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A High Performance Membrane for Sorption and Pervaporation Separation of Ethyl *tert*-Butyl Ether and Ethanol Mixtures

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ABSTRACT

A new kind of membrane was prepared by blending 5 wt% poly(1-vinylpyrrolidone-*co*-acrylic acid) with cellulose acetate propionate for the separation of ethyl *tert*-butyl ether and ethanol mixtures. The membrane properties were evaluated by pervaporation and sorption of mixtures of ethyl *tert*-butyl ether/ethanol. The experimental results show that the selectivity and the fluxes of this membrane depend upon the feed composition and upon the temperature. The minimum values of ethanol concentration in the permeate and in the sorption solution were obtained in the vicinity of the azeotropic point. Compared with the pure CAP membrane, the new membrane shows high performance for the separation of ETBE and EtOH mixtures, especially under high temperature conditions.

Key Words. Pervaporation; Sorption; ETBE; Ethanol; Blended membrane

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INTRODUCTION

The need for methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) in high quality fuels has increased rapidly with the development of environmental concerns in recent years (1, 2). ETBE is especially recognized as an environmentally friendly product. Because of reaction equilibrium limitations and some azeotropes, the existing production process is a high capital and energy intensive separation process.

As mentioned in our previous work (3, 4), pervaporation has been widely considered to be an alternative separation process for azeotropic mixtures. Many research works in the pervaporation separation of the MTBE and methanol mixtures (5–11) have been reported. In 1995, Noezar et al.'s (12) report of binary blends of a cellulose derivative with another polymer or cellulose derivative led to membranes with much better permeabilities and higher selectivities for ethanol–ETBE separation. Jonquieres et al. (13) studied pervaporative transport modeling in the ternary system ETBE/EtOH/polyurethaneimide. We studied the pervaporation characteristics of the cellulose acetate propionate (CAP) membrane for the separation of the EtOH/ETBE mixture (3). The results showed that high selectivity and reasonable fluxes could be obtained with the CAP membrane. We also studied the performance of a blended membrane of cellulose acetate butyrate (CAB) with CAP which showed that good performance could be achieved by changing the experimental conditions (4).

The purpose of this work is to search for a better performance membrane for ETBE/ethanol separation. The characteristics of pervaporation separation, swelling, and sorption will be studied. A comparison with all previous works will be reported.

EXPERIMENTAL

Cellulose acetate propionate (CAP) (46 wt% propionyl content, average MW = 75,000), poly(1-vinylpyrrolidone-*co*-acrylic acid) (PVP) (VP/AA ratio 75:25, MW = 95,000), and ethanol (EtOH) were provided by Aldrich Chemical Co. Ethyl *tert*-butyl ether (ETBE) was kindly supplied by the Institut Francais du Pétrole (IFP). All these chemical products were used directly without any further purification.

Polymer blending was performed by a solution method. PVP and CAP were dissolved in acetate acid to obtain the desired polymer solution at room temperature. Homogeneous membranes were prepared by casting the solution on the plate surface of PVC films and evaporating the solvent at room temperature for 48 hours under no air flowing conditions. After drying, the transparent membranes detached from the surface of the PVC films automatically. The average thickness of these membranes was around 30 μm.

The experiments were explained in our previous works (3, 4). The pervaporation properties were characterized by the total, EtOH, and ETBE fluxes (J_{total}, J_{EtOH}, J_{ETBE}), and the separation factor α. The fluxes were normalized to a membrane thickness of 5 μm, assuming a proportionality between the fluxes and the membrane thickness. The characteristics of the sorption of the membrane were evaluated from the swelling ratio, S, and the sorption selectivity, β.

RESULTS AND DISCUSSION

Determination of the Composition of the Blended Membrane

Much higher selectivity with the CAP membrane could be obtained for the separation of EtOH/ETBE mixtures (3). The EtOH wt% in the permeate can reach as much as 97.5%. CAP can preferentially interact with EtOH through hydrogen bond formation or even dissolve in EtOH solution at high temperature, but the permeability of this membrane is not very good and the selectivity decreases quickly with increasing temperature. Therefore, in our present work, blended membranes of CAP with PVP were tested with the hope that they would show high selectivity and good permeability for the separation of EtOH/ETBE mixtures, especially at high temperature.

