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Kun Liu[a][b]; X. Feng[a]; Zhangfa Tong[b]; L. Li[a]
[a] Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada [b] College of Chemistry and Chemical Engineering, Guangxi University, Nanning, China

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Kun Liu and X. Feng
Department of Chemical Engineering, University of Waterloo, Waterloo,
Ontario, Canada

Zhangfa Tong
College of Chemistry and Chemical Engineering, Guangxi University,
Nanning, China

L. Li
Department of Chemical Engineering, University of Waterloo, Waterloo,
Ontario, Canada

Abstract: This paper reports on the removal of trace water from mixtures of n-butyl acetate, n-butanol, and acetic acid by pervaporation using a polyvinyl alcohol (PVA) membrane. The separations of binary (i.e., n-butyl acetate and water) and quaternary (n-butyl acetate, n-butanol, acetic acid, and water) mixtures were investigated. The quaternary mixtures are relevant to n-butyl acetate production by esterification via reactive distillation. A series of pervaporation experiments were performed, including a simulated production process in which the relationship between pervaporation time and water content in the feed was studied. The results show that the PVA membrane has very high permselectivity for water and maintains significant selectivity for a considerable period of time even when the water concentration is present at relatively high concentrations of water in organic mixtures.

Keywords: Pervaporation, PVA membrane, removal, water, n-butyl acetate

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Address correspondence to Kun Liu, College of Chemistry and Chemical Engineering, Guangxi University, Nanning, China. E-mail: kunliuuw2004@163.com

INTRODUCTION

Nowadays, traditional separation techniques are facing more and more challenges, including high-energy consumption (e.g., distillation) and limited separation ability in particular cases (e.g., removal of trace water from organic mixtures). Pervaporation is a relatively new separation technique that holds the promise of successfully meeting some of these challenges (1). As a low-energy, membrane-based separation process, it is often suitable for separating close boiling, heat-sensitive, and azeotropic mixtures.

Polyvinyl alcohol (PVA) is one of the most widely used polymeric materials in membrane separation technology. Since PVA is hydrophilic, such membranes are successfully used to separate water and water-like components from organic mixtures. The availability of commercial PVA and PVA composite membranes has spurred a great deal of research into their performance and enhancement. For example, Gulsen and Oya (2) studied the separation of acetic acid/water using PVA modified with polyacrylic acid; Rhim et al. (3) investigated the separation of the same system (acetic acid/water) using cross-linked PVA membranes; Yeh et al. (4) have reported on the dehydration of water/alcohol mixtures using PVA/clay membranes; Rhim et al. (5) also studied the separation of water/ethanol mixtures using metal ion-exchanged PVA/sulfosuccinic acid (SSA) membranes; and Huang and Yeom (6) studied pervaporation separation of water/ethanol mixtures; Hilmioglu (1) and Rhim et al. (7) reported on the use of PVA membranes to separate methyl tert-butyl ether (MTBE)/methanol mixtures; Habib (8) has studied the use of PVA membranes to remove water from aqueous mixtures of ethanol, propanol, hexanol, ethyl acetate, and acetic acid; and Zhu and Chen (9) reported the pervaporation-esterification coupling using cross-linked PVA composite catalytic membranes.

The production of n-butyl acetate is a niche application for pervaporation. N-butyl acetate is an important compound used in the painting and coating and the pharmaceutical and perfume industries, among others. Due to its low toxicity and low environmental impact, it has become an important replacement for more toxic and less environmentally friendly solvents. At present, the industrial production of n-butyl acetate involves direct esterification of n-butanol and acetic acid. The reaction is equilibrium-limited, and, as a result, conversion to the ester is generally low.

