



Use of pervaporation to separate butanol from dilute aqueous solutions: Effects of operating conditions and concentration polarization

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ABSTRACT

This study deals with the separation of *n*-butanol from aqueous solutions by pervaporation. The effects of feed concentration, temperature, and membrane thickness on the separation performance were investigated. Over the low feed butanol concentration range (0.03–0.4 wt%) studied, the butanol flux was shown to increase proportionally with an increase in the feed butanol concentration, whereas the water flux was relatively constant. An increase in temperature increased both the butanol and water fluxes, and the increase in butanol flux was more pronounced than water flux, resulting in an increase in separation factor. While the permeation flux could be enhanced by reducing the membrane thickness as expected for all rate-controlled processes, the separation factor was compromised when the membrane became thinner. The effect of membrane thickness on the separation performance was analyzed taking into account the boundary layer effect. This could not be fully attributed to the concentration polarization, which was found not significant enough to dominate the mass transport. A variation in the membrane thickness would vary the local concentration of permeant inside the membrane, thereby affecting the permeation of butanol and water differently. Thus, caution should be exercised in using permeation flux normalized by a given thickness to predict the separation performance of a membrane with a different thickness because the membrane selectivity can be affected by the membrane thickness even in the absence of boundary layer effect.

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1. Introduction

Membrane separation technologies offer numerous advantages over other mass transfer processes, including high selectivity, low energy consumption, moderate cost to performance ratio, and compact and modular designs. As a result, they are generally considered to be “clean technologies.” Pervaporation is a rapidly developing membrane technology as an energy-efficient process for separating liquid mixtures (e.g., azeotropic mixtures and mixtures with similar volatilities) that are difficult to separate by conventional methods [1]. Pervaporation can be used for the purification of chemicals. Depending on the type of membranes used, pervaporation can be applied for dehydration of organic solvents, recovery of organic compounds from aqueous solutions, and the separation of organic mixtures.

However, pervaporation is a rate-controlled process, and the permeation flux through a membrane is generally low. Therefore, pervaporation becomes economically more attractive when the

preferentially permeable component is present in the feed at low concentrations [2].

The mass transport in pervaporation is generally described by the solution–diffusion model [1], based on which the mechanism of transport is considered to be a three-step process consisting of (i) sorption of the permeant from at the feed liquid to the upstream side of the membrane, (ii) diffusion of the permeant through the membrane, and (iii) desorption at the downstream side of the membrane under a low-pressure. Thus, the permeability is a function of the solubility in and diffusivity through the membrane. The membrane selectivity is thus affected by both the solubility (which is a thermodynamic property) and the diffusivity (which is a kinetic property). The solubility of a compound in a polymer is determined by the permeant–membrane interaction, whereas the diffusivity, on the other hand, is generally governed by the molecular size, shape, and mass of the permeant. When both the sorption and diffusion aspects favor a given component, a very high pervaporation selectivity for this component will be obtained.

Butanols are aliphatic four-carbon alcohols that are widely used in the manufacture of resins, cleaning agents, plasticizers and in the reaction with acids to form ester compounds. In urea resin manufacturing, the thick wastewater produced contains butanol and a small quantity of formaldehyde that have to be recovered for

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reuse [3]. In addition, the depleting supply of crude oil has created a renewed interest in technologies that utilize renewable resources for energy production, and the acetone–butanol–ethanol (ABE) fermentation process continues to attract attention as a potential process for the production of chemical feedstock and liquid fuel. If used as fuel for internal combustion engines, butanols can better tolerate water contamination than ethanol and is more suitable for distribution through existing pipelines for gasoline. In addition, since the enthalpies of vaporization of butanols are less than half of that of ethanol, an engine running on butanols is expected to be easier to start in cold weather than one running on ethanol or methanol. On the other hand, butanols are much less volatile than ethanol, making it safer to use as a gasoline oxygenate in hot weather, thereby eliminating the need for very special blends during the summer and winter months. However, due to the low product concentration involved in ABE fermentation, their recovery from the fermentation broth by distillation is uneconomical. As a result, alternative techniques are being developed for ABE recovery from fermentation broths [4–6], and pervaporation holds great promise as a more efficient technique.

The increasing usage and production of butanols in the biochemical industries make butanol separation from aqueous solutions an important topic of research [7–10]. Recently, various studies have been carried out on butanol pervaporation using hydrophobic membranes, and silicone-based membranes are used extensively [5]. Butanol extraction from acetobutylic fermentation broth by sweeping gas pervaporation was studied by Larrayoz and Puigjaner [11] using a silicone tubing with inside and outside diameters of 2 and 4 mm, respectively. The pervaporation performance of flat poly(dimethyl siloxane) (PDMS) membranes, with and without silicalite fillers, has been investigated for the separation of butanol/water and butanol/water/acetone mixtures, and it was shown that the fillers tend to lower the permeation flux but increase the selectivity [12]. The pervaporation of butanol from a model solution/fermentation broth was also tested using polytetrafluoroethylene, polypropylene, silicalite/PDMS membranes [4,5]. In addition, dense films of poly[1-(trimethylsilyl)-1-propyne], a glassy polymer with a network of interconnecting nanopores in the polymer matrix that forms a large fraction of free volumes, were also evaluated for *n*-butanol recovery from aqueous solution [13,14]; unfortunately, the membrane performance was shown to be unstable, and this limits the practical application of the membrane.