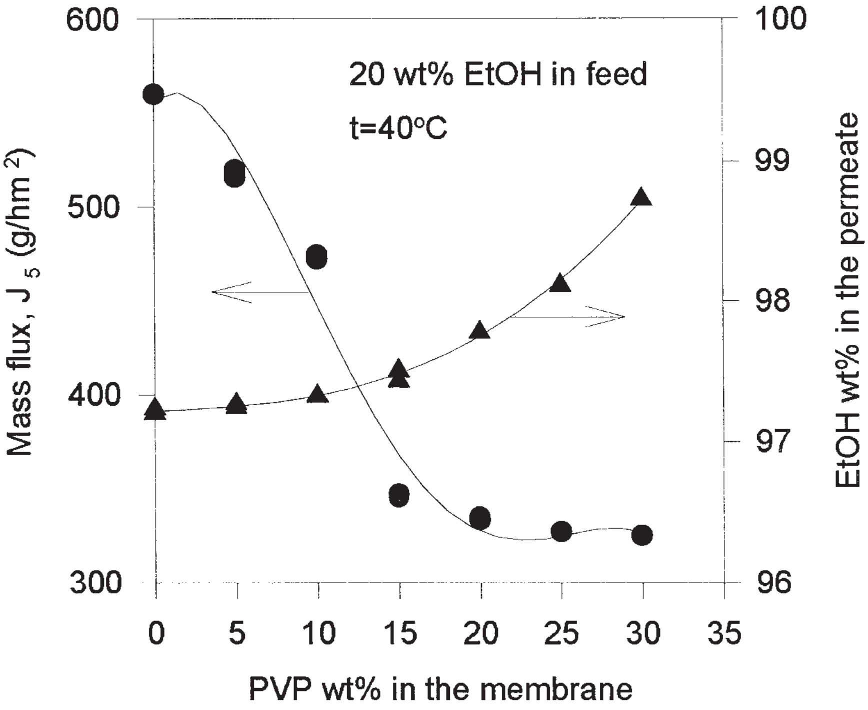

FIG. 1 Influence of PVP content on the performance of membranes.

As shown in Fig. 1, the total flux decreases rapidly. However, the EtOH wt% in the permeate increases as the PVP content in the membrane increases. In order to achieve stability of the blended membrane and to exceed the azeotropic point for the separation of ETBE and EtOH mixtures and much higher fluxes, a blended membrane of 5 wt% PVP with 95 wt% CAP was chosen and used in the following experiments. Under our experimental conditions, this blended membrane is stable; no change in properties was observed.

Pervaporation Characteristics of the Blended Membrane

The influence of the EtOH wt% in the feed and the experimental temperature on the fluxes were systematically studied (Fig. 2). As shown in this figure, the total fluxes increase quickly with increasing temperature and EtOH wt% in the feed. This is because the molecules of the mixture move more quickly when the temperature is increased, and therefore the diffusion coefficients of EtOH and ETBE in the membrane increase. As the EtOH wt% in the feed increases, the swelling ratios of the membrane increase, and this causes the fluxes to increase.

For a comparison of the selectivity of the blended membrane at different experimental conditions, the separation factor (α) and the EtOH wt% in the permeate (Y_{EtOH}) were chosen as constants to be compared. Figures 3 and 4 show