In order to increase the esterification conversion, a number of techniques have been explored. For example, Liao and Tong (10) have investigated many aspects of the esterification process for the production of n-butyl acetate by catalytic distillation. As a result, a commercial plant with an n-butyl acetate manufacturing capacity of 1000 ts/yr has been constructed. In this process, n-butyl acetate is withdrawn from the bottom of the distillation column, and the overhead distillate is condensed and cooled to induce phase separation. While the organic phase is refluxed into the column, the aqueous phase, which still contains small amounts of organic compounds (i.e., n-butyl acetate and unreacted n-butanol and acetic acid) is removed from the system. The specific compositions of the aqueous phase are affected by the feedrate of the reactants, the extent of conversion of the reaction, and the operating temperature and pressure. The wastewater stream in the top of the column may be subjected to further treatment.

The reactive distillation process appears to be a niche application for membrane pervaporation in order to separate and recover the organic compounds from the dilute aqueous solutions. Since pervaporation involves a phase change of the permeate from liquid to vapor, from an energy consumption point of view, pervaporation is especially suitable for circumstances where the preferentially permeating species are the minor component of the feed mixture.

In our previous work (11), we reported on the use of pervaporation to remove organics in the water phase at the top of the column using a polyether block amide (PEBA) membrane. In this work, we focus on the removal of impurities (water, n-butanol, and acetic acid) from the primary n-butyl acetate product by pervaporation using PVA membranes. The presence of these impurities can affect the quality of the product; e.g., the water can lead to hydrolysis of n-butyl acetate. The effects of feed concentration, temperature, and pervaporation time on the permeation flux and separation factor are reported. In particular, the relationship between the water content in the feed and the pervaporation time is used to simulate conditions that might be found in an actual production facility.

The most widely accepted model to explain pervaporation is the Solution-Diffusion Model. The model describes that pervaporation separation depends on the difference in sorption and diffusion properties among the various components in the feed solution, as well as on the permselectivity of the membrane. The presence of multi-components can affect the membrane by, for example, changing the permeation behavior of the membrane. They can also have mutually interactive effects through the following (12):

a. Free volume effect, generally increasing the diffusivity of the component.

b. Coupling effect, due to the interaction between components in the membrane, that can increase or decrease diffusivity.

In general, the pervaporation performance can be evaluated by permeation fluxes and separation factors for the various components. These values depend on variables such as temperature, feed concentration, membrane material, and feed and permeate side pressures.

For a binary system consisting of components i and j, the separation factor, α is defined as the ratio of the concentrations of the components on the permeate side (y) to the ratio of the concentrations of the components on the feed side (x):

$$\alpha = (y_i/y_j)/(x_i/x_j) \tag{1}$$

The enrichment factor, E, of the membrane for component i is defined as the ratio of the concentration of the compound i in the permeate (y_i) to the concentration of compound i in the feed (x_i).

$$E_i = y_i/x_i \tag{2}$$

EXPERIMENTAL

Materials

The PVA membrane was supplied by GFT Ltd in Germany. It is a composite membrane consisting of a thin layer of PVA supported on a microporous polyacrylonitrile substrate. The thickness of the support is measured to be ~0.16 mm. Ethyl butyrate was purchased from Aldrich Chemical Co. (USA), and n-butanol and acetic acid were purchased from Fisher Scientific Ltd of Canada. All reagents were quoted as having a purity greater than 99% and were used without further purification.

Pervaporation

The effective area of the membrane in the permeation cell was 14 cm^2. The feed solution was circulated from a 1000 mL feed tank to the permeation cell at a certain rate in order to minimize any concentration polarization. A constant operating temperature of (±0.1°C) was maintained thermostatically over a range from 30°C to 70°C. During the experiments, the upstream feed solution was at atmospheric pressure, while the downstream (permeate side) pressure was maintained at roughly 5 mmHg absolute. The permeate vapor (mainly water) was collected in one of two parallel Pyrex cold traps immersed in liquid nitrogen, permitting continuous operation of the system. In order to reach steady-state conditions, the apparatus was run for at least 2 h before collection of the permeate began and was run for at least 1 h between sample collections. The total permeation flux, i.e., the sum of the partial fluxes, was determined from the weight of the condensate trapped over a given time period by an electronic balance of (±0.01 mg). In all cases, the condensate was a single phase. The total organic concentration in the permeate was determined by total organic carbon analyzer (Shimadzu TOC-500) for both binary BaW (99.8% n-butyl acetate and 0.2% water—by weight percent) and the quaternary BaBAW (n-butyl acetate 98.45%, n-butanol, 1.3% acetic acid, and 0.2% water—by weight percent) mixtures.