On the other hand, certain poly(ether-block-amide) (PEBA) copolymers have attracted significant attention as a promising membrane material. They are thermoplastic elastomers having alternating sequences of hard polyamide (PA) and soft polyether (PE) segments with a micro-phase separated morphology [15]. By adjusting the composition or the lengths of the polyamide/polyether segments, optimal properties for a particular application may be achieved. Bøddeker et al. [3] studied the separation of ethanol, butanol isomers and benzyl alcohol from water, membranes made from PEBA 40 (thickness 50 μm) were found to have a better permeability than other elastomeric membranes (e.g., silicone-based membranes) tested. The separation of a small amount of *n*-butyl acetate, *n*-butanol and acetic acid from aqueous solutions, pertinent to *n*-butyl acetate production via esterification by reactive distillation, was studied using a PEBA membrane [16]. Other studies using PEBA membranes were done for the separation of ethyl butyrate, isopropanol and pyridine from low concentration aqueous solutions [17,18]. The potential of using PEBA membranes for ABE extraction from dilute aqueous solutions was demonstrated by Liu et al. [19].

In the present study, PEBA 2533 was chosen as the membrane material for *n*-butanol separation because of its good organophilic

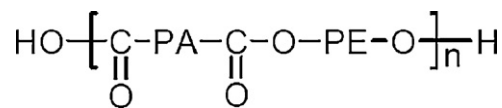


Fig. 1. Structure of poly(ether-block-amide). PA and PE represent hard polyamide (i.e., Nylon 12) segments and soft polyether (i.e., polytetramethylene oxide) segments.

properties. It consists of linear chains of hard polyamide (i.e., Nylon 12) segments covalently linked to soft polyether (PE) (i.e., polytetramethylene oxide) segments via ester groups, as shown in Fig. 1. The separation performance of the PEBA membrane for model water/*n*-butanol mixtures at concentrations encountered in fermentation processes was considered. The effects of feed butanol concentration and temperature on the permeation flux and selectivity were studied. It may be mentioned that in previous studies involving PEBA membranes for pervaporation separations, the membrane performance was essentially evaluated with membranes of given thicknesses. However, the present study showed that not only was the permeation flux affected by the membrane thickness as expected for all rate-controlled processes, the separation factor was influenced as well, which could not be completely attributed to concentration polarization. While a thin membrane is often desired for increased permeation flux, the separation factor tends to be compromised as the membrane becomes thinner. Thus the effects of membrane thickness on the membrane performance were also investigated and analyzed. Contrary to the perception that the membrane thickness has little impact on the selectivity, it was shown that the membrane thickness influenced the partial permeation fluxes of butanol and water differently, and as a result, the separation factor was affected as well in the pervaporation system where the permeation behavior of individual components was non-ideal.

2. Experimental

2.1. Materials

N,N-Dimethyl acetamide from VWR Canlab was used as the solvent to dissolve the polymer in preparing the membrane casting solutions. *n*-Butanol was purchased from Fisher Scientific. All solvents were of analytical grade and were used without further purification. Water was de-ionized and distilled before use.

2.2. Membrane preparation

A homogeneous PEBA polymer solution (15 wt%) was prepared by dissolving an appropriate amount of PEBA 2533 in *N,N*-dimethyl acetamide at 70 °C under vigorous agitation. The membrane was prepared by the solution casting method. Briefly, the hot polymer solution was cast onto a glass plate at 70 °C to various thicknesses with a casting knife, followed by solvent evaporation in an oven for at least 24 h. The membranes were then further dried until the trace amount of solvent remaining in the membranes was completely removed. The membrane thickness was measured by a Mitutoyo digital micrometer.

2.3. Pervaporation

The experimental setup for pervaporation test has been described previously [16]. The membrane was mounted in a stainless steel permeation cell, with an effective membrane area of 13.85 cm². The feed mixture was pumped from the feed tank (ca. 1 L) to the permeation cell through a center opening and flowed radially along the membrane surface. The retentate was collected

through a thin channel located peripherally near the edge of the membrane and recycled to the feed tank. To minimize the boundary layer effect, a relatively high feed circulation rate (1.6 L/min) was used, corresponding to a linear flow velocity on the membrane surface of >20 cm/s. Vacuum was provided on the downstream side of the membrane using a vacuum pump. The permeate stream was condensed and collected in cold traps immersed in liquid nitrogen. After a steady state of permeation was reached, the permeate sample collected over a given period of time was weighed and then analyzed for composition using a Total Organic Carbon Analyzer (Shimadzu TOC-500) to determine the permeation flux and permeate concentration. Pervaporation experiments were conducted at various temperatures (i.e., 29, 40, 50 and 60 °C) and different feed concentrations using the same membrane. To investigate the influence of membrane thickness on the pervaporation separation performance, dense membranes with different thicknesses (i.e., 30, 50, 59, 65, and 81 μm) were prepared and tested as well.

