewpoints of physical and chemical structure of membrane

ABSTRACT

This paper focuses on the effects of the addition of an ionic liquid, 1-Allyl-3-butylimidazilium bis(trifluoromethane sulfonyl)imide ([ABIM]TFSI), which has a high affinity for benzene, into the poly(vinyl chloride) (PVC) membrane on the pervaporation characteristics of the removal of benzene from aqueous solutions of dilute benzene. When aqueous solutions of 100~500 ppm benzene were permeated through the [ABIM]TFSI)/PVC membranes, they showed a high benzene/water selectivity and permeability of these membranes was enhanced with increasing [ABIM]TFSI content significantly. These pervaporation characteristics are discussed from the viewpoint of chemical and physical structure of [ABIM]TFSI/PVC membranes in detail. The mechanism of permeation and separation was analyzed by the solution-diffusion model.

1. Introduction

The volatile organic compounds (VOCs) such as aromatic and chlorinated hydrocarbons have a negative effect on ecology and the human body, directly and indirectly. Removal of VOCs dissolved in water is very important for our life as the water contaminated with VOCs is used as drinking water sources. An active carbon method, ozone processing, and other methods have been developed to remove VOCs from water [1]. However, their separation performance is not high and the operation cost is high.

The membrane separation techniques such as microfiltration, ultrafiltration, reverse osmosis, dialysis, electrodialysis, gas separation, pervaporation, and so on have been applied to industrial, medical, and

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biological fields. Especially, pervaporation (PV) is a promising membrane technique for the separation of VOCs/water mixtures [2-6].

The typical polymer membrane that can selectively permeate VOCs in water is the poyl(dimethysiloxane) (PDMS) membrane. Thus, many membranes composed of PDMS have been prepared for the separation of VOCs/water mixtures [7-17]. However, the PDMS membrane most notably has weak mechanical strength. Poly(vinyl chloride) (PVC) is excellent in the membrane preparation and the strength of their membranes is very strong. However, the selectivity for VOCs of the PVC membrane is not high. Then, we attended to an ionic liquid to give the VOCs selectivity to PVC membranes. Recently, ionic liquids have been noted in a great number of fields because they have specific properties such as low vapor pressure, in-volatility, non-combustibility, high ion conductivity and so on, and are regarded as environmentally friendly. Therefore, they are also playing an increasingly important role in the separation of science fields [18, 19].

Studies on polymer membranes containing ionic liquids in the membrane separation areas are reported for the separation of gases such as CO_2, CH_4, N_2, H_2, and SO_2 and propylene/propane, acetylene/olefin mixtures [20]. In PV separation, the transport of 1,3-propanedial from aqueous mixture [21] and the removal of acetone and butan-1-ol from water [22] were reported by Izák et al. Dyson et al. reported the separation properties of buta-1-ol/water mixtures and supported the ionic liquid PDMS membrane in PV [23]. Heitmann et al. studied the recovery of *n*-butanol by ionic liquid-based PV membranes [24]. Mai et al. studied the selective recovery of acetone-butanol-ethanol from aqueous mixture by PV using the ionic liquid immobilized PDMS and the butanol enrichment factor of the ionic liquid immobilized PDMS was three-times higher than that of the PDMS membrane [25].

In this study, in order to obtain higher VOCs selective membranes, the PVC membrane as a hydrophobic polymer membrane was prepared and 1-allyl-3-butylimidazolium bis(trifluoromethane sulfonyl)imide ([ABIM]TFIS) as an ionic liquid having high affinity for VOCs and low affinity for water was included in the PVC membrane. The permeation and separation characteristics of aqueous solutions of dilute benzene through [ABIM]TFIS/PVC membranes during PV were investigated and are discussed from the viewpoints of chemical and physical structures of these membranes.

2. Experimental

2.1 Materials

Poly(vinyl chloride) (PVC) was supplied by Kaneka Co., Ltd. at an average degree of polymerization of 480 as the membrane material. 1-Allyl-3-butylimidazilium bis(trifluoromethane sulfonyl)imide ([ABIM]TFSI)(**I**) which was purchased from Kanto Chemical Co., Ltd. was selected as an ionic liquid for the selective removal of VOCs from water. All other solvents and reagents were purchased from Wako Pure Chemical Industries, Ltd. and were of analytical grade and were used without further purification.