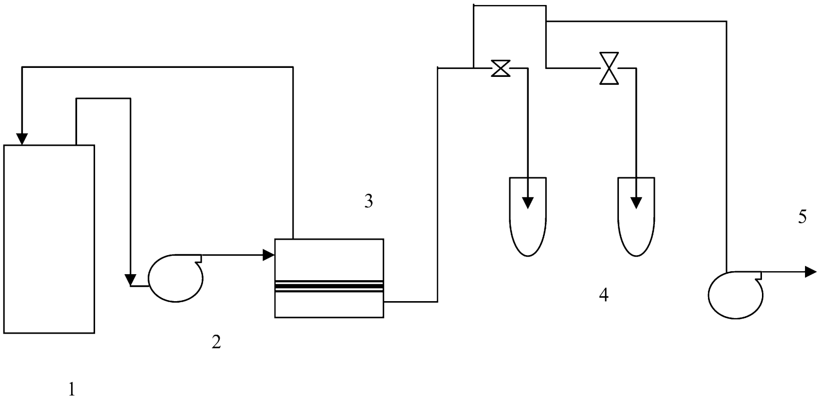

Figure 1. Experimental setup 1-feed tank; 2-circulation pump; 2-pervaporation module; 4-cold trap; 5-vacuum pump.

Each condensate was analyzed three times. Figure 1 is a schematic of the experimental setup for pervaporation.

RESULTS AND DISCUSSION

In all the experimental results, the water concentrations in the permeate side were found to be more than 99% by weight. The membrane enrichment factor [Eq. (2)] for water is roughly 500.

Effect of Temperature on Pervaporation

Operating temperature is an important factor in pervaporation (12). According to the Solution-Diffusion Model, as the temperature increases, the frequency and amplitude of the thermal motion of the polymer chains in the membrane also increase. This effectively increases the free volume of the system, allowing for increased molecular diffusion which results in greater partial and total fluxes of the permeate increases. From the plasticization of membrane and the interaction between permeates and the membrane material, it can be explained that strong interactions can be formed and reduce the membrane plasticization effect at lower temperature (4).

The diffusion phenomenon is complicated by the solution behavior of the permeate in the membrane. Specifically, the ability of the compound to dissolve into the membrane decreases with increasing temperature. Therefore the membrane swelling decreases at higher temperatures. This results in a decrease in free volume and a decrease in the diffusion and permeation, as well.

Therefore, given the different behavior with increasing temperature, if the diffusion predominates, the permeation will be enhanced at higher temperatures. If the solubility predominates, the permeation will be reduced at higher temperatures. It is possible that the two opposite effects will nearly cancel each other so that the permeability is little affected by temperature.

Figure 2 shows the results of the effect of temperature on the pervaporation for the binary BaW and the quaternary BaBAW mixtures. In both cases, the water flux first decreases and later increases with temperature. This behavior suggests that the water solubility dominates the pervaporation process at lower temperatures, while the diffusion process dominates the process at higher temperatures. The overall effect, however, is that the flux does not have a strong dependency on temperature.

Figures 3 shows the effect of increasing temperature on the organic content of the permeate. For both the binary BaW and quaternary BaBAW systems, the organic content of the permeate remains low ($<0.2\%$) over the temperature range investigated, but there is a pronounced increase in concentration with temperature, although the concentration remains quite low. This behavior would be expected in terms of the Solution-Diffusion Model, since organics (even polar organics) would show less solubility in the membrane compared to water so that the diffusion mechanism would be expected to predominate, resulting in the increasing pervaporation with temperature that we observe.