From the experimental data of pervaporation, the membrane performance can be assessed in terms of total permeation flux (J), separation factor (α), and pervaporation separation index (PSI) shown below:

$$J = \frac{W}{At} \quad (1)$$

$$\alpha = \frac{Y/(1-Y)}{X/(1-X)} \quad (2)$$

$$\text{PSI} = J(\alpha - 1) \quad (3)$$

where W is the mass of the permeate sample collected over a period of t , and A is the effective area of the membrane for permeation. X and Y are the weight fractions of butanol in feed and permeate, respectively. The partial permeation fluxes can be readily obtained from the total flux and the permeate concentration.

3. Results and discussion

3.1. Effect of feed concentration

The influence of *n*-butanol concentration in the feed on the membrane performance for the separation of *n*-butanol from water by pervaporation at different temperatures was studied using a PEBA 2533 membrane of 30 μm thickness. Fig. 2 shows the total and partial permeation fluxes versus feed butanol concentration in the range of 70–4000 ppm. At a given temperature, with an increase in butanol concentration in the feed solution, water flux increased slightly and the butanol flux increased almost proportionally. The linearity of the butanol flux–concentration relationship suggests that constant butanol permeability can be assumed in the dilute feed concentration range studied. This can be explained on the basis of membrane–permeant interactions. An increase in butanol concentration in the feed tends to increase the free volume and chain mobility of the organophilic membrane. Consequently, the diffusion of water molecules through the membrane is enhanced. However, because of the low concentrations of butanol in the feed solutions, the membrane is only moderately plasticized (swollen) on the feed side by permeant sorption [20]. As a result, butanol sorption on the membrane at the feed side is close to ideal (i.e., in the Henry's law regime). This is consistent with the results of molecular dynamics simulation performed for mass transport of ethanol and water through poly(dimethyl siloxane) membranes [21], which show that there are two competing effects at the feed–membrane interface. An increase in the feed ethanol concentration significantly influences the dynamics of the polymer swelling, while the presence of a large quantity of water molecules in the feed restricts the membrane swelling. In cases where the membrane swelling is

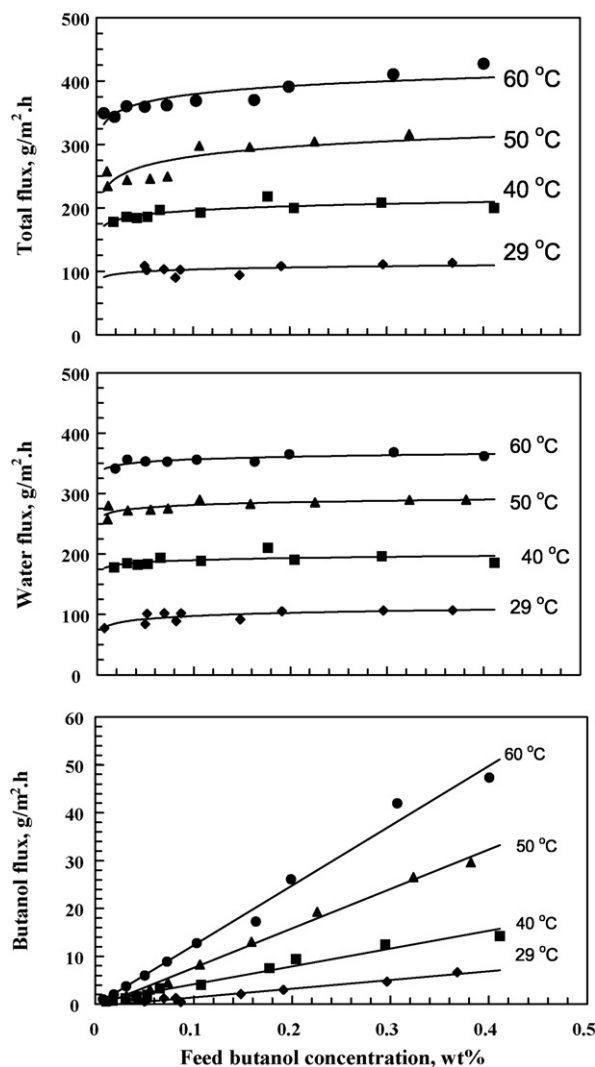


Fig. 2. Effect of butanol concentration in the feed on the total and partial permeation fluxes at different temperatures. Membrane thickness 30 μm .

minimal (for example, for very dilute feed systems), the permeation flux of the organic compound will vary linearly with the feed concentration. The relative constancy of the water flux has been reported by Favre et al. [22] who ascribed the effect to the quasi-constancy of the water activity in aqueous solutions where the concentrations of organic compounds are low. This is in agreement with the solution thermodynamics of dilute aqueous solutions, that is, the activity of water is essentially constant, while the activity of the low concentration organic compounds increases linearly with its concentration. Matsumura et al. [23] also reported a linear relationship between the partial permeation flux of butanol and the feed butanol concentration for pervaporation of butanol from dilute aqueous solutions using a rather thick (180 μm) homogeneous PDMS membrane.