(I)

2.2 Preparation of PVC and [ABIM]TFSI/PVC membranes

PVC powder was dissolved in tetrahydrofuran (THF) at 30 °C to make a 4 wt% casting solution. The PVA membrane was prepared by pouring the casting solution onto Teflon plates, and allowing the solvent to evaporate completely at 30 °C for 24 h. After the PVC was dissolved in THF at 30 °C to a concentration of 4 wt%, [ABIM] TFSI was added to this THF solution for preparation of the casting solution. The PVC containing [ABIM]TFSI ([ABIM]TFSI/PVC) membranes were prepared by pouring the casting solution onto Teflon plates, and then allowing the solvent to evaporate completely at 30 °C for 24 h.

2.3 FT-IR measurements

The IR spectra of the PVC and [ABIM]TFSI/PVC membranes were measured by FT-IR (Perkin-Elmer, SPECTRUM2000).

2.4 Permeation measurements

Pervaporation (PV) was performed using the apparatus described in previous studies [26-28]. The experimental conditions were: permeation temperature, 40 °C; pressure on the permeate side, 1.33 Pa. The effective membrane area was 13.8 cm^2. In all PV experiments in this study, the air-side surface of the PVC and [ABIM]TFSI/PVC membranes faced the feed side of the permeation cell. An aqueous solution of 0.05 wt% benzene was used as the feed solution. The feed solution was circulated between the PV cell and the feed tank to maintain a constant concentration of feed solution in the PV cell. After the feed and permeate containing benzene and water were dissolved in a specific amount of ethanol, the compositions of the feed solution and the permeate were determined by a gas chromatograph (Shimadzu GC-14A) equipped with a flame ionization detector (FID) and a capillary column (Shimadzu Co. Ltd.; PorapacQ) heated to 180 °C. The permeation rate for the aqueous benzene solution during PV was determined from the weight of the permeate collected in a cold trap, the permeation time and the effective membrane area. To facilitate a comparison of the permeation rate of membranes with different thickness, the normalized permeation rate (kg m/m^2 h), which is the product of the permeation rate and the membrane thickness, was used. The results of the permeation of an aqueous benzene solution by PV were reproducible, and the errors inherent in these permeation measurements ranged within a few percent for the permeation rates through the membranes. Permeation results in this study were after the steady state flux.

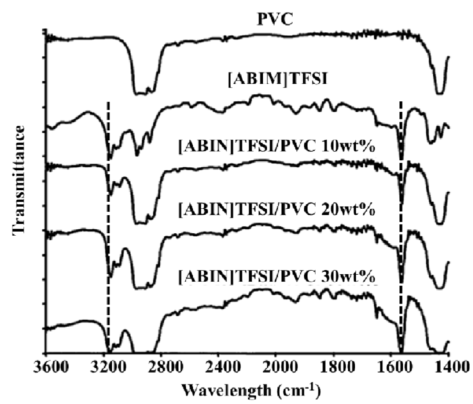

Fig. 1. FT-IR spectra of [ABIM]TFSI, PVC and [ABIM]TFSI/PVC membranes.

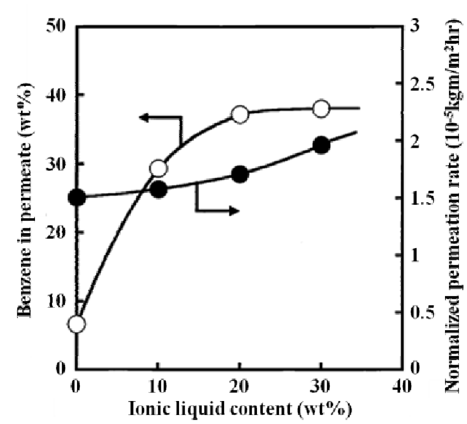

Fig. 2. Effects of the ionic liquid content on the normalized permeation rate (●) and the benzene concentration in the permeate (○) through the PVC and [ABIM]TFSI/PVC membranes during PV.

The composition of the benzene and water mixtures in the feed and permeate yielded the separation factor, $\alpha_{sep.Bz/H2O}$, as expressed by Equation (1),

$$\alpha_{sep.Bz/H2O} = (P_{Bz}/P_{H2O})/(F_{Bz}/F_{H2O}) \quad (1)$$

here F_{Bz} and F_{H2O} are the weight fractions of benzene in the feed and water and P_{Bz} and P_{H2O} are those in the permeate, respectively. Losses of dissolved [ABIM]TFSI from [ABIM]TFSI/PVC membranes were not observed.