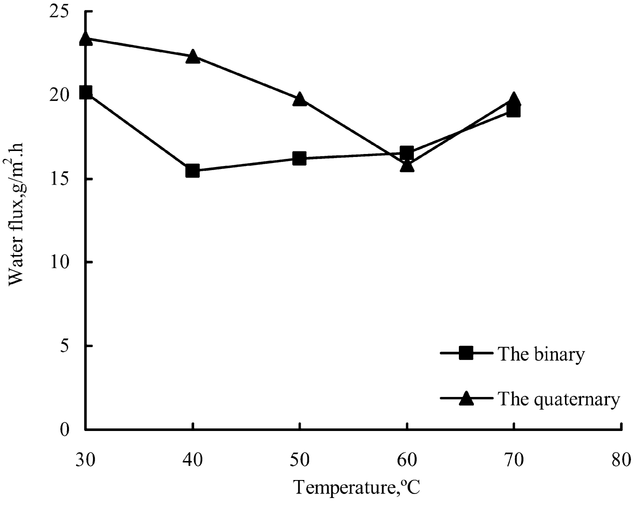

Figure 2. Effect of temperature on the water flux in binary and quaternary mixtures, respectively.

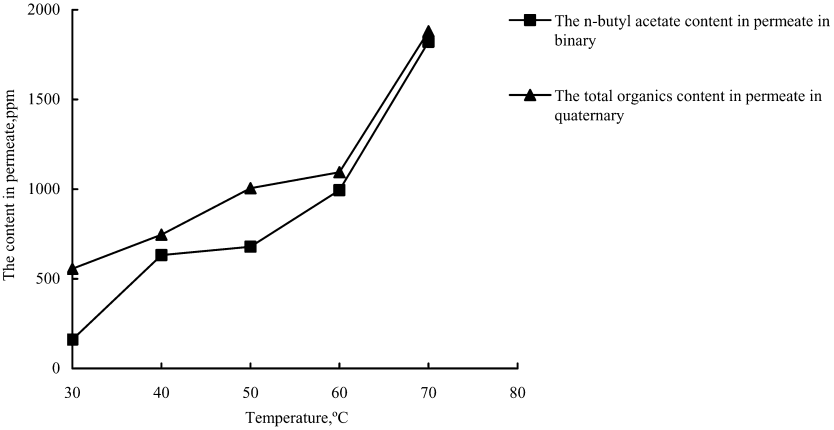

Figure 3. Effect of temperature on n-butyl acetate and total organics content in permeate in binary as well as quaternary mixtures, respectively.

Effect of Water Concentration in Feed on Pervaporation Performance at 30°C

Figure 4 shows that the total flux across the PVA membrane increases linearly with an increase in the water concentration for a BaW binary system. This behavior would be expected since, in addition to the increased concentration gradient across the barrier, the increased amount of water in the feed would lead to increased swelling of the hydrophilic membrane, resulting in greater diffusion.

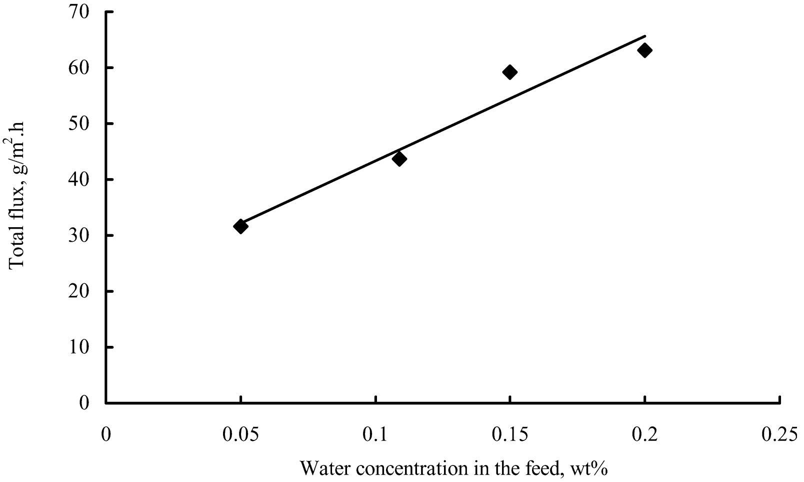

Figure 4. Relationship between water concentration in the feed and total flux.

