HTPB-Based Polyurethaneurea Membranes for Recovery of Aroma Compounds from Aqueous Solution by Pervaporation

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ABSTRACT: Hydroxyterminated polybutadiene (HTPB)-based polyurethaneurea (PU), HTPB-PU, was synthesized by two-step polymerization and was firstly used as membrane materials to recover aroma, ethyl acetate (EA), from aqueous solution by pervaporation (PV). The effects of the number–average molecular weight (M_n) of HTPB, EA in feed, operating temperature, and membrane thickness on the PV performance of HTPB-PU membranes were investigated. The membranes demonstrated high EA permselectivity as well as high EA flux. The DSC result showed two transition temperatures in the HTPB-PU membrane and contact angle measurements revealed the difference of hydrophobicity of the membrane at both sides, which were induced by glass plate and air, respectively, due to movement of the soft hydrophobic polybutadiene (PB) segments in HTPB-PU chains. Furthermore, the PV performance of the HTPB-PU membrane with the hydrophobic surface facing the feed was much better than that with the hydrophilic surface. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 552–559, 2007

Key words: membranes; morphology; polyurethaneurea; separation techniques; surfaces

INTRODUCTION

Volatile organic compounds (VOC) of foods and beverages, generally referred to as aroma compounds, contribute significantly to the flavor. Analysis of different kinds of fruits indicates more than 6000 compounds as participants of their aroma. For instance, juices of passion fruit and orange have about 200 compounds responsible for their aroma.[1] But most of these VOCs are lost during the processing of food. This has resulted in great economical losses.[2]

PV is being recognized as an energy-efficient alternative to other traditional separation methods including air stripping, adsorption, distillation, and oxidation for recovery of aroma from aqueous solution.

Nowadays, a major hurdle limits PV commercialization for recovery of aroma from aqueous solution. Namely, it is a lack of proper membrane materials with high flux and separation factor for recovery of so many kinds of organic compounds. Many hydrophobic materials used for aroma recovery have been studied, such as, polyether-*block*-amide (PEBA),[3–6] polyoc-

tylmethylsiloxane, polydimethylsiloxane (PDMS),[7–10] ethylene–propylene–diene monomer (EPDM)[1,11] and poly(vinylidene fluoride-*co*-hexafluoropropene) [P(VDF-*co*-HFP)].[12] Among them, PEBA, PDMS, and P(VDF-*co*-HFP) were ever used to recover ethyl acetate (EA) from water. Djebbara et al.[4] reported that the separation factor for PDMS and PEBA membranes were 425 and 134, the EA flux were 2980 and 2030 g/m² h, respectively, at 30°C. These materials are not only hydrophobic but also elastic and both properties are in favor of the permselectivity of EA. Semicrystalline P(VDF-*co*-HFP) membrane was used by Tian et al.[12] to recover EA from water and showed good mechanical strength and film-forming property. When EA in feed was 3.0 wt % the separation factor was 160 and the EA flux was 500 g/m² h at 30°C. In general, membrane materials applied in organophilic pervaporation (PV) should satisfy several requirements except for good PV performances (permeability and permselectivity), such as, stability in contact with the separated liquid mixture, thermal stability, and stable transport and mechanical characteristics over time. The literatures indicated that despite the diversity of available polymeric materials, only a few have been studied as membrane materials in PV for aroma recovery. It has been evident[3–6,13,14] that the introduction of some polar segments to the elastic materials is good for improving their mechanical strength and film-forming property.

Polyurethaneurea is a suitable membrane material, which could provides hydrophobic and flexible soft

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segment (polyol) for facilitating organic diffusion and a rigid hard segment (diisocyanate and chain extender, viz. diol, diamine) for mechanical strength,[15] and has been used to remove 1,1,1-trichloroethane, toluene, dichloromethane, and phenol from aqueous solutions.[15,16–19]

HTPB-based polyurethaneurea membranes have soft segment of polybutadiene (PB) and rigid segment of urea, which have been used earlier for separation of ethanol-water mixture[20,21] and gas mixtures.[22] None report for the esters-water mixtures, such as EA-water mixture, can be found. In fact, esters are numerically the largest group of aroma compounds.[23] In this article hydrophobic HTPB was chosen as polyol to synthesize HTPB-PU and then to prepare HTPB-PU membrane. EA was chosen as a model aroma compounds. The objectives of this study are trying to know the recovery performance of EA from aqueous solution using the HTPB-PU membrane first, and then some internal and external dependences of the recovery of EA from aqueous solutions.