The butanol concentration in the permeate is shown in Fig. 3, where the good permselectivity of the membrane for butanol/water separation is demonstrated. At a feed butanol concentration of 0.4 wt%, a permeate butanol concentration of as high as over 10 wt% can be obtained. However, the separation factor, which characterizes the degree of enrichment of the permeate product relative to the feed, is shown to decrease with the feed butanol concentration (see Fig. 4), and the rate at which it decreases tails off at higher concentrations of butanol in the feed solution. *n*-Butanol is a strong

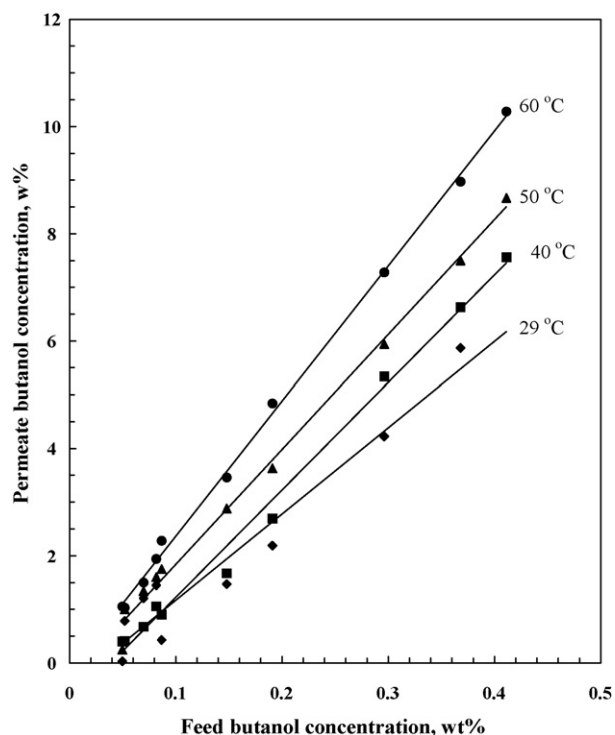


Fig. 3. Effect of feed concentration on the permeate concentration at different temperatures. Membrane thickness 30 μm .

polar solvent and thus has a strong cohesion effect in water due to strong hydrogen bonding. This will increase the coupling effect on permeation between water and *n*-butanol, resulting in a decrease in the separation factor. This trend is consistent with previous reports for the separation of ABE from dilute aqueous solutions [19] and the separation of other organic compounds from water involved in butyl acetate production via esterification [16]. The pervaporation

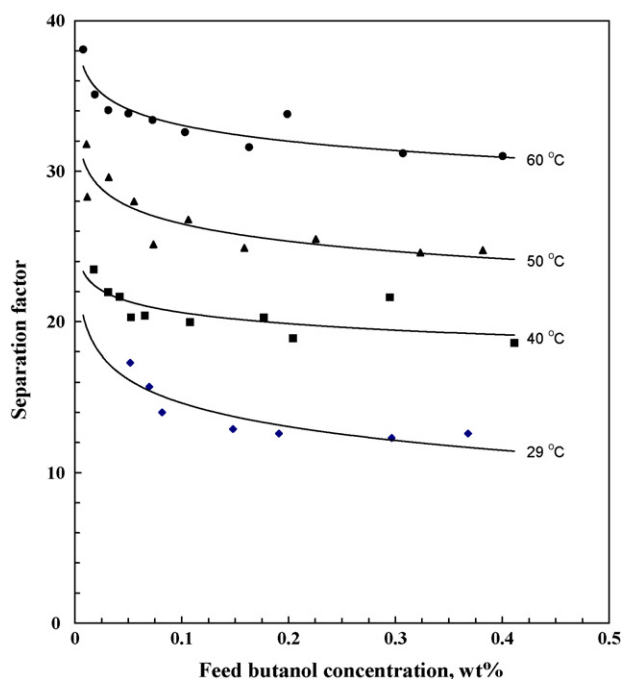


Fig. 4. Separation factor vs. feed butanol concentration. Membrane thickness 30 μm .

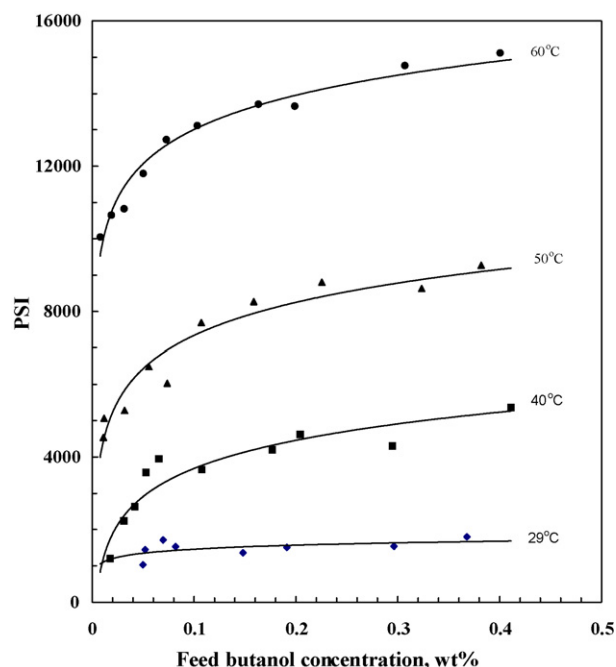


Fig. 5. The pervaporation separation index at feed concentrations and temperatures. Membrane thickness 30 μm .

separation index, presented in Fig. 5, is shown to increase as the feed butanol concentration increases and it gradually levels off at higher feed concentrations. The dependency of pervaporation separation index on the feed concentration becomes more significant at higher temperatures.