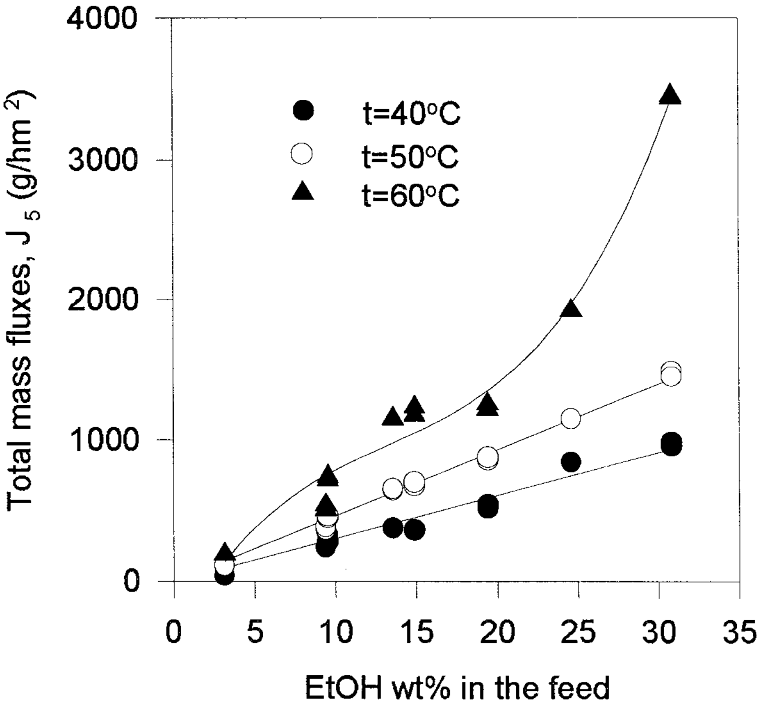

FIG. 2 Performance of fluxes of the membrane.

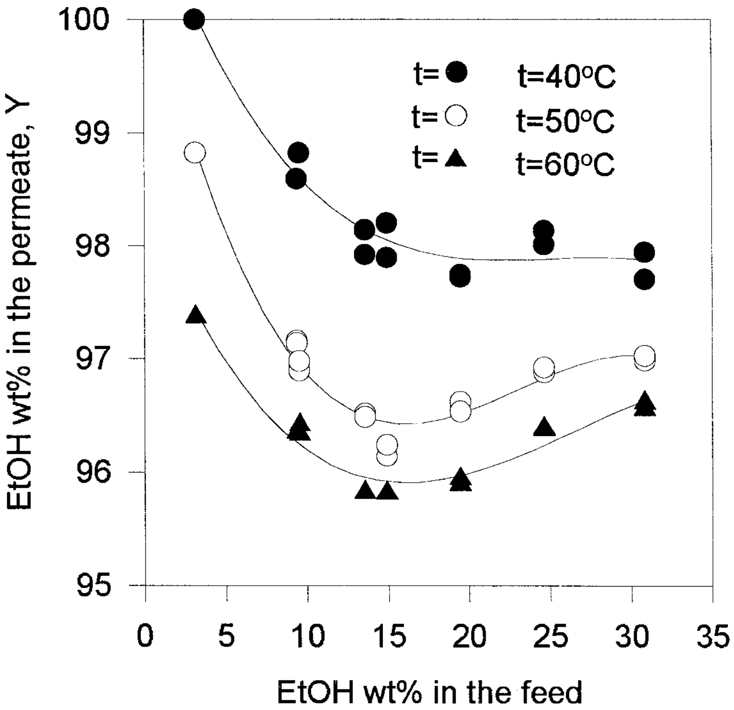

FIG. 3 Y_{EtOH} vs the wt% of EtOH in the feed for various temperatures.