EXPERIMENTAL

Materials

HTPB (hydroxyl value = 1.05 mmol KOH g^{-1}) with the number–average molecular weight of 2000, 2500, and 3000 (M_n, in g/mol) were received from Qilushihua (Shandong, China); Dibutyltindilaurate (DBTDL, catalyst) and toluene 2,4-diisocyanate (TDI, L.R) obtained from Hangzhou Electronical Group Auxiliary Chemical (Hangzhou, China), were used without further purification. Solvent tetrahydrofuran (THF) was dried by molecular sieves and distilled under nitrogen. Chain-extender, 3,3′-dichloro-4,4′-diaminodiphenymethane (MOCA), was obtained from Hangzhou Congsun Chemical (Hangzhou, China).

Synthesis and characteristics of HTPB-PU

Firstly, HTPB was heated to 100°C under vacuum for 2 h to remove water and gases and then cooled down to room temperature. Prepolyurethane was prepared by the reaction of HTPB and TDI in THF at 30°C for 1 h in the presence of 0.05 wt % DBTDL as catalyst maintaining NCO : OH mole ratio of 2 : 1. Polyurethaneurea was prepared by adding the chain-extender MOCA (OH : NH$_2$ = 1 : 1) to the prepolyurethane under mechanical stirring. After 15 min of the reaction, the entrapped bubbles were removed from the viscous solution by vacuum evacuation. The structures of prepolyurethane and HTPB-PU are shown in Scheme 1. The solution with solid content of 30 wt % was cast on a clean glass plate and was left overnight at room temperature followed by thermal curing at 80°C for 3 h. The thickness of the obtained membranes was about 100 μm.

The chemical structures of HTPB, prepolyurethane, and HTPB-PU samples were confirmed by Fourier transform infrared (FTIR) using a Bruck Vector22 type spectrometer. The samples for FTIR measurements were obtained by spreading a thin film of their solutions in THF on a potassium bromide flake and evaporated the solvent under vacuum at room temperature.

The differential scanning calorimetry (DSC) curve of the HTPB-PU was obtained through a Perkin–Elmer Pyris 1 DSC under N$_2$ atmosphere at a heating rate of 20°C/min from −150 to 200°C.

Static contact angles for water of HTPB-PU membranes were measured by sessile drop method[24] using a contact angle meter (OCA 20, Dataphysics Instruments GmbH Germany) at 25°C and at about 65% relative humidity. The volume of the water drops used was always 2 μL. All reported values were average of at least eight measurements taken at different locations of the film surface and have a typical error of the mean of ±1°.

Thermal stability of the HTPB-PU was examined with a Perkin–Elmer Pyris 1 Thermogravimetric analyzer (TGA). The temperature profile was from 60 to 600°C at a heating rate of 20°C/min.

Degree of swelling and sorption of membrane

The swelling experiment was conducted according to the method proposed by Trifunovic.[25] Thick pieces (0.4–0.8 g, 300 μm) of HTPB-PU membranes were weighed (m_0) and immersed in 20 mL of aqueous solution with known EA weight fraction (W_{EA}^0) and kept in tightly sealed flasks at 30°C for 72 h to reach thermodynamic equilibrium. The swollen polymer was removed from the solution after thermodynamic equilibrium and the free liquid on the surface of it was carefully removed by using a paper tissue. The swollen membrane was weighed again (m_t). The remaining EA weight fraction (W_{EA}^t) in solution was determined by gas chromatographic (GC) analysis. The degree of swelling was calculated as follows:

$$DS = \frac{m_t - m_0}{m_0} \times 100\% \qquad (1)$$

The weight fraction of the EA (W_{EA}^M) and water (W_W^M) inside the membrane can be expressed as follows:

$$W_{EA}^M = \frac{m_{EA}^M}{m_t - m_0} = \frac{(W_{EA}^0 - W_{EA}^t)m_s}{m_t - m_0} \qquad (2)$$