3.2. Effect of temperature

The above data showed that at a given feed concentration, increasing the operating temperature will increase both the permeation flux and separation factor. The temperature dependency of the permeation flux is found to follow an Arrhenius type of relation, as shown in Fig. 6, where the partial permeation fluxes of butanol and water are plotted against reciprocal temperature. It appears the butanol flux is more sensitive to temperature than water flux over the feed concentration range studied. The overall activation energies (E_j) characterizing the temperature dependencies of the permeation fluxes, which can be obtained from the slopes of the straight lines in Fig. 6, are shown in Fig. 7. The activation energy for water permeation is in the range 23.1–25.8 kJ/mol, which is lower than the activation energy for butanol permeation (35.6–58.6 kJ/mol). This explains that the separation factor increases with an increase in temperature as noticed previously (see Fig. 4).

The data in Fig. 7 also show that while the activation energies for permeation of both components tend to increase with an increase in the feed butanol concentration, the influence of feed concentration on butanol activation energy is more significant. This may be attributed to the low butanol content in the dilute feed solutions. The permeation process involves three consecutive steps: dissolution (or sorption), diffusion and desorption. The desorption step is generally not considered to be the rate controlling step, and the membrane permeability is mainly determined by the solubility and diffusivity of the permeating component in the membrane [1]. Butanol permeates through the membrane preferentially in spite of its larger molecular size than water molecules, and this suggests that the permselectivity derives mainly from

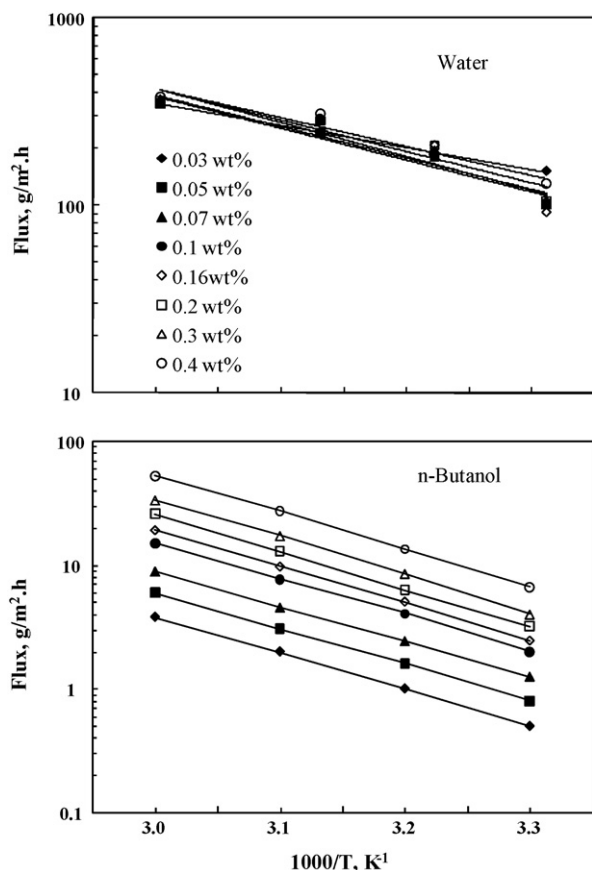


Fig. 6. Temperature dependence of permeation fluxes. Membrane thickness 30 μm .

the solubility selectivity. It means the dissolution of the permeant in the membrane is a dominating step in the pervaporation transport for butanol/water separation. The heat of mixing for dissolution of permeating species in the membrane will influence the

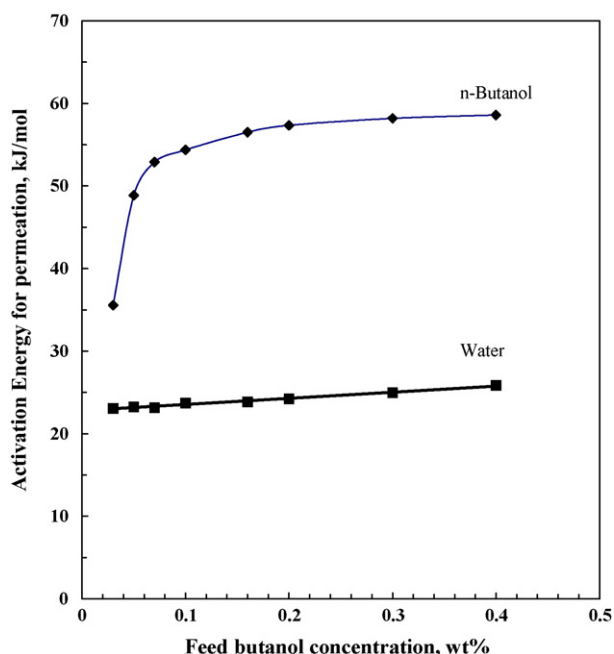


Fig. 7. Activation energy for water and butanol permeation.

activation of energy for permeation [24]. Note that the activation energy so obtained has accounted for the effect of increased trans-membrane driving force for permeation when the temperature increases. As a first approximation, the activation energy (E_p) characterizing temperature dependence of the membrane permeability can be estimated by subtracting the heat of evaporation (which roughly measures the temperature dependence of the driving force) from the activation energy (E_j) obtained above. In consideration of the heat of evaporation of *n*-butanol and water (which is 52.4 and 44.0 kJ/mol at 25 °C, respectively [25]), it appears to suggest a negative value of E_p , which is also an indication that the permeant dissolution step is dominating in the pervaporation separation. Because E_p consists of the activation energy for diffusion (which is always positive) and the heat of dissolution (which is often negative due to the exothermic mixing process), when the heat of dissolution is dominant, negative values of E_p will result. This is consistent with the hypothesis that the membrane permselectivity for butanol/water separation results from the solubility selectivity of the membrane because of organophilic nature of the membrane.