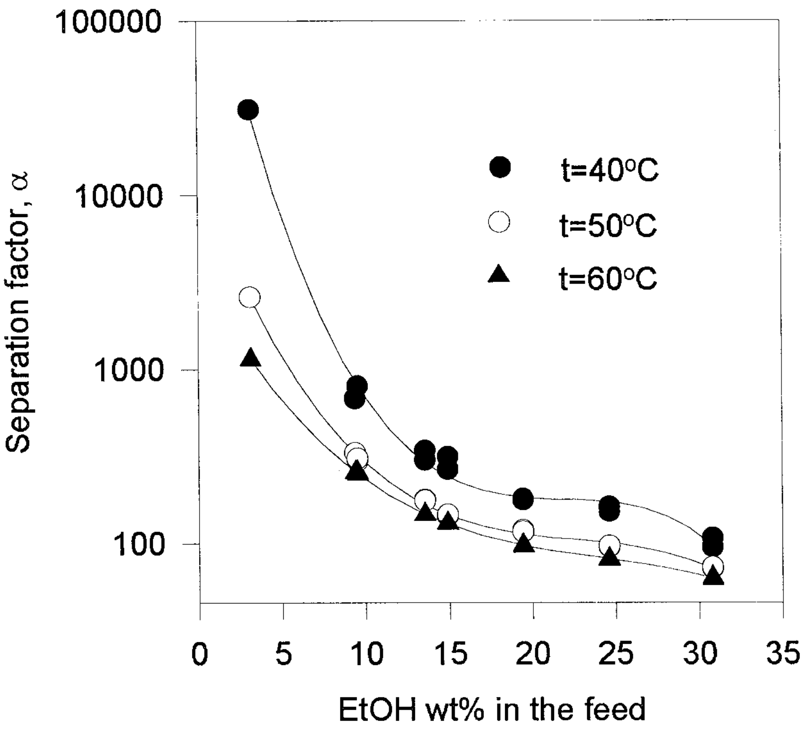

FIG. 4 α vs the wt% of EtOH in the feed for various temperatures.

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Y_{EtOH} and α, respectively, versus the EtOH wt% in the feed at various temperatures.

For the same feed, the EtOH wt% in the permeate decreases with increasing temperature. When the temperature is not changed, the EtOH wt% in the permeate decreases until the minimum value is reached and then it increases as the EtOH concentration in the feed increases. The lowest selectivity value is observed in the vicinity of the azeotropic composition of the mixture. The separation factor decreases to nearly a constant value when the temperature and EtOH wt% are increased. When the EtOH wt% in the feed is low, the separation factor decreases quickly with increasing temperature. But when the EtOH wt% in the feed is increased, the influence of temperature on the separation factor is not as great as it is at a low EtOH concentration in the feed. The main reason for this is swelling of the membrane with changing temperature. For mixtures of ETBE and EtOH, the azeotropic composition is at about 21 wt% EtOH under 1 atm. Although interactions between the polymer and EtOH molecules are strong if the mixtures are near the azeotropic point, the interactions of ETBE with EtOH molecules are also very strong. Therefore, the lowest selectivity appears to be in the vicinity of the azeotropic point; namely, a EtOH content in the 15 to 25% range. As the EtOH wt% in the feed increases further, the selectivity increases due to interactions of the membrane with EtOH, even though the membrane is much more swollen.

Influence of Temperature and EtOH wt% in Feed on Membrane Sorption

The permeation of molecules through a nonporous polymer membrane is generally described by a solution–diffusion mechanism that occurs in three steps: sorption, diffusion, evaporation (14). The component with the highest solubility and largest diffusion coefficient in the polymers usually permeates preferentially. Therefore, the properties of the membrane may be strongly decided by the sorption characteristic.

The results of swelling ratio vs EtOH wt% in the feed at different temperatures are plotted in Figs. 5 and 6. It can be seen from these figures that the swelling ratios of the membrane are almost independent of the temperature, so there is no marked influence on the structure of the membrane when the temperature is raised. As the EtOH wt% in the feed increases, the swelling ratios increase to maximum values and then decrease. The most likely reason is the strong interactions of EtOH molecules with the polymer and the ETBE molecules, which causes the swelling ratios to increase with increasing EtOH wt%. When the EtOH wt% in the feed increases further, the interactions of EtOH molecules among themselves is enhanced, and this causes the swelling ratios to decrease.