$$W_W^M = \frac{m_t - m_0 - m_{EA}^M}{m_t - m_0} \qquad (3)$$
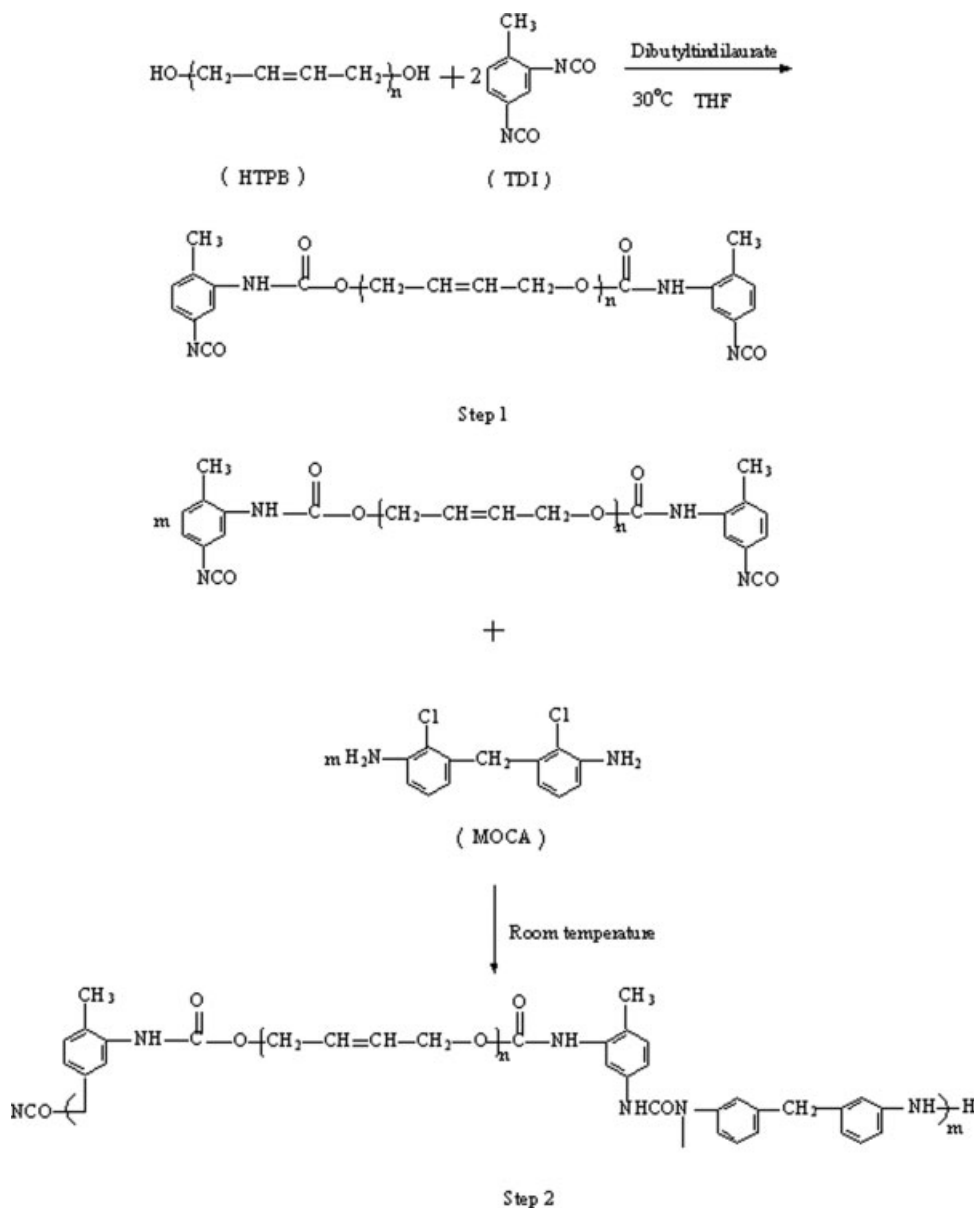
Scheme 1 Preparation of prepolyurethane and HTPB-PU.

where m_{EA}^M is the mass of EA in the polymer after the sorption process and m_S is the mass of 20 mL of the aqueous solution added. The sorption selectivity, $\alpha_{sorp,i/W}$, was calculated by:

$$\alpha_{sorp,i/W} = (W_{EA}^M/W_W^M)/(W_{EA}^0/W_W^0) \quad (4)$$

where W_W^0 is the weight fraction of water in the feed.