2.5 Composition of solution sorbed into membranes

The PVC and [ABIM]TFSI/PVC membranes were completely dried under reduced pressure at room temperature. The dried membranes were immersed in an aqueous solution of 0.05 wt% benzene in a sealed vessel at 40°C until equilibrium was reached. The membranes were then taken out of the vessel, and wiped quickly with a filter. The solution absorbed into the swollen membranes was completely desorbed under reduced pressure, and was collected in a cold trap. The composition of the solution in the membrane was determined by measuring the benzene concentration in the collected solution using gas chromatography (Shimazu GC-14A).

The composition of the solution sorbed into the membranes and that of the feed solution yielded the sorption selectivity, $\alpha_{sorp.Bz/H2O}$, as expressed in Equation (2),

$$\alpha_{sorp.Bz/H2O} = (M_{Bz}/M_{H2O})/(F_{Bz}/F_{H2O}) \quad (2)$$

where F_{Bz} and F_{H2O} are the weight fractions of benzene and water in the feed and M_{Bz} and M_{H2O} are those in the permeate, respectively.

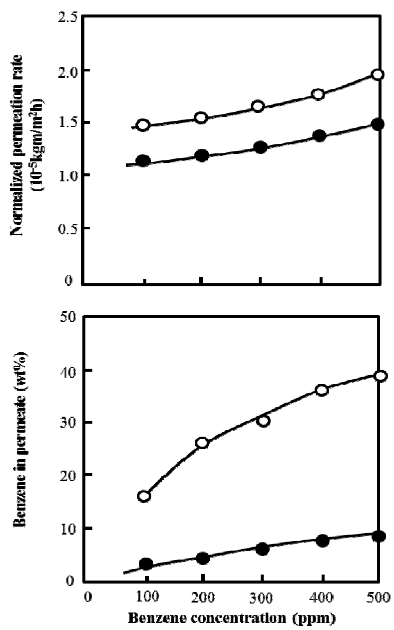

Fig. 3. Normalized permeation rate and benzene concentration in the permeate for an aqueous solution of 0.05 wt% benzene through the PVC membrane without [ABIM]TFSI (●) and the [ABIM]TFSI/PVC membrane containing 30 wt% [ABIM]TFSI (○) in PV as a function of the benzene concentration in the feed solution.

2.6 Contact angle measurements

The contact angles for water on the surface of PVC and [ABIM]TFSI/PVC membranes were measured using a contact angle meter (Kyowa Interface Science, DropMaster 500) at 25 °C. The contact angles, θ, were determined by Equation (3) [29]:

$$\theta = \cos^{-1}\{(\cos\theta_a + \cos\theta_r)/2\} \quad (3)$$

where θ_a and θ_r are the advancing contact angle and the receding contact angle, respectively.

2.7 Degree of swelling of membranes

The PVC and [ABIM]TFSI/PVC membranes were dried completely under reduced pressure at 40 °C and weighed. These membranes were immersed into an aqueous solution of 0.05 wt% benzene in a sealed vessel at 40 °C. After the weight of the membranes became constant, they were taken out of the vessel, wiped quickly with filter paper and weighed. The degree of swelling (DS) of the membrane was determined by Equation (4):

$$DS = W_s/W_d \quad (4)$$

where W_s is the weight of the membrane swollen in an aqueous solution of 0.05 wt% benzene and W_d is the weight of the dried membrane.

2.8. Membrane density

The density of PVC and [ABIM]TFSI/PVC membranes was determined by measuring their weights in air and ethanol with an electric specific weight measure (Shinko Electron Co. Ltd. DMA-220) at 30 °C.

3. Results and discussion

3.1 Characterization of [ABIM]TFSI/PVC membranes

In Figure 1 FT-IR spectra of the PVC membrane, [ABIM]TFSI and [ABIM]TFSI/PVC membranes are shown. As can be seen from these spectra, with increasing [ABIM]TFSI content peaks at 1560 and 3150 cm^{-1} originated from the [ABIM]TFSI molecule increased. These results suggested that the content of [ABIM]TFSI immobilized in the [ABIM]TFSI/PVC membrane obviously increased with an increase of an additional amount of ionic liquid in the preparation of [ABIM]TFSI/PVC membranes.