Figures 7 and 8 show that the EtOH wt% in the sorption solution decreases

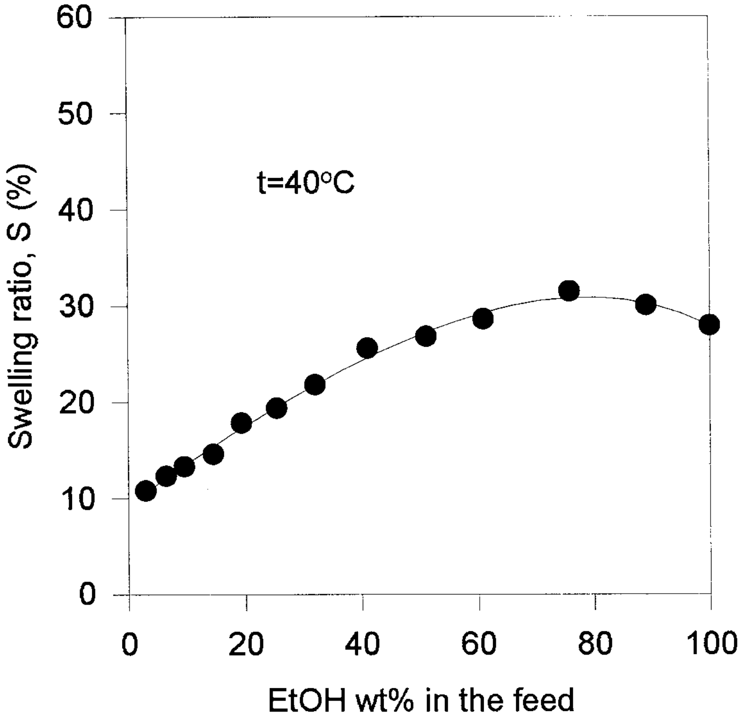

FIG. 5 Swelling ratio vs wt% of EtOH at 40°C.

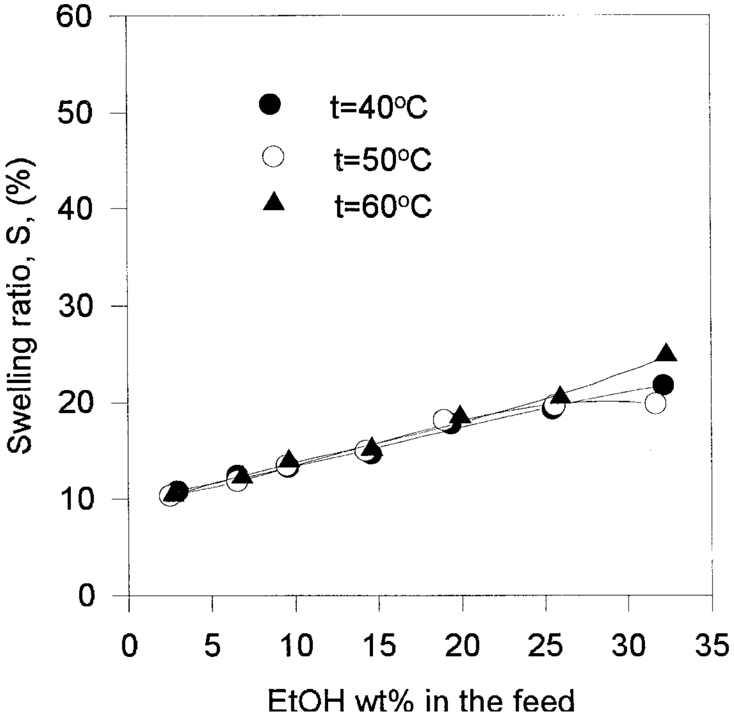

FIG. 6 Swelling ratio vs wt% of EtOH at various temperatures.

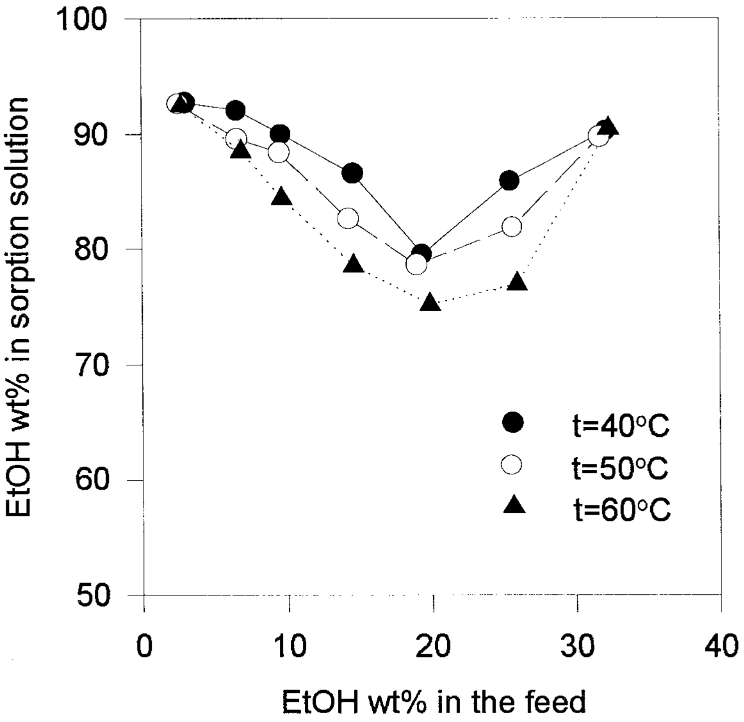

FIG. 7 Influence of experimental conditions on sorption selectivity.