Effect of Pervaporation Time on Pervaporation Performance

Figure 5 illustrates that the membrane performance can be maintained over a period of 9 h with no significant degradation. Here, the experiments were done in 30°C and 50°C, respectively. Because the concentrations of n-butanol and acetate acid are so low, the slight changes seen during the time of the experiments are probably not statistically significant and are not the important feature of the experiment. It may be noted that membrane does not "clog" or "wear out" during the experiment. For this system to be useful, however, it would have to be stable for a much longer time.

Figure 6 shows that the pervaporation of n-butyl acetate in binary BaW mixture is low and decreases slowly over time. The slow decrease may be a reflection of the increasing swelling of the membrane with water over time, resulting in a decreased penetration of the organic. Figure 6 also shows similar data for the quaternary BaBAW mixture. The data suggest a possible increase in the total organics in the permeate over time. This behavior may reflect a greater membrane selectivity for n-butanol and/or acetic acid, relative to the less polar butyl acetate measured in the experiment with the binary mixture.

Effect of Pervaporation Time on Concentration of Water in the Feed of a BaW Binary Mixture

Figure 7 shows the relationship between pervaporation time and the remaining concentration of water in the feed for the case of the binary BaW mixture at 30°C and an initial water concentration of 0.2%. The data can be fitted to

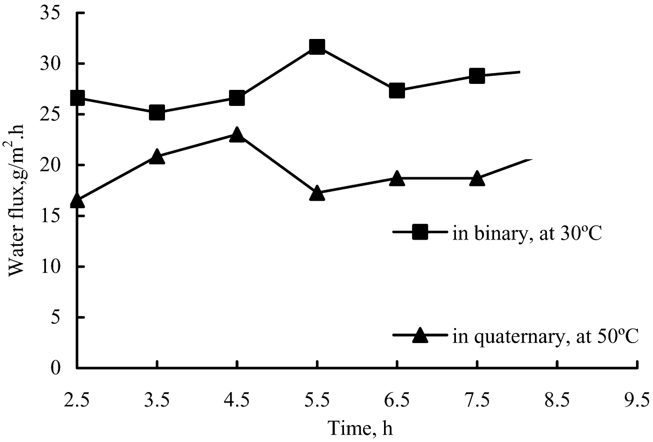

Figure 5. Effect of pervaporation time on the water flux in binary system at 30°C and in quaternary system at 50°C, respectively.

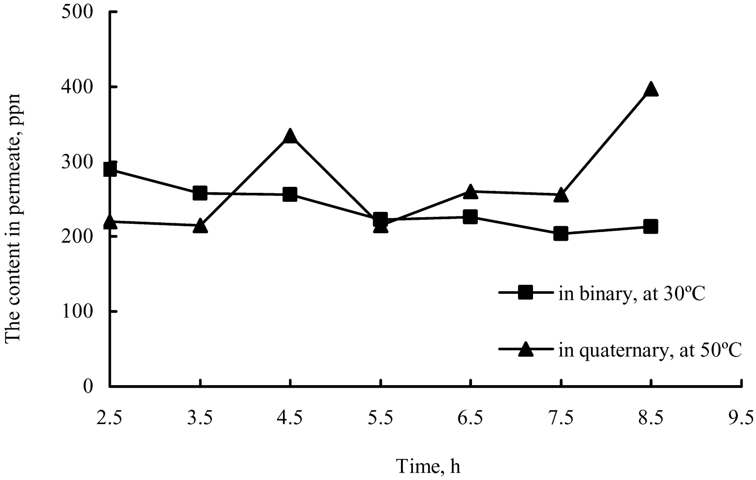

Figure 6. Effect of time on n-butyl acetate and the total organics content in permeate in binary at 30°C as well as in quaternary at 50°C, respectively.