3.3. Effect of membrane thickness

Thin membranes are often used in order to achieve a high permeation flux. It is usually perceived that in an ideal case where the membrane is homogeneous and free of defects, the permeation flux is inversely proportional to the membrane thickness while the membrane thickness has no impact on the membrane selectivity. This is why in some studies the reported permeation fluxes were normalized to a given membrane thickness by assuming a reciprocal relationship between permeation flux and the membrane thickness (see, for example, [26–33]). However, pervaporation involves a phase change from liquid to vapor, and there is no guaranty that the concentration profile in the membrane and the local state of the membrane at a given point relative to the feed/membrane interface will remain the same when the membrane thickness varies. Thus the effects of membrane thickness on the pervaporation performance were investigated as well.

Fig. 8 shows the partial permeation fluxes as a function of reciprocal membrane thickness at various feed butanol concentrations. As expected, an increase in membrane thickness will reduce the permeation rates of both butanol and water. However, it is very clear that the permeation flux and membrane thickness do not follow a simple inverse proportionality relationship. It would be misleading to predict the permeation flux of a thin membrane from the thickness-normalized permeation flux obtained with a thick membrane.

The permeation flux of butanol is shown to follow a linear (but not proportional) function of reciprocal membrane thickness. This seems to suggest that concentration polarization occurred in the boundary layer on the feed side. Based on the resistance-in-series model [34,35], which has been widely used to describe the boundary layer effect, the overall resistance to mass transfer ($1/k_{ov}$) is the sum of the membrane resistance ($1/k_m$) and the boundary layer resistance ($1/k_L$):

$$\frac{1}{k_{ov}} = \frac{1}{k_L} + \frac{1}{k_m} \quad (4)$$

where k_{ov} and k_L are the overall mass transfer coefficient and the mass transfer coefficient in the liquid boundary layer, respectively, and k_m is the mass transfer coefficient in the membrane and is equal to the membrane permeability divided by the membrane thickness. Assuming zero pressure on the permeate side and for dilute feed solutions, the overall mass-transfer coefficient k_{ov} can be determined from the experimental data of butanol fluxes as a function

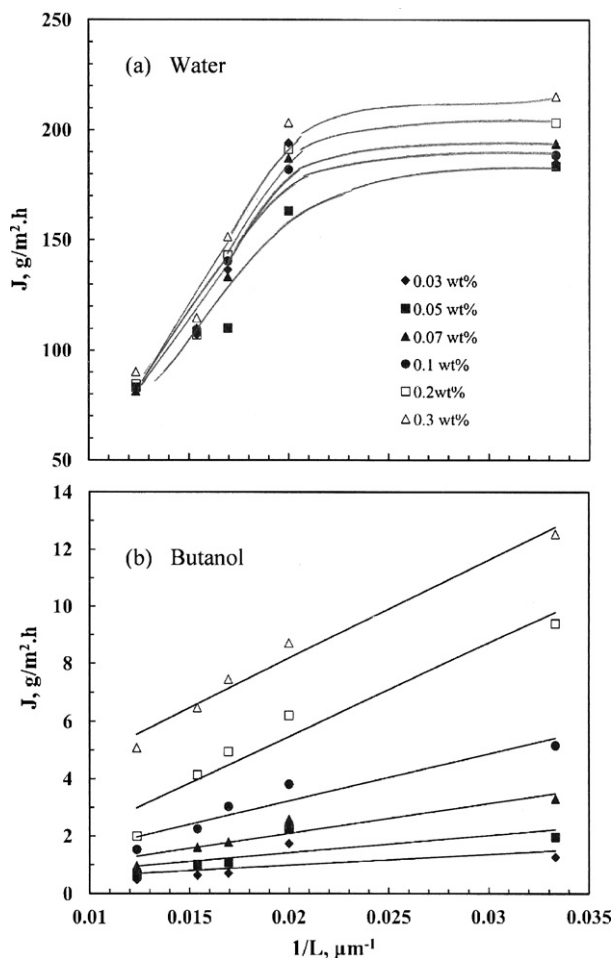


Fig. 8. Permeation fluxes of water and butanol vs. reciprocal membrane thickness. Temperature 40°C .