3.2 Permeation and separation characteristics for an aqueous solution of dilute benzene

Figure 2 shows the normalized permeation rate and benzene concentration in the permeate for an aqueous solution of 0.05 wt% (500 ppm) benzene through [ABIM]TFSI/PVC membranes during PV as a function of the ionic liquid content. Both the normalized permeation rate and benzene concentration in the permeate increased with increasing [ABIM]TFSI content. These results suggest that the addition of [ABIM]TFSI in the PVC membrane enhanced both the permeability and benzene/water selectivity compared with those of the PVC membrane.

3.3 Effect of feed concentration

In Figure 3 the effect of benzene concentration (100- 500 ppm) in the feed liquid on the normalized permeation rate and benzene concentration in the permeate through the PVC membrane without [ABIM]TFSI and the PVC membrane containing 30 wt% [ABIM]TFSI is shown. As can be seen in Figure 3, the permeation rate and the benzene/water selectivity of both PVC membranes with or without [ABIM]TFSI increased with increasing benzene concentration in the feed. However, with an increase of the benzene concentration in the feed, the increase in the permeation rate and the benzene/water selectivity of the PVC containing [ABIM]TFSI are greater than those of the PVC membrane without [ABIM]TFSI. These results suggest that [ABIM]TFSI molecules can sorb a small amount of benzene in the feed more efficiently than the PVC membrane matrix, resulting in an increase in the benzene concentration in the [ABIM]TFSI/PVC membrane. We have reported similar results in the selective removal of dilute benzene from water by membranes containing *tert*-butyl calix [4] arene [30].

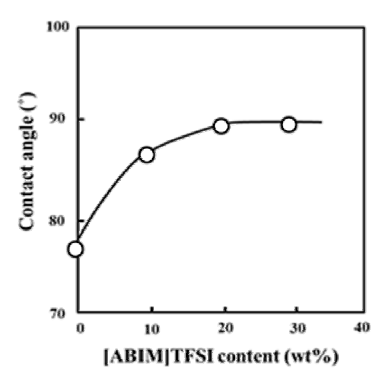

Fig. 4. Effect of the ionic content on the contact angle for water on the surface of the [ABIM]TFSI/PVC membranes.

3.4 Chemical structure of [ABIM]TFSI/PVC membranes

To clarify the role of [ABIM]TFSI in the enhancement of the benzene/water selectivity and permeability of the [ABIM]TFSI/PVC membranes, we characterized the [ABIM]TFSI/PVC membranes based on their chemical and physical structures. Figure 4 shows the contact angle for water on the surface of [ABIM]TFSI/PVC membranes as a function of [ABIM]TFSI. The contact angle of water for all [ABIM]TFSI/PVC membranes increased with increasing [ABIM]TFSI content up to 30 wt% of [ABIM]TFSI. The increase in the contact angle suggests that the addition of [ABIM]TFSI to the PVC membrane significantly increases the hydrophobicity of the membrane surface with increasing [ABIM]TFSI content. However, in this figure, there is some limiting value of the contact angle at 90°. This fact suggests that there is a kind of critical concentration of [ABIM]TFSI in the membrane at which membrane surface is completely occupied with[ABIM]TFSI. Consequently, the addition of [ABIM]TFSI up to 30 wt% results in an increase in the affinity of benzene for PVC membrane.

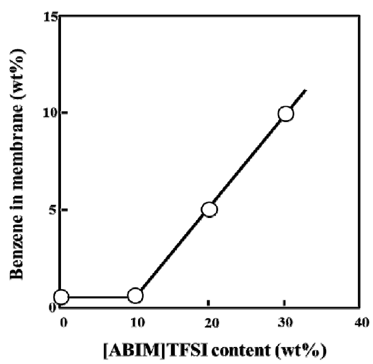

Fig. 5. Benzene concentration in the [ABIM]TFSI/PVC membrane immersed in an aqueous solution of 0.05 wt% benzene as a function of the ionic liquid content.

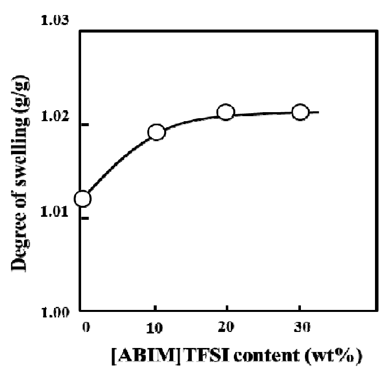

Fig. 6. Effect of the ionic liquid content on the degree of swelling aqueous solution of 0.05 wt% benzene.