Eq. (3) and the correlation coefficient R^2 is 0.9981 in Eq. (3), which is also plotted in Fig. 7.

$$Water(wt\%) = 2 \times 10^{-5}t^2 - 0.004t + 0.2043 \tag{3}$$

where t is time expressed in hours.

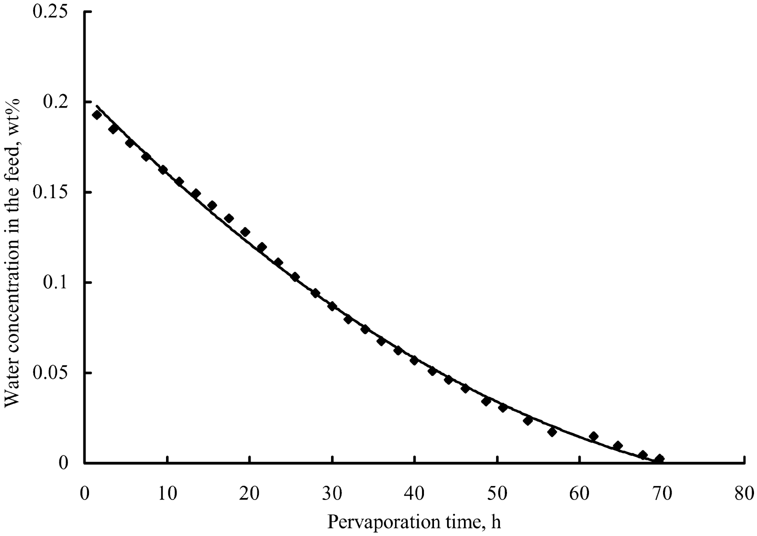

Figure 7. Effect of pervaporation time on water concentration in the feed in binary mixtures 30°C.

This process simulates a condition that one might encounter in an actual production of n-butyl acetate. The result clearly shows that the perevaporation leads to a continual removal of trace amounts of water from the feed solution which is exactly what one wants to see in production.

The experiment shown here is for the binary BaW, while the actual production process would involve removal of water from a quaternary mixture (BaBAW). However, given the similarity of the two mixtures, we anticipate similar results with the quaternary mixture. One can expect that the presence of the more polar n-butanol and acetic acid in the quaternary mixture could lead to more interaction between the compounds and the membrane and between the compounds and the water. The effect of the interactions could possibly affect the behavior shown in Fig. 7.

Effect of Pervaporation Time, Temperature and Feed Concentration on the Selectivity of the Membrane

The separation factor [Eq. (1)] is a measure of the selectivity of the membrane and is affected by many factors. Figures 8, 9, and 10 show the effect on selectivity of the variables time, temperature, and water concentration in the feed, respectively.

Figure 8 shows that the separation factor for water in the binary system remains high ($>10^6$) throughout the period of time evaluated in this experiment (2 to 8 h). In the quaternary mixture, there appears to be an overall decrease in the separation factor during the same time period. One possible

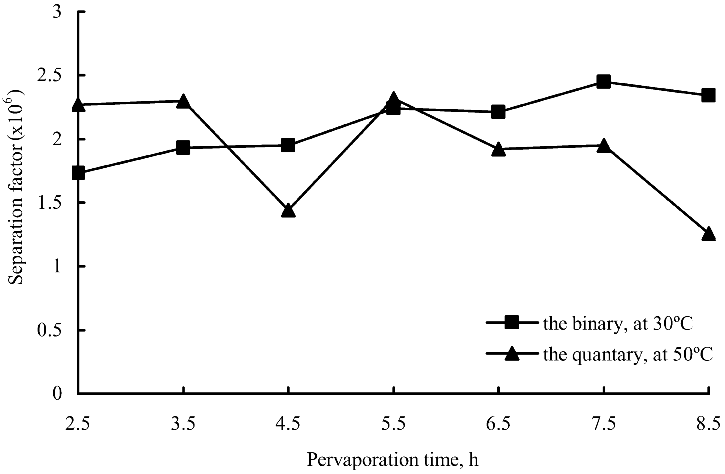

Figure 8. Effect of pervaporation time on the separation factor in the binary mixtures at 30°C and the quaternary mixtures at 50°C.