PV measurement

A traditional PV apparatus was used in this study.[26] The permeation flux, J and the separation factor, $\alpha_{EA/W}$ for all membranes were calculated according to the following equations:

$$J = \frac{\Delta W}{S \Delta t} \quad (5)$$

$$\alpha_{EA/W} = \frac{y_{EA}/y_W}{x_{EA}/x_W} \quad (6)$$

where ΔW is the permeation weight during the operation time Δt, S the membrane area 18.09 cm^2, x and y the weight fraction in the feed and the permeate, respectively. For all measurements, the downstream pressure was maintained at 5 mmHg by a vacuum pump. The permeate vapor was condensed with liquid nitrogen. The permeation rate was determined by measuring the weight of the permeate liquid. The compositions of the feed solutions and the permeate liquid were measured by gas chromatography (GC, China Chromatography 120).
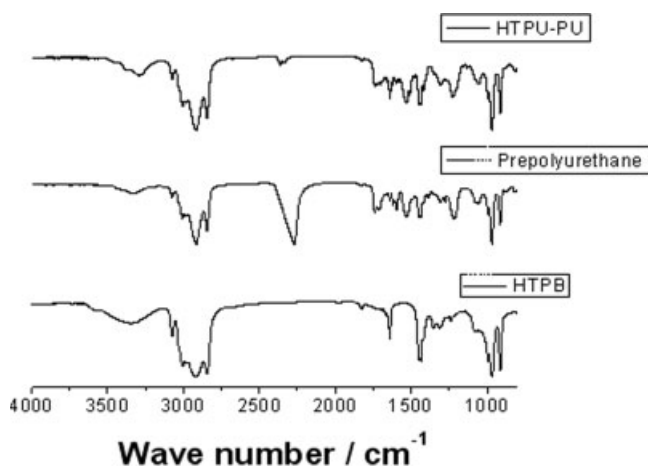
Figure 1 FTIR spectra of HTPB, prepolyurethane, and HTPB-PU.

Figure 3 TGA curve of HTPB-PU.

RESULTS AND DISCUSSION

Characterization of HTPB

The FTIR spectra of HTPB, HTPB-PU, and prepolyurethane are shown in Figure 1. Compared with HTPB the strong absorption in the 2270 cm^{-1} region (asymmetric–NCO stretch) appeared in prepolyurethane, and almost disappeared in the FTIR spectrum of HTPB-PU, so the reaction of chain extend was complete. In prepolyurethane new other peaks of 1738 cm^{-1} (C=O) and 1531 cm^{-1} (N—C) are also observed compared with HTPB and confirmed the forming of urethane group (—NHCOO—).

Figure 2 shows DSC thermogram of the HTPB-PU. Two glass transition temperatures (T_g), −75 and 65°C are displayed. This result suggests that there are two kinds of incompatible microdomain in the HTPB-PU membrane. It is well known that multicomponent polymer blends often have a heterogeneous structure because of the immiscibility of each component. T_g value obtained by DSC measurements could be used

to investigate the heterogeneity of a polymer. It is well known that the HTPB soft segment is very hydrophobic and the urethane hard segment is very hydrophilic, this suggests that the higher T_g in the block copolymer membranes was due to the urethane component and the lower T_g from the HTPB component.

Figure 3 shows the TGA curve of HTPB-PU. The weight loss of HTPB-PU starts after 250°C. It means HTPB-PU has good thermal stability for the PV process.