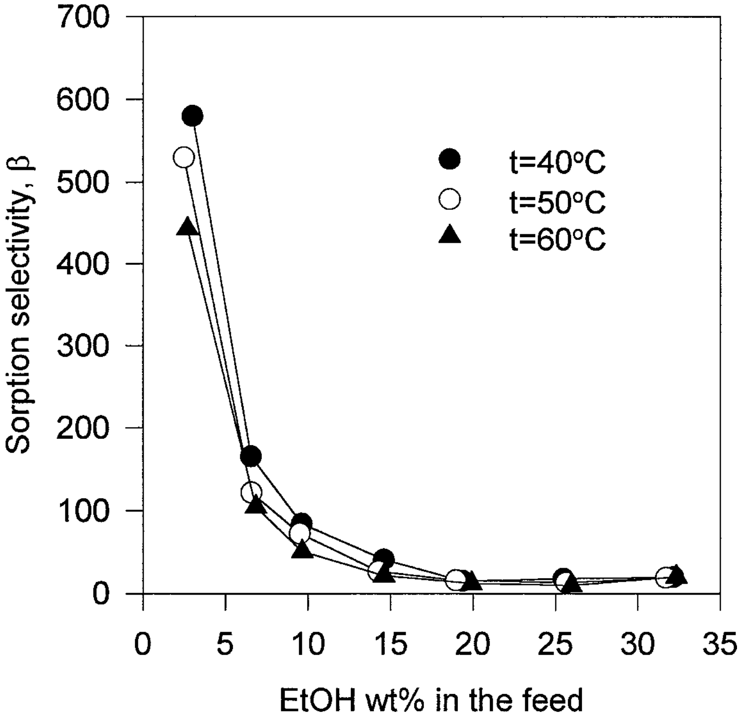

FIG. 8 Influence of experimental conditions on sorption selectivity.

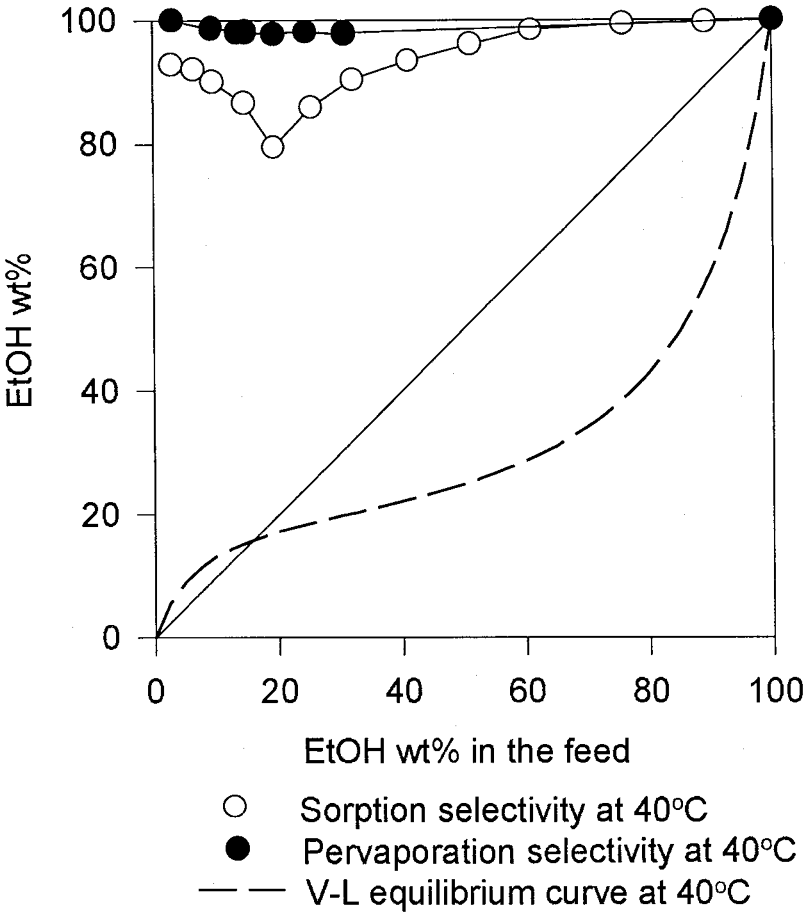

FIG. 9 Comparison of sorption and pervaporation with the vapor–liquid equilibrium curve.