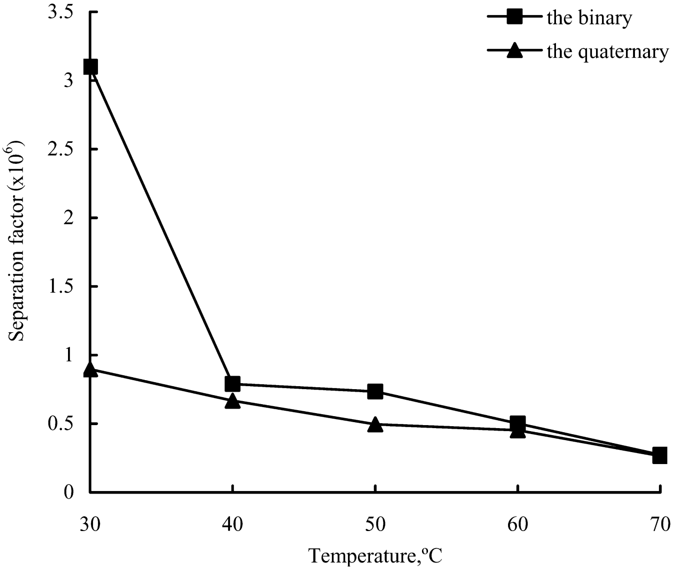

Figure 9. Effect of temperature on the separation factor in the binary and the quaternary mixtures.

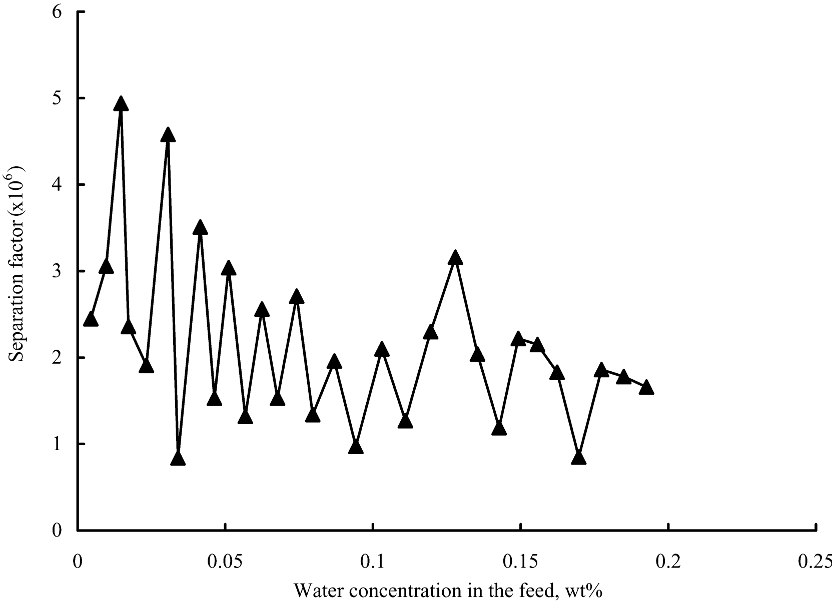

Figure 10. Effect of the water concentration in the feed solution on the separation factor in the binary mixtures at 30°C.

reason is that, due to their polarity, additional amounts of n-butanol and acetic acid can diffuse through the membrane over time.

In Figure 9, the separation factor is seen to decrease, owing, perhaps, to the greater diffusion of the organics through the membrane with increasing temperature, as noted previously.