Figure 4 gives the variation of the contact angle for water with the M_n of HTPB on the glass-side and the air-side surfaces of HTPB-PU membranes. Both the contact angles of water on the air-side and glass-side surfaces of the membranes increased with increasing the M_n of HTPB. This is due to the increase of M_n of HTPB that will result in the increase of hydrophobic segments in the HTPB-PU membranes. In addition, the contact angle of water of the air-side surface is higher than that of the glass-side surface. This indicates that the hydrophobic segments of PB were more preferentially concentrated at the air-side surface than
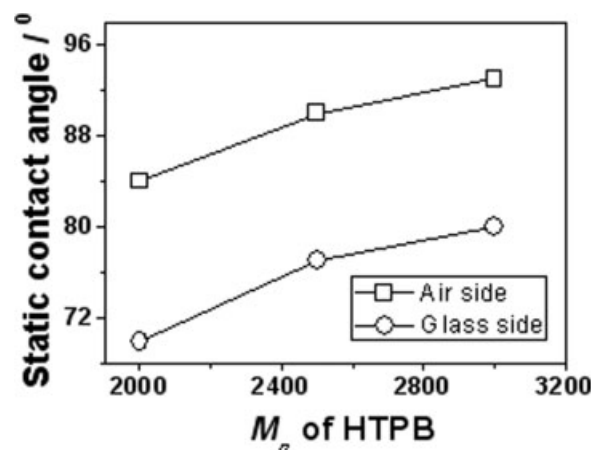

Figure 2 DSC thermogram of HTPB-PU.

Figure 4 The variation of the contact angle for water with M_n of HTPB with the HTPB-PU membrane's both surfaces.

Figure 7 Effect of the EA in feed on $\alpha_{EA/W}$, $\alpha_{diff,EA/W}$, and $\alpha_{sorp,EA/W}$ for HTPB-PU membrane at 30°C (M_n of HTPB, 2500).

increasing EA in feed from 0.62 to 3.10 wt %, the EA flux also increased up to 190 g/m² h with increasing EA in feed, but the increasing of the water flux was slight. The increasing of the separation factor with EA in feed, here, is mainly due to diffusion selectivity-controlled in the solution–diffusion mechanism of PV process.

In general, the separation and permeation characteristics for organic liquid mixtures through polymer membranes by PV are based on the solubility of the permeants into the polymer membrane (sorption process), and the diffusivity of the permeants in the polymer membrane (diffusion process). It is very important to determine the sorption selectivity and diffusion selectivity to estimate the separation mechanism of an aqueous EA solution through the HTPB-PU membranes. The separation factor for mixtures of EA and water in PV can be defined by eq. (7)[28]

$$EA/W = \alpha_{sorp,EA/W}\alpha_{diff,EA/W} \tag{7}$$

the separation factor, EA/W, are determined from eq. (6) and the sorption selectivity, $\alpha_{sorp,EA/W}$, from eq. (4). Thus the diffusion selectivity, $\alpha_{diff,EA/W}$, could be drawn from eq. (7).

Figure 7 shows the effect of EA in feed on $\alpha_{EA/W}$, $\alpha_{diff,EA/W}$, and $\alpha_{sorp,EA/W}$ for HTPB-PU membrane at 30°C. As can be seen that $\alpha_{diff,EA/W}$ was much greater than $\alpha_{sorp,EA/W}$. The results suggest that the separation of the HTPB-PU membrane for EA/water mixture is mainly governed by diffusion process at the EA concentration range of the feed studied. In other words, the increasing of EA concentration is in favor of the permeation of EA because of the more increasing of $\alpha_{diff,EA/W}$ compared with $\alpha_{sorp,EA/W}$. Thus, the EA flux increases dramatically and the water flux increased a little with increasing EA concentration in feed as shown in Figure 6(b), and the separation factor, $\alpha_{EA/W}$, increased with increasing EA concentration as shown in Figure 6(a), ultimately. These results

are in accordance with the HTPB-PU membrane structure mentioned earlier. Uragami proved that organic molecules mainly permeated through the hydrophobic phase of a membrane that has microphase structure, while water molecules mainly permeated through hard segments.[29] The PB segment is very hydrophobic and long that formed the main matrix of the whole membrane. It is also a soft segment, which is in favor of the diffusion of EA. But the diffusion of water is much harder because the low content of hard and polar segments in the membrane. In addition, the low degree of swelling of the HTPB-PU membranes, which was only 13.4% in feed with 3.10 wt % EA concentration, will be resistant to water permeation.

