



Pervaporative separation of *n*-butanol from dilute aqueous solutions using silicalite-filled poly(dimethyl siloxane) membranes

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ABSTRACT

Pervaporative separation of *n*-butanol from dilute aqueous solutions (<0.5 wt%) using a silicalite-filled poly(dimethyl siloxane) composite membrane was investigated. The effects of operating conditions (e.g., feed composition, temperature) on the permeation flux, separation factor and pervaporation separation index were evaluated. It was shown that at a given temperature, water flux increased almost linearly with an increase in feed butanol concentration, whereas the butanol flux increased in a concave fashion due to silicalite fillers that have a strong affinity to butanol molecules. Consequently, the permeate butanol concentration initially increased and then gradually leveled off when the feed butanol concentration was high enough, and the leveling off started to occur at a lower butanol concentration at a higher temperature. The temperature dependence of permeation flux followed a typical Arrhenius relation, and a variation in temperature would increase or decrease the membrane selectivity, depending on feed butanol concentration. These results are especially important for potential use of the membrane for in situ butanol extraction from fermentation where butanol becomes inhibitory at a low concentration of 4–6 g/L.

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1. Introduction

In recent years, pervaporation has been widely studied for the separation of close boiling, azeotropic, isomeric and other mixtures that are difficult to separate by conventional techniques. In pervaporation, the separation is based on selective permeability of the membrane to the components in a mixture to be separated. The membrane permeability is primarily determined by the solubility and diffusivity of the permeating component in the membrane, and not the relative volatility as in distillation. Unlike other membrane processes, pervaporation involves a liquid to vapor phase change and the permeate obtained is a low pressure vapor. In addition to the energy consumption used to operate the vacuum pump to create driving force for permeation, the phase change requires additional energy which should be at least equal to the heat of evaporation of the permeate. Thus, from an energy consumption point of view, it is preferable if the membrane can be targeted at selective permeation of the minor component in the mixture.

For the separation of organic compounds from aqueous solutions where the organic compounds are the minor components, poly(dimethyl siloxane) (PDMS) and other rubbery organophilic

membranes are often preferred. The rapid chain segment motion in the silicone and other rubbery polymers leads to a large free volume that favors the diffusion of the permeating molecules. While homogeneous membranes may be adequate in basic permeability studies, composite membranes comprising of a thin active skin layer and a microporous substrate are desired for practical applications in order to enhance the mass transfer rate without compromising their mechanical stabilities. The substrate should be highly porous to minimize its resistance to mass transfer of the permeating components. Otherwise, the overall permselectivity of the composite membrane will be lowered. On the other hand, the pores on the substrate membrane should be small enough so as to prevent intrusion and filling of the pores with the top layer material during surface coating, which is commonly used in membrane formation.

Based on the solution-diffusion mechanism, the membrane performance can be enhanced by improving either selective sorption or selective diffusion or, if possible, both. Therefore, efforts have been made to incorporate microporous “filler” materials with high sorption selectivity into a membrane matrix, and zeolites are the most popular filler materials due to their well-defined microstructure and hydrophilicity/hydrophobicity. Over the past few years, zeolite-filled membranes have received significant attention for various applications (see, for example, [1–8]). Silicalite, an organophilic silica molecular sieve [9], has shown to be especially effective for improving membrane permselectivity because of its unique crystalline microporous structure and surface chemistry. As a result, water permeability is generally reduced as water

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molecules are excluded from entering the pores of the filler particles. This causes not only a decreased sorption of water but also an increased path length for water molecules to travel through the membrane because they have to take a more tortuous path [1]. It has been found that the mass transport of small organic molecules is generally enhanced, but depending on the relative size and shape of the molecules, bulky molecules may be partly or totally excluded from entering the zeolite pores due to the molecular sieving effect [2].

This study deals with pervaporative separation of butanol from dilute aqueous solutions. Butanol is widely used in the manufacture of resins, plasticizers, cleaning agents and ester compounds as well as in the food and cosmetic industries as an extractant. In addition, the depleting supply of crude oil has recently created extensive interest in converting biomass and agricultural wastes for energy production, and biobutanol has become an attractive transportation fuel. If used as a fuel for internal combustion engines, butanol has many advantages over ethanol, including a higher (30% more) energy density, a higher octane rating, more miscible with gasoline and diesel fuel but less miscible with water, and a lower Reid vapor pressure (which is 7.5 times lower than ethanol). Many studies have been carried out on the use of pervaporation to separate butanol/water mixtures using either hydrophobic membranes for butanol concentration [10–13] or hydrophilic membranes for butanol dehydration [14–17].