Figure 10 shows the change in the separation factor as a function of the increase in the water concentration in the feed solution in the binary mixture. Again, the separation factor remains high, $>10^6$.

CONCLUSION

In this study, pervaporation using a PVA membrane was used to remove trace amounts of water from n-butyl acetate/water binary mixtures and n-butyl acetate/n-butanol/acetic acid/water mixtures. The effects of operation time, temperature, and water concentration in the feed were studied. The following conclusions can be drawn from the experimental results:

1. The PVA membrane can be used in pervaporation to separate trace amounts of water from n-butyl acetate mixtures.
2. Under the conditions of this study, the membrane demonstrated a high and stable permselectivity for water that varied little with temperature, while the concentration of organic components increased with temperature. The optimal temperature for water removal was 30°C. The membrane showed a good selectivity to water.
3. The water flux was in the range of 20–30 g/m^2-h and showed little variation over the duration of the experiment (9 h). Similarly the low concentration of the organics in the permeate side did not change much over time.
4. These results suggest that pervaporation with the PVA membrane could be successfully applied to an actual production process.

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REFERENCES

1. Hilmioglu, N.D. and Tulbentci, S. (2004) Pervaporation of MTBE/methanol mixtures through PVA membranes. *Desalination*, 160: 263–270.
2. Gulsen, A. and Oya, S. (2003) Characteristics of permeation and separation for acetic acid-water mixtures through poly (vinyl alcohol) membranes modified with poly (acrylic acid). *Sep. Sci. Technol.*, 38 (9): 1963–1980.

3. Rhim, J.W., Yoon, S.W., Kim, S.W., and Lee, K.H. (1997) Pervaporation separation and swelling measurement of acetic acid-water mixtures using crosslinked PVA membranes. *J. Appl. Polym. Sci.*, 63: 521–527.
4. Yeh, J.M., Yu, M.Y., and Liou, S.J. (2003) Dehydration of water-alcohol mixtures by vapor permeation through PVA/clay nanocomposite membrane. *J. Appl. Polym. Sci.*, 89: 3632–3638.
5. Rhim, J.W., Lee, S.W., and Kim, Y.K. (2002) Pervaporation separation of water-ethanol mixtures using metal-ion-exchanged poly (vinyl alcohol) (PVA)/sulfosuccinic acid (SSA) membranes. *J. Appl. Polym. Sci.*, 85: 1867–1873.
6. Huang, R.Y.M. and Yeom, C.K. (1990) Pervaporation separation of aqueous mixtures using crosslinked poly (vinyl alcohol) (PVA). Permeation of ethanol-water mixtures. *J. Membr. Sci.*, 51: 273–292.
7. Rhim, J.W. and Kim, Y.K. (2000) Pervaporation separation of MTBE-methanol mixtures using cross-linked PVA membranes. *J. Appl. Polym. Sci.*, 75: 1699–1707.
8. Habib, S. (1996) Removal of water from aroma aqueous mixtures using pervaporation processes. *Sep. Technol.*, 6: 69–75.
9. Zhu, Y.S. and Chen, H.F. (1998) Pervaporation separation and pervaporation-esterification coupling using crosslinked PVA composite catalytic membranes on porous ceramic plate. *J. Membr. Sci.*, 138: 123–134.
10. Liao, A.P. and Tong, Z.F. (1995) Synthesis of n-butyl acetate catalyzed by amberlyst. *Chem. React. Eng. Technol.*, 11: 406–408.
11. Liu, K., Tong, Z.F., and Feng, X. (2004) Pervaporation separation of organic compounds from water during butyl acetate production via esterification, Frontiers on Separation Science and Technology (Proceedings of the 4th International Conference on Separation Science and Technology China), World Scientific Publishing Co. Pte. Ltd., 819–826.
12. Huang, R.Y.M. (1991) *Pervaporation Membrane Separation Processes*; Elsevier: Amsterdam, 35–38.