of feed butanol concentrations:

$$J_i = k_{ov} C_b \quad (5)$$

where C_b is the bulk concentration of butanol in the feed. This relationship is found to be valid for the system studied here, as shown by Fig. 9 where the butanol flux is plotted versus feed butanol concentration for membranes with different thicknesses. Eq. (4) suggests that at constant hydrodynamic conditions (which was the case in the present study), plotting the overall resistance against membrane thickness will yield a straight line, as shown in Fig. 10. The mass transfer coefficient in the boundary layer (k_L) can be determined from the intercept of the plot and is found to be 1.0×10^{-5} m/s. This is consistent to the boundary layer mass transfer coefficients reported in the literature, which is often in the range of $(0.2\text{--}3.3) \times 10^{-5}$ m/s, for lab scale of pervaporation for the separation of a variety of organic compounds from dilute aqueous solutions using different membranes [36–38]. Based on butanol permeation, the relative contribution of boundary layer resistance to the overall mass transfer resistance is shown in Table 1. It is revealed that depending on the membrane thickness, the boundary layer resistance represents only 5–12% of the overall mass transfer resistance, whereas the membrane itself constitutes 88–95% of the total resistance for butanol permeation. Although the boundary layer resistance tends to be more significant for thinner membranes, the boundary layer effect is in general not significant enough to dominate the butanol permeation under the experimental conditions.

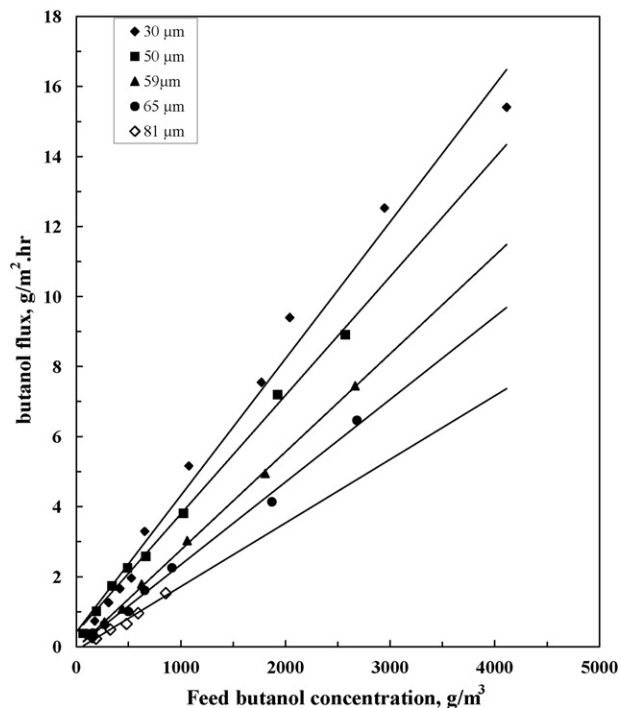


Fig. 9. Permeation flux of butanol vs. feed butanol concentration for membranes with different thicknesses. Temperature 40°C .

Based on the above analysis, the resistance-in-series model appears to work well in describing the boundary layer effects based on butanol permeation. However, it should be mentioned that this approach is not without reservation. In principle, the concentration polarization affects the permeation fluxes of the more and less permeable components differently because of the buildup of the less permeable component on the membrane surface. Because of the concentration polarization, the concentration of water on

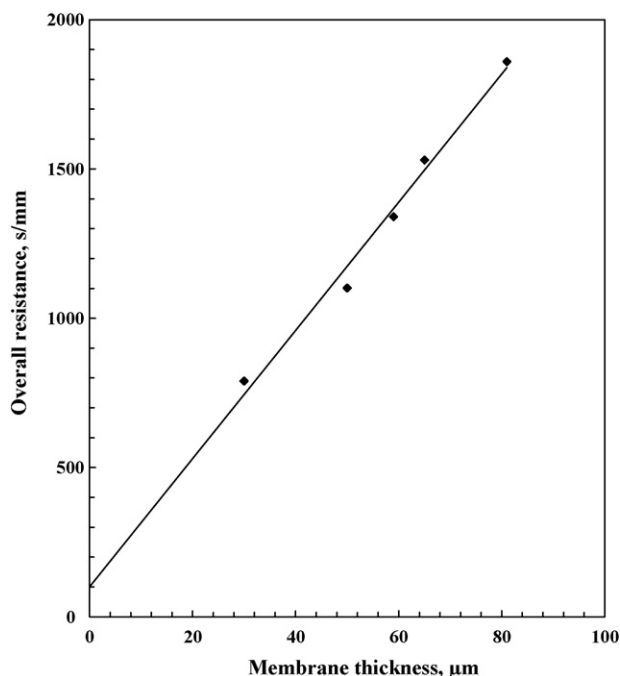


Fig. 10. Effect of membrane thickness on the overall resistance for butanol permeation. Temperature 40°C .

Table 1

Overall resistance for butanol permeation and a breakdown of the relative contribution of the membrane and the boundary layer

Membrane thickness (μm)	Overall resistance ($\times 10^{-3}$) ($\text{m/s})^{-1}$	Percentage membrane resistance	Percentage boundary layer resistance
30	789	87.4	12.6
50	1101	90.9	9.1
59	1340	92.5	7.5
65	1530	93.5	6.5
81	1860	94.6	5.4

Note: Overall permeation resistance = $1/(\text{overall mass transfer coefficient})$.