Butanol production by fermentation is severely limited by product inhibition, resulting in a low reactor productivity and a low final butanol product concentration (0.04–1.5 wt%) [18], which are the primary factors impeding commercial acceptance of butanol production from biomass. This, however, appears to represent a niche application for pervaporation to alleviate product inhibition and to facilitate product recovery by simultaneous removal of butanol as soon as it is produced. For this potential application, organophilic membranes will be appropriate. In consideration that butanol becomes inhibitory at a low concentration of 0.4–0.6 wt%, it is of interest to investigate the pervaporation behavior for butanol removal from dilute solutions that are relevant for in situ removal of butanol. In this paper, a silicalite-filled poly(dimethyl siloxane) thin film composite membrane was evaluated, and the effects of feed concentration of *n*-butanol (0.01–0.4 wt%) and operating temperature (25–65 °C) on the separation performance were studied. This information will be useful to the assessment of technical feasibility of using pervaporation for in situ recovery of butanol. It may be mentioned that butanol recovery by pervaporation from dilute solutions is not well studied, and the prior work reported in the literature is often for feed concentrations too high to be relevant to the in situ recovery. Jonquieres and Fane [19] reported separation of butanol/water mixtures with a silicalite/PDMS membrane at three different concentrations (i.e., 1, 2.5 and 5 wt%) at a temperature of 40 °C. El-Zanati et al. [13] studied butanol separation from water at 33 °C in a feed concentration range of 0.6–5.0 wt% using a reportedly Sulzer 2200 membrane (which might not be true as this poly(vinyl alcohol)-based commercial membrane is a hydrophilic membrane appropriate for dehydration of organic solvents). As will be reported in this work, the membrane behaved quite differently in terms of permselectivity at low feed concentrations because of the silicalite fillers in the membrane, and it would be unreliable to obtain the membrane permselectivity at low concentrations by extrapolating the experimental data obtained at high concentrations.

2. Experiments

n-Butanol was supplied by Fisher Scientific. The membrane used in the experiments was a silicate-filled composite PDMS membrane (Pervap 1070) manufactured by GFT (now Sulzer Chemtech). It is comprised of a thin selective skin layer of PDMS filled with a certain

amount of hydrophobic silicalite particles and a microporous asymmetric polyacrylonitrile substrate, which is backed on a non-woven polyester fabric for increased mechanical strength. The precise composition of the active skin layer is proprietary. The pervaporation experiments were carried out using a laboratory scale pervaporation unit; the setup and the procedure have been described elsewhere [20]. The membrane was mounted in a stainless steel permeation cell with an effective permeation area of 13.85 cm².

The permeation cell was designed to allow the feed to enter the permeation cell through a center opening and then flow radially along the membrane surface, while the retentate exited through a thin channel located peripherally near the edge of the membrane. The feed solution was admitted to the membrane cell via a centrifugal pump and the retentate was circulated back to the feed tank. A relatively high flow rate (1.6 L/min, corresponding to a linear flow velocity on the membrane of >20 cm/s) was used to minimize the boundary layer effect. Vacuum was provided on the down stream-side of the membrane using a vacuum pump, and the permeate pressure was maintained at ~5 mmHg for all experiments. The permeate was initially collected in one of the cold traps immersed in liquid nitrogen, and it was then sampled periodically (~1 h) by switching to the other cold trap. This allows permeate to be sampled without interrupting the pervaporation system.

The permeate flux was determined gravimetrically from the weight of the permeate sample collected over a given period of time. The concentration of butanol in the permeate was determined using a Total Organic Carbon Analyzer (Shimadzu TOC-500); double distilled water was used as a diluent to the permeate sample during composition analysis. For each set of experiments, the operating parameter was varied one at a time and covered the following ranges: feed concentration 0.01–0.4 wt% butanol and operating temperature 25–65 °C. Based on the experimental data of pervaporation, the membrane performance can be characterized in terms of permeation flux (*J*) and separation factor (α) shown below:

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

$$\alpha = \frac{x_P/(1-x_P)}{x_F/(1-x_F)} \quad (2)$$

where *Q* is the mass of permeate collected over a time interval *t*, *A* is the effective membrane area for permeation, and *x_P* and *x_F* are the mass fractions of butanol in the permeate and feed, respectively. The partial permeation fluxes can be easily obtained from the total flux and the permeate concentration. Sometimes the pervaporation separation index (PSI) may also be used as a composite parameter to characterize the overall performance of the membrane:

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

3. Results and discussion

To study the effect of *n*-butanol concentration in the feed solution on the performance of the PDMS composite membrane, pervaporation experiments were performed at different concentrations and temperatures. Figs. 1 and 2 show the effects of feed composition on the total permeation flux and butanol concentration in the permeate at different temperatures, respectively. At a given temperature, the total flux increased with an increase in the feed butanol concentration over the low feed concentration range (0.01–0.5 wt%) studied. An increase in temperature will increase the permeation flux, but the concentration dependency of the flux does not appear to be affected significantly by the temperature. While this pattern can often be observed for pervaporation of dilute solutions, it is interesting to notice that the permeate butanol concentration initially increased and then gradually leveled off when the feed butanol concentration is high enough. A striking point

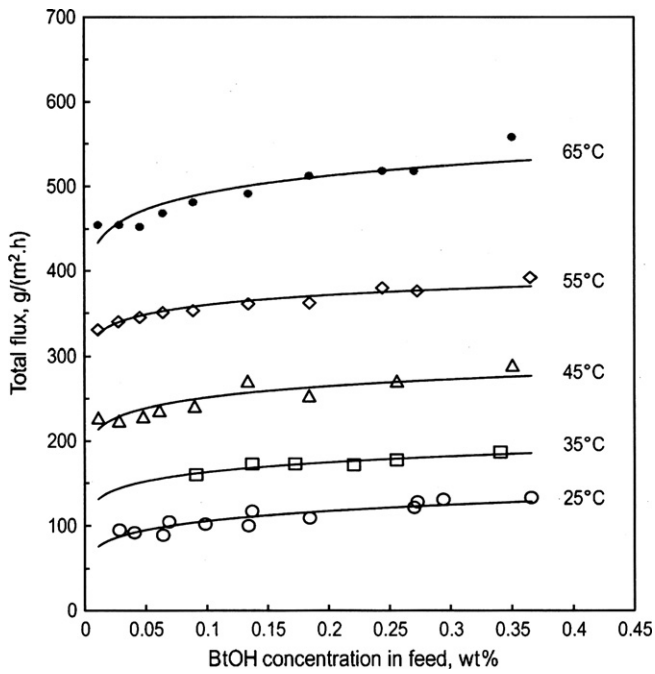


Fig. 1. Effect of butanol concentration in the feed on the total permeation flux at different temperatures.

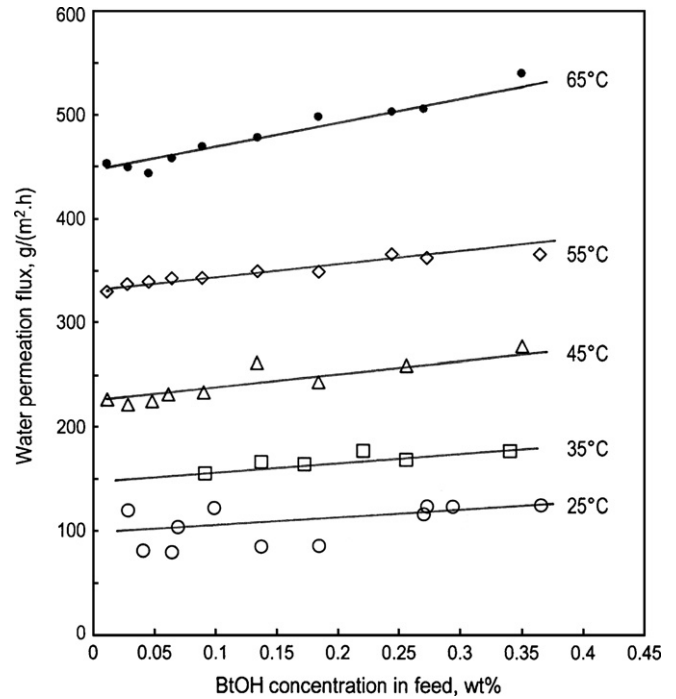


Fig. 3. Effect of feed butanol concentration on the permeation flux of water at different temperatures.

worthy of mention is that at a higher temperature, the permeate butanol concentration tends to increase more significantly with an increase in feed butanol concentration and so is its rate of leveling off. Consequently, the “leveling off” in permeate butanol concentration starts to occur at a lower concentration when the temperature increases, as shown in Fig. 2. This feature can be attributed to the filler particles in the membrane that cause competitive sorption to the permeating species, as will be discussed later. To our

knowledge, no similar trend has been observed for other pervaporation membranes containing filler particles or silicalite-filled PDMS membranes for butanol/water separation at high concentrations.