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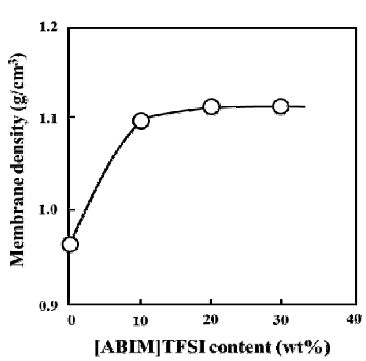

Fig. 7. Membrane density of [ABIM]TFSI/PVC membranes as a function of the ionic liquid content.

Table 1
PV characteristics of PVC, [ABIM]/PVC and PMMA-*g*-PDMS[a] membrane.

Membrane	NPR[b] (10^{-5} kgmm^{-2}h^{-1})	Benzene in permeate (wt%)	Ref.
PVC	1.39	8.1	This work
[ABIM]TFSI/PVC[c]	1.91	38.4	This work
PMMA-*g*-PDMS	0.72	24.3	30

Feed: aqueous solution of 0.05 wt% benzene, Permeation temperature: 40 ºC, Pressure on permeate side: 1.33 Pa
a) Poly (methyl methacrylate-graft-poly(dimethyl siloxane)
b) Normalized permeation rate
c) [ABIM]TFSI content: 30 wt%

Figure 5 shows the effect of the [ABIM]TFSI content on the benzene concentration sorbed in the [ABIM]TFSI/PVC immersed in an aqueous solution containing 0.05 wt% benzene. The benzene concentration in [ABIM]TFSI/PVC membranes were much higher than those in the PVC membrane without [ABIM]TFSI. Furthermore, the benzene concentration sorbed into all membranes increased significantly with increasing [ABIM]TFSI content. The increase in the benzene concentration in all membranes containing [ABIM]TFSI correlates with the results of the contact angle measurements, as shown in Figure 4. As can be seen from Figure 5, a similar trend occurs for the membrane density. In this case also, it is suggested that there is some maximum loading of the ionic liquid in the membrane.

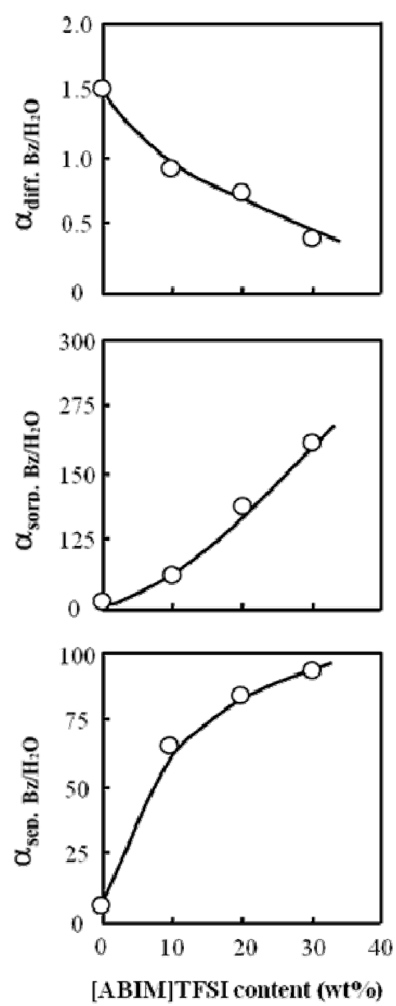

Fig. 8. Effects of the ionic liquid content on the separation factor, sorption selectivity and diffusion selectivity through [ABIM]TFSI/PVC membranes during PV at 40 °C.

3.5 Physical structure of [ABIM]TFSI/PVC membranes

In Figure 6, the degree of swelling of the [ABIM]TFSI/PVC membranes immersed in an aqueous solution of 0.05 wt% benzene as a function of the [ABIM]TFSI content. The degree of swelling of [ABIM]TFSI/PVC membranes increased with increasing [ABIM]TFSI content. The increase in the degree of swelling is due to enhanced benzene sorption into the membrane by the addition of [ABIM]TFSI. The increase in the normalized permeation rate with increasing [ABIM]TFSI content in Figure 1 can be attributed to the fact that the degree of swelling of [ABIM]TFSI/PVC membranes increased with increasing [ABIM]TFSI content. Figure 7 shows the effect of the [ABIM]TFSI content on the membrane density of [ABIM]TFSI/PVC membranes. As can be seen in Figure 7, the membrane densities of [ABIM]TFSI/PVC membranes was much higher than that of the PVC membrane. With increasing [ABIM]TFSI content, the membrane density of [ABIM]TFSI/PVC membranes increased.