TABLE 1
Performance of Various Membranes for the Separation of the EtOH/ETBE Mixture

Membrane	EtOH wt% in feed	EtOH wt% in the permeate	Total flux (g/m^2·h)	Temperature (°C)	Reference
Cellulose acetate (CA)	20	100	90	40	12
Cellulose acetate butyrate (CAB)	20	79.70	2980	40	12
Cellulose triacetate	20	100	70	40	12
Polyurethaneimide	20	<50	<650	30	13
CAP	20	97.5	560	40	3
CAP	20	96.73	751	50	3
CAP	20	95.28	1058	60	3
70% CAP + 30% CAB	20	94.7	1140	40	4
70% CAP + 30% CAB	20	93.1	1640	50	4
70% CAP + 30% CAB	20	92.57	2450	60	4
95% CAP + 5% PVP	20	97.75	525	40	This work
95% CAP + 5% PVP	20	96.60	868	50	This work
95% CAP + 5% PVP	20	95.93	1240	60	This work

with increasing EtOH wt% in the feed. Minimum values of EtOH concentration in the sorption solution are obtained when the feed contains 15–25% EtOH which is in the vicinity of azeotropic composition. Above the azeotropic point, the EtOH wt% in the sorption solution increases as the EtOH wt% in the feed increases. The sorption selectivity of the membrane decreases to near a constant with an increase of the EtOH wt% in the feed. Figures 7 and 8 also show the EtOH wt% in the sorption solution and the sorption selectivity are influenced by the temperature. When the temperature increases, the sorption selectivity decreases. It is likely that for a mixture of ETBE and EtOH the interactions between these molecules are much stronger at the azeotropic composition. Therefore, when EtOH molecules pass through the membrane, much EBTE will also pass through the membrane in the vicinity of azeotropic composition, although the interaction between the molecules of EtOH and the membrane is very strong. The interactions between the molecules of mixtures and the polymer weaken as the temperature increases, so the sorption selectivity decreases.

Comparison of the Results of Pervaporation and Sorption

In order to investigate the potential of the blended membrane for the separation of the EtOH/ETBE mixture, the results of sorption and pervaporation at 40°C were compared with the vapor–liquid equilibrium calculated by ASPEN PLUS RELEASE 9.2 with the UNIFAC method. As shown in Fig. 9, the pervaporation curve, the vapor–liquid equilibrium curve, and the polymer–liquid mixture equilibrium curve show the same tendency with a change of the EtOH wt% in the feed. The selectivity of pervaporation is considerably higher than that of distillation, indicating the membrane permeates EtOH preferential. Figure 9 also shows the blended membrane absorbs EtOH molecules preferentially based on data from the sorption experiments, although the sorption selectivity value is smaller than that of pervaporation selectivity.

From above discussion we conclude that pervaporation selectivity is determined by the sorption and diffusion steps, and that the diffusion coefficient of EtOH is much larger.

Table 1 summarizes the performance of various membranes for the separation of the EtOH/ETBE mixture. From this table it can be seen that higher selectivity and mass fluxes can be allowed with the blended membrane. The performance of the new membrane is higher than that of a pure CAP membrane for the separation of ETBE and EtOH mixtures, especially under high temperature conditions.

CONCLUSION

A new kind of membrane was prepared by blending poly(1-vinylpyrrolidone-*co*-acrylic acid) with cellulose acetate propionate. The experimental results showed that the selectivity and the fluxes with this membrane depend on the feed composition and the temperature. When the ethanol concentration in the feed and the experimental temperature are increased, the total flux increases and the selectivity decreases. But as the ethanol concentration in the feed is changed, a minimum value of the selectivity is observed in the vicinity of the azeotropic composition of the mixture. The same tendency is shown in sorption experiments. Compared with a pure CAP membrane, the new membrane shows high performance for the separation of ETBE and EtOH mixtures at high temperature conditions.

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