Effect of temperature on PV performance

Figure 8 shows temperature effect on the PV performance of HTPB-PU membrane with the air-side surface facing the feed. Both EA content in permeate and separation factor decrease and flux increases with increasing temperature from 30 to 60°C. This is a normal PV performance. It is interesting that a high separation factor with more than 300 is kept even at 60°C,

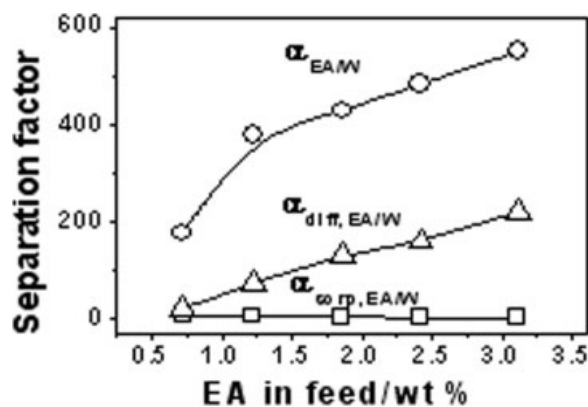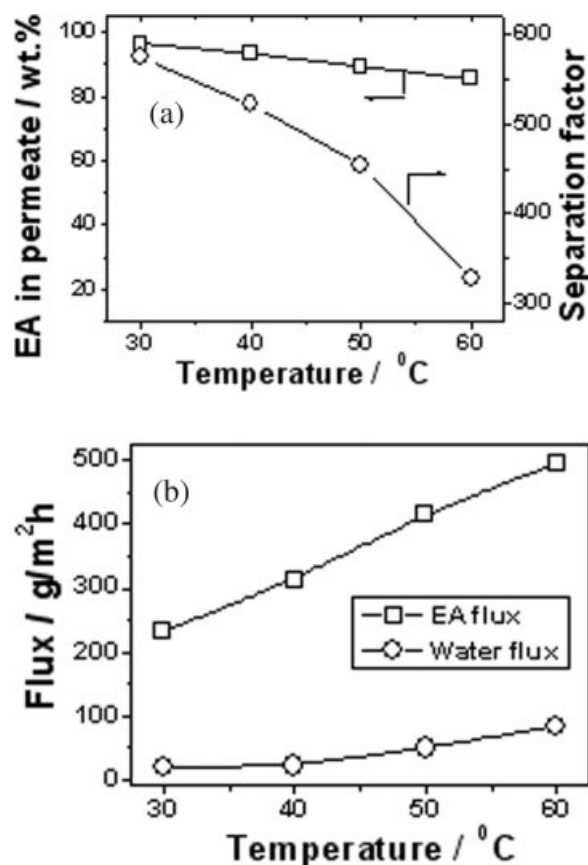**Figure 8** Temperature effect on the PV performance of HTPB-PU membrane with air-side facing the feed (Membrane thickness, 100 μm; M_n of HTPB, 2500; feed concentration, 3.1 wt %).

and the increasing of the water flux is still lower than that of the EA flux though the water molecular volume is much smaller than EA molecular volume.

Figure 9 shows Arrhenius plots of PV of EA and water mixture. Two linear lines for EA and water were obtained at the range of the temperature studied, and the permeation activation energies of EA and water through the membrane are 21.41 and 44.03 mol K^{-1}, respectively. The high permeation activation energy of water could be used to account for its lower flux than EA.

Effect of membrane thickness on PV performance

Figure 10 shows the effect of the thickness of HTPB-PU membrane on the separation of EA/water mixture with two sides of the membranes facing the feed. Both EA flux and the separation factor of HTPB-PU membrane decrease with increasing the thickness of the dry membrane. The variation of EA flux with thickness is in consistent with literatures' results studied on VOC removal from water.[30]

The variation of the separation factor of PV membranes for removal of volatile organic compounds with the membrane thickness exhibits two different trends in literatures. One was that the separation factor increased as the membrane thickness increases.[31] While Yeom et al.'s research[32] showed opposite.