3.6 Mechanism of benzene/water selectivity in [ABIM]TFSI/PVC membranes

With respect to the permeation and separation characteristics for organic liquid mixtures though polymer membranes by PV, it is very important to determine the sorption selectivity and diffusion selectivity in the solution-diffusion model [31-32]. With these membrane properties, the separation mechanism of an aqueous benzene solution through the [ABIM]TFSI/PVC membranes can elucidated. In general, the separation factor for mixtures of benzene and water in PV can be defined by Equation (5).

$$\alpha_{sep.}\alpha_{Bz/H2O} = \alpha_{sorp\cdot Bz/H2O} \times \alpha_{diff.Bz/H2O} \quad (5)$$

The diffusion selectivity, $\alpha_{diff.Bz/H2O}$, from Equation (5) can be determined as shown in Equation (6) using the separation factor, $\alpha_{sep.Bz/H2O}$ from Equation (1) and the sorption selectivity, $\alpha_{sorp.\ Bz/H2O}$, from Equation (2).

$$\alpha_{diff.Bz/H2O} = \alpha_{sep}.\alpha_{Bz/H2O} / \alpha_{sorp.\ Bz/H2O} \quad (6)$$

In Figure 8, the separation factor, sorption selectivity and diffusion selectivity for an aqueous solution of 0.05 wt% benzene are shown as a function of the [ABIM]TFSI content in the [ABIM]TFSI/PVC membranes. As can be seen in Figure 8, the sorption selectivites of all of the membranes with various [ABIM]TFSI contents were greater than the diffusion selectivities. This observation suggests that the removal of benzene from a dilute aqueous solution of benzene using [ABIM]TFSI/PVC membranes is mainly governed by the sorption process. The increase in the sorption selectivity with increasing the [ABIM]TFSI/PVC content can be supported by the increase in the benzene concentration in [ABIM]TFSI/PVC membranes in Figure 5. On the other hand, the decrease in the diffusion selectivity with increasing [ABIM]TFSI/PVC content can be explained by the increase in the membrane density in Figure 7, that is, benzene molecules of larger molecular size compared with the water molecule are difficult to diffuse through denser membranes.

3.7 Comparison of permeation and separation characteristics of some polymer membranes

To estimate the performance of [ABIM]TFSI/PVC membranes prepared in this study, an attempt is made to compare it with those of other polymer membranes. It is well-known that the poly(dimethyl siloxane) (PDMS) membrane has a high permselectivity for organic solvents but its membrane strength is extremely low. Then, a graft copolymer membrane from poly (methyl methacrylate) (PMMA) and PDMS is selected as a comparison object. In Table 1, permeation and separation characteristics for a dilute benzene aqueous solution through PVC, [ABIM]TFSI/PVC and PMMA-*g*-PDMS membranes in PV are listed. As can be seen from this table, both the permeation rate and benzene-permselectivity of the [ABIM]TFSI/PVC membrane are higher than those of the PMMA-g-PDMS membrane. Furthermore, the former membrane strength is much higher than the latter one.

4. Conclusions

The effect of the addition of ionic liquid, [ABIM]TFSI, into a hydrophobic PVC membrane for the removal of benzene from water by PV was investigated. The PVC membranes containing [ABIM]TFSI showed higher permeability and benzene/water selectivity, and with increasing [ABIM]TFSI content, both permeability and benzene/water selectivity were improved. These results are worth noting in the membrane separation field. The enhanced permeation properties of [ABIM]TFSI/PVC membranes were investigated based on their chemical and physical structure. The permeation and separation characteristics for an aqueous solution of dilute benzene by PV can be explained by enhanced benzene sorption into [ABIM] TFSI/PVC membranes. The sorption selectivity increased significantly by adding [ABIM]TFSI into the PVC membrane. The increase in the benzene/water selectivity in the PVC membrane was the primary cause for a simultaneous increase in the PV selectivity. Therefore, the strong affinity of [ABIM]TFSI molecule to hydrophobic compounds plays a significant role in the enhancement of benzene affinity in these membranes. In addition, [ABIM]TFSI influenced the physical structure of [ABIM]TFSI/PVC membranes. In particular, the benzene concentration of all [ABIM]TFSI/PVC membranes remarkably increased with increasing [ABIM]TFSI content. In this study, we demonstrated that membranes with high permeability and high benzene/water selectivity could be designed by adding [ABIM]TFSI into the PVC membrane.