the membrane surface will be higher than in the bulk feed, which means the driving force for water permeation would be increased by the boundary layer effect, and thus the mathematical form of the resistance-in-series model as represented by Eq. (4) will be invalid to describe water permeation. In consideration of the dilute feed solutions, the variations of water concentration on the membrane surface due to concentration polarization are relatively small and should be insignificant to impact water permeation flux. In this case, the water flux should be approximately proportional to the reciprocal membrane thickness as the membrane dominates the overall mass transport of water through the membrane. However, the experimental results show that this is not the case, as shown in Fig. 8(a). It appears that when the membrane is sufficiently thin, the permeability of water through the membrane is no longer significantly affected by the membrane thickness. This can be explained in consideration that the feed side of the membrane is swollen by the liquid feed, whereas the permeate side is dry due to vacuum applied. For a membrane that is thin enough, while a decrease in membrane thickness shortens the path for the permeating species to pass the membrane, which tends to increase the permeation rate, the dry "region" within the membrane near the permeate side is expected to be closer to the feed side on a relative scale across the membrane thickness, which tends to lower the permeation rate. The latter aspect is anticipated to be significant for water because of the organophilicity of the membrane. As a result, the membrane thickness will not drastically influence the water flux any more.

On the other hand, the membrane thickness is found to influence the separation factor significantly, as shown in Fig. 11. While a decrease in the membrane thickness tends to improve the permeation flux, the separation factor becomes compromised. This cannot be attributed merely to concentration polarization as the boundary layer effect does not dominate butanol permeation. Based on all the results of permeation flux and separation factor, it is apparent that in addition to the boundary layer effect that occurs outside the membrane, the local permeant concentration within the membrane and the concentration profile across the membrane are also influenced when the membrane thickness changes. This is expected to be especially significant for systems with strong permeant–permeant and permeant–membrane interactions. With an increase in the membrane thickness, the permeation rate decreases and thus the local concentration of the permeant in the membrane decreases. In other words, the local "state" of the membrane (e.g., the degree of swelling at a given point and the swelling gradient across the membrane) will be affected by the membrane thickness. Just like the well-known observation that the feed concentration affects membrane permselectivity due to permeant–membrane interactions, it is not surprising that the membrane thickness has an impact on the permeability. Therefore, caution should be exercised in using thickness-normalized permeation fluxes to estimate or predict the separation performance of pervaporation membranes with different thicknesses because the permeation fluxes are not necessarily proportional to the reciprocal

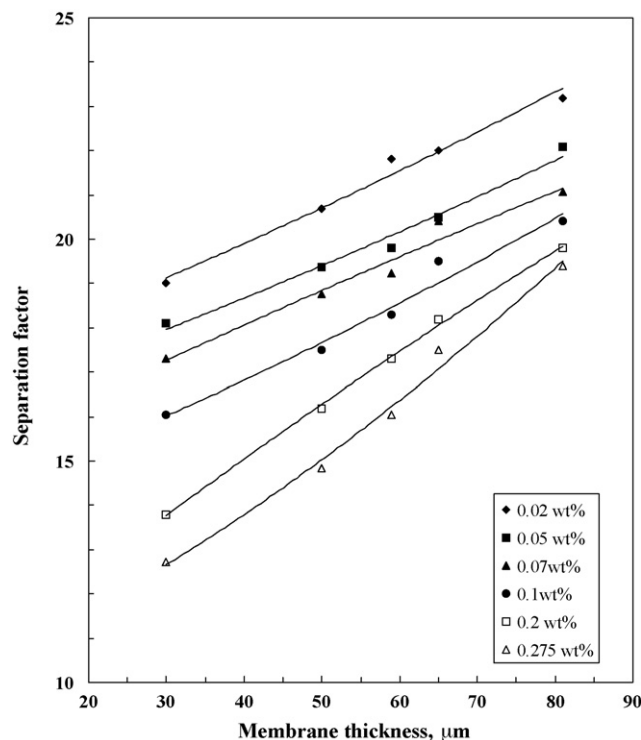


Fig. 11. Effect of membrane thickness on separation factor. Temperature 40 °C.

membrane thickness and thus the separation factor can be affected by the membrane thickness even under circumstances where the boundary layer effects are unimportant.

4. Conclusions

The separation of *n*-butanol from aqueous solutions by pervaporation with PEBA 2533 membranes was studied, and the performance of the membranes for separating model water/butanol mixtures at concentrations commonly encountered in fermentation processes was considered. It was shown that the permeation flux of butanol was approximately proportional to the feed butanol concentration, while the permeation flux of water was relatively constant over the low feed concentration range (0.03–0.4 wt%) studied. An increase in temperature increased both the permeation flux and separation factor, and the temperature dependency of the permeation flux followed an Arrhenius type of relationship. The present study also showed that not only was the permeation flux affected by the membrane thickness as expected for all rate-controlled processes, the separation factor was influenced as well. While a thin membrane is often desired for increased permeation flux, the separation factor became compromised as the membrane became thinner. The effect of membrane thickness on the membrane performance was analyzed on the basis of the resistance-in-series model. It was demonstrated that the observed effect of membrane thickness on the separation performance could not be entirely attributed to the boundary layer effect occurring outside the membrane, and the variations in the local permeant concentrations inside the membrane with membrane thickness appeared to be also significant. Therefore, caution should be exercised in using thickness-normalized permeation fluxes to predict the separation performance of membranes with any given thicknesses because the membrane selectivity can be affected by the membrane thickness even if the boundary layer effect is insignificant.

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