The separation factor in this study was inversely proportional to the thickness of the membrane because HTPB-PU membrane is very hydrophobic. In other words, the decrease of membrane thickness resulted in the smaller resistance of EA permeation, but the high hydrophobicity still makes water diffuse harder.
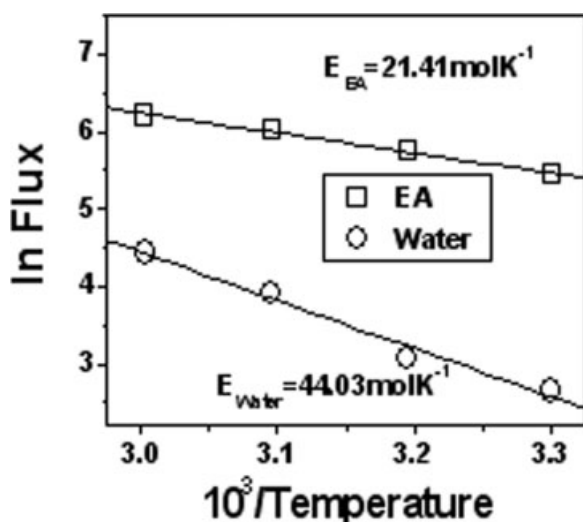

Figure 9 Arrhenius plots of the HTPB-PU membrane with M_n of HTPB, 2500.
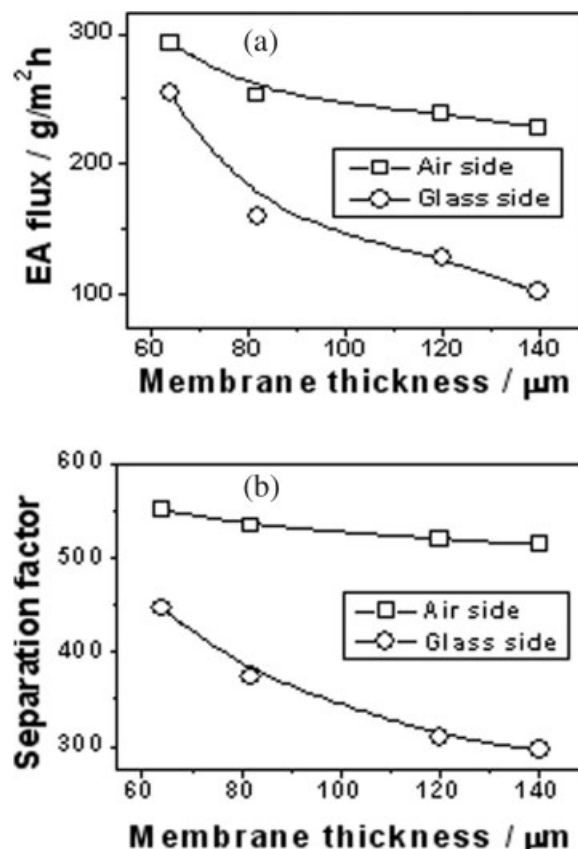
Figure 10 Effect of membrane thickness on the PV performance of HTPB-PU membrane (M_n of HTPB, 2500; feed concentration, 3.1 wt %; temperature, 30°C).

CONCLUSIONS

From the present study the following conclusions can be drawn:

1. Hydroxyterminated polybutadiene (HTPB) based polyurethaneurea (HTPB-PU) was synthesized and HTPB-PU membranes were first used for recovery of EA from aqueous solution. The HTPB-PU showed the microphase separation structure, good film-forming property, excellent thermal stability and high EA selectivity.
2. The separation factor increased and the EA flux decreased with increasing the M_n of HTPB used for making the HTPB-PU membrane. In addition, both separation factor and EA flux are higher with air-side surfaces facing the feed than with glass-side surfaces facing the feed.
3. Both EA flux and the separation factor of the HTPB-PU membrane increase with increasing the EA in feed from 0.62 to 3.10 wt % at 30°C due to the diffusivity controlled the PV process.
4. With increasing operating temperature the EA flux increases and the separation factor decreases, but more than 300 is still kept even at 60°C for the

feed with 3.10 wt % due to the high permeation activation energy of water.