Acknowledgements

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References

[1] R.W. Baker, In Membrane Separation System, Recent Developments and Future Directions; R.W. Baker, E.L. Cussler, W. Eykamp, W.J. Koros, R.L. Riley, H. Strathmann, H., Eds.; Noyes Data Corp., Park Ridge, NJ, 1991, 2.1 Process Overview, pp 151-160.
[2] R. Psaume, Y. Aurell, C. J. Mora, J. L. Bersillon, Pervaporation: importance of concentration polarization in the extraction of trace organics from water, J. Membr. Sci. 36 (1988) 373-384.
[3] I. Blume, J.G. Wijmans, R.W. Baker, The separation of dissolved organics from water by pervaporation, J. Membr. Sci. 49 (1990) 253-286.
[4] Y. Fang, V.A. Pham, T. Matuura, J.P. Santerre, R.M. Narbaitz, Effect of surface-modifying macromolecules and solvent evaporation time on the performance of polyethersulfone membranes for the separation of chloroform/water mixtures by pervaporation, J. Appl. Polym. Sci. 54 (1994) 1937-1943.
[5] D. Yang, S. Majumdar, S. Kovenklioglu, K. Sirkar, Hollow fiber contained liquid membrane pervaporation system for the removal of toxic volatile organics from wastewater, J. Membr. Sci. 103 (1995) 195-210.
[6] W.W.Y. Lau, J. Finlayson, J.M. Dickson, J. Jiang, M.A. Brook, Pervaporation performance of oligosilylstyrene-polydimethylsiloxane membrane for separation of organics from water, J. Membr. Sci. 134 (1997) 209-217.
[7] S. Mishima, T. Nakagawa, Sorption and diffusion of volatile organic compounds in fluoroalkyl methacrylate-grafted PDMS membrane, J. Appl. Polym. Sci. 75 (2000) 773-783.
[8] A.M. Urtiaga, D. Gorri, I. Ortiz, Mass-Transfer modeling in the pervaporation of VOCs from diluted solutions, AIChE J. 48 (2002) 572-581.
[9] H.J. Kim, S.S. Nah, B.R. Min, A new technique for preparation of PDMS pervaporation membrane for VOC removal, Adv. Environ. Res. 6 (2002) 255-264.
[10] M. Bennett, B.J. Brisdon, R. England, R.W. Field, Performance of PDMS and organofunctionalised PDMS membranes for the pervaporative recovery of organics from aqueous streams, J. Membr. Sci. 137 (1997) 63-88.
[11] S. Das, A.K. Banthia, B. Adhikari, Pervaporation separation of aqueous chlorophenols by a novel polyurethane urea–poly (methyl methacrylate) interpenetrating network membrane, J. Membr. Sci. 280 (2006) 675-683.
[12] S. Deng, S., Sourirajan, T. Matsuura, A study of polydimethylsiloxane/aromatic polyamide laminated membranes for separation of acetic acid/water mixtures by pervaporation process, Sep. Sci. Technol. 29 (1994) 1209-1216.
[13] J. Wenchang, K. S. Subhas, H. Sun-Tak, Sorption, diffusion and permeation of 1,1,1-trichloroethane through adsorbent-filled polymeric membranes, J. Membr. Sci. 103 (1995) 243-252.

[14] Y.-H. Chang, J.-H. Kim, S.-B. Lee, H.-W. Rhee, Polysiloxaneimide membranes for removal of VOCs from water by pervaporation, J. Appl. Polym. Sci. 77 (2000) 2691-2702.
[15] M. Peng, S. Liu, VOC removal from contaminated groundwater through membrane pervaporation. (I): Water-1,1,1-trichloroethane system, J. Environ. Sci. 15 (2003) 815-820.
[16] J. Xu. A. Ito, Removal of VOC from water by pervaporation with hollow-fiber silicone rubber membrane module, Desal. Wat. Treat. 17 (2010) 135-142.
[17] D. Jeong, J. Oh, I. Yum, Y. Lee, Removal of VOCs from their aqueous solution by pervaporation with PDMS-zeolite composite membrane, Desal. Wat. Treat. 17 (2010) 242-247.
[18] R.D. Noble, In Green Separation Processes, Fundamentals and Applications; C.A. Afonso, J.G. Crespo, Eds.; Wiley-VCH, Weinheim, 2005, Chapter 3.1, pp103-126. S. Seinigeweg, J. Grmechling, In Green Separation Processes, Fundamentals and Applications; C.A. Afonso, J.G. Crespo, Eds.; Wiley-VCH, Weinheim, 2005, Chapter 3.2, pp127-154. I.F.J. Vankelecom, L.E.M. Gevers, T. Schafer, J.G. Crespo, In Green Separation Processes, Fundamentals and Applications; C.A. Afonso, J.G. Crespo, Eds.; Wiley-VCH, Weinheim, 2005, Chapter 3.6, pp251-289.
[19] X. Han, D.W. Armstrong, Ionic Liquids in Separations, Acc. Chem. Res. 40 (2007) 1079-1086.
[20] R.D. Noble, D.L. Gin, Perspective on ionic liquids and ionic liquid membranes, J. Membr. Sci. 369 (2011) 1-4.
[21] P. Izák, M. Kockerling,U. Kragl, Solute transport from aqueous mixture throught supported ionic liquid membrane by pervaporation, Desalination 199 (2006) 96-98.
[22] P. Izák, W.Ruth, Z. Fei, P.J. Dyson, U. Kragl, Selective removal of acetone and butan-1-ol from water with supported ionic liquid–polydimethylsiloxane membrane by pervaporation, Chem. Eng. J. 139 (2008) 318-321.
[23] P. Izák, K. Friess, V. Hynek, W. Ruth, Z. Fei, J.P. Dyson, U. Kragl, Separation properties of supported ionic liquid–polydimethylsiloxane membrane in pervaporation process, Desalination 241 (2009) 182-187.
[24] N.L. Mai, S.H. Kim, S.H. Ha, H.S. Shin, Y.-M. Koo, Selective recovery of acetone-butanol-ethanol from aqueous mixture by pervaporation using immobilized ionic liquid polydimethylsiloxane membrane, Korean J. Chem. Eng. 30 (2013) 1804-1809.
[25] S. Heitmann, J. Krings, P. Kreis, A. Lennert, W.R. Pitner, A. Górak, M.M. Schulte, Recovery of n-butanol using ionic liquid-based pervaporation membranes, Sep. Purif. Technol., 97 (2012) 108-114.
[26] T. Uragami, T. Doi, T.,Miyata, Control of permselectivity with surface modifications of poly[1-(trimethylsilyl)-1-propyne] membranes, Inter. J. Adhesion & Adhesive 19 (1999) 405-409.
[27] T. Uragami, T. Meotoiwa, T. Miyata, Effects of morphology of multicomponent polymer membranes containing calixarene on permselective removal of benzene from a dilute aqueous solution of benzene, Macromolecules 29 (2003) 2041-2048.
[28] T. Uragami, K. Tsukamoto, T. Miyata, Performance of butyrylcellulose membranes for benzene/cyclohexane mixtures containing a low benzene concentration by pervaporation, Biomocromolecules 5 (2004) 2116-2121.
[29] T. Uragami, K. Tsukamoto, K. Inui, T. Miyata, Pervaporation characteristics of a benzoylchitosan membrane for benzene-cyclohexane mixtures, Macromol. Chem. Chem. Phys. 199 (1998) 49-54.
[30] T. Uragami, T. Meotoiwa, T. Miyata, Effects of the Addition of Calixarene to Microphase-Separated Membranes for the Removal of Volatile Organic Compounds from Dilute Aqueous Solutions, Macromolecules 34 (2001) 6806-6811.
[31] R.C. Binnding, R.J. Lee, J.F. Jennins, E.C. Mertin, Separation of liquid mixtures by permeation, Ind. Eng. Chem. 53 (1961) 45-50.
[32] P. Aptel, J. Cuny, J., Jozefonvicz, G. Morel, J. Neel, Liquid transport through membranes prepared by grafting of polar monomers onto poly(tetrafluoroethylene) films. III. Steady-state distribution in membrane during pervaporation, J. Appl. Polym. Sci. 18 (1974) 365-378.