5. Both EA flux and the separation factor decrease with increasing the HTPB-PU membrane thickness.

References

1. Pereira, C. C.; Rufino, J. R. M.; Habert, A. C.; Nobrega, R.; Cabral, L. M. C.; Borges, C. P. J Food Eng 2005, 66, 77.
2. Karlson, H. O. E.; Trägårdh, G. J Membr Sci 1993, 76, 121.
3. Baudot, A.; Marin, M. J Membr Sci 1996, 120, 207.
4. Djebbara, M. K.; Nguyenb, Q. T.; CleÂmenta, R.; Germain, Y. J Membr Sci 1998, 146, 125.
5. Sampranpiboon, P.; Jiraratananon, R.; Uttapap, D.; Feng, X.; Huang, R. Y. M. J Membr Sci 2000, 173, 53.
6. Jiraratananon, R.; Sampranpiboon, P.; Uttapap, D.; Huang, R. Y. M. J Membr Sci 2002, 210, 389.
7. Börjesson, J.; Karlsson, H. O. E.; Trägårdh, G. J Membr Sci 1996, 119, 229.
8. Schäfer, T.; Bengtson, G.; Pingel, H.; Böddeker, K. W.; Crespo, J. P. S. G. Biotechnol Bioeng 1999, 62, 412.
9. Kanani, D. M.; Nikhade, B. P.; Singh, P. B. G.; Pangarkar, V. G. Ind Eng Chem Res 2003, 42, 6924.
10. Sampranpiboon, P.; Jiraratananon, R.; Uttapap, D.; Feng, X.; Huang, R. Y. M. J Membr Sci 2000, 174, 55.
11. Huang, R. Y. M.; Moon, G. Y.; Pal, R. Ind Eng Chem Res 2002, 41, 531.
12. Tian, X. Z.; Zhu, B. K.; Xu, Y. Y. J Membr Sci 2005, 248, 109.
13. Miyata, T.; Takagi, T.; Uragami, T. Macromolecules 1996, 29, 7787.
14. Uragami, T.; Yamada, H.; Miyata, T. J Membr Sci 2001, 187, 255,
15. Hollein, M. E.; Hammond, M.; Slater, C. S. Sep Sci Technol 1993, 28, 1043.
16. Ji, W.; Sikdar, S. K.; Hwang, S. T. J Membr Sci 1994, 93, 1.
17. Hoshi, M.; Ieshige, M.; Saitoh, T.; Nakagawa, T. J Appl Polym Sci 2000, 76, 654.
18. Hoshi, M.; Kogure, M.; Saitoh, T.; Nakagawa, T. J Appl Polym Sci 1997, 65, 469.
19. Gupta, T.; Pradhan, N. C.; Adhikari, B. J Membr Sci 2003, 217, 43.
20. Lee, K. R.; Teng, M. Y.; Hsu, T. N.; Lai, J. Y. J Membr Sci 1999, 162, 173.
21. Huang, S. H.; Chao, J. Y. Eur Polym J 1998, 34, 449.
22. Chen, S. H.; Yu, K. C.; Houng, S. L.; Lai, J. Y. J Membr Sci 2000, 173, 99.
23. Morton, I. D.; Macleod, A. J. Food Flavours, Part C: The Flavour Of Fruits; Elsevier: New York, 1990; pp 1–41.
24. Tretinnikov, O. N. Langmuir 1997, 13, 2988.
25. Trifunovic, O.; Trägårdh, G. J Membr Sci 2003, 216, 207.
26. Uragami, T.; Ohshima, T.; Miyata, T. Macromoleculars 2003, 36, 9430.
27. Higuchi, A.; Yoon, B. O.; Asano, T. J Membr Sci 2002, 198, 311.
28. Miyata, T.; Nakanishi, Y.; Uragami, T. Macromolecules 1997, 30, 5563.
29. Uragami, T.; Meotoiwa, T.; Miyata, T. Macromoleculars 2001, 34, 6806.
30. Peng, M.; Vane, L. M.; Liu, S. X. J Hazard Mater B 2003, 98, 69.
31. Lau, W. W. Y.; Finlayson, J.; Dickson, J. M. J Membr Sci 1997, 134, 209.
32. Yeom, C. K.; Kim, H. K.; Rhim, J. W. J Appl Polym Sci 1999, 73, 601.