To help understand the permeation behavior of the membrane, the partial fluxes of water and butanol are shown in Figs. 3 and 4, respectively. It can be seen that at a given temperature the water flux slightly increased with the feed butanol concentration. This is understandable as butanol sorbed into the membrane will swell

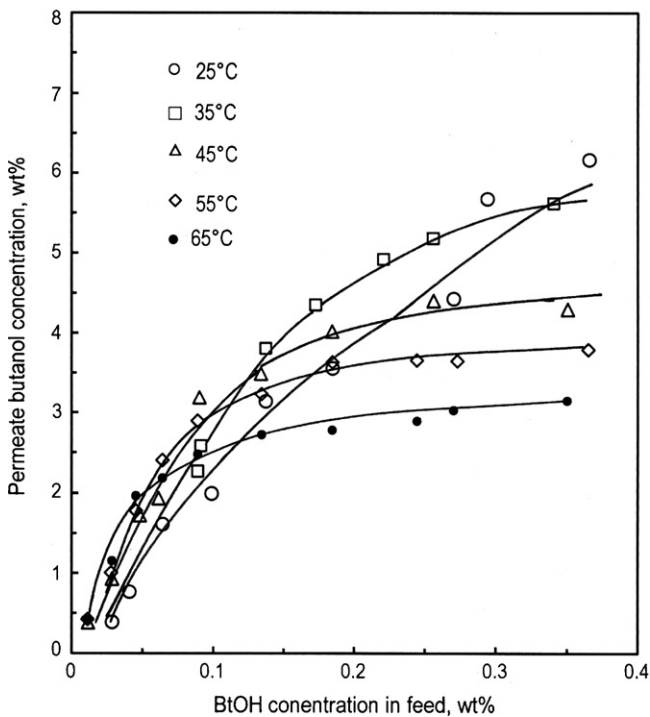


Fig. 2. Permeate butanol concentration versus feed concentration at different temperatures.

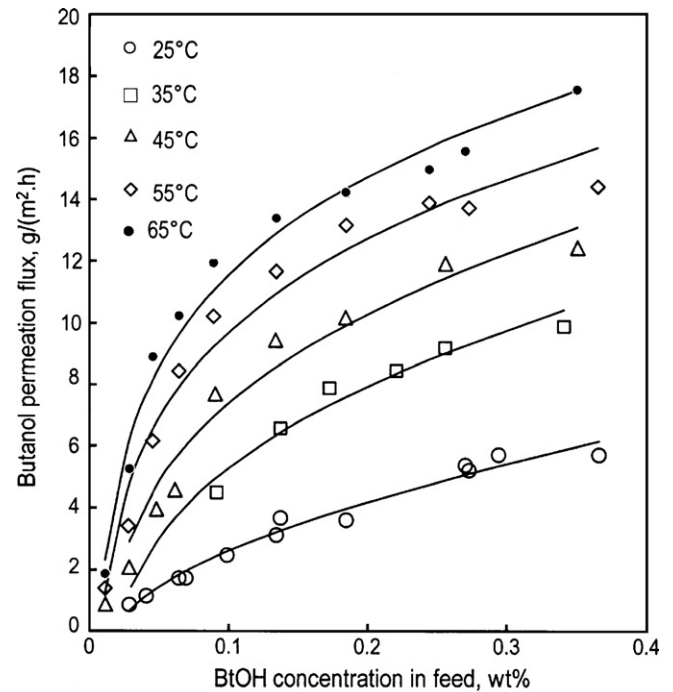


Fig. 4. Effect of feed butanol concentration on the permeation flux of butanol at different temperatures. Solid lines represent calculated values.

the membrane, resulting in an increased free volume and polymer chain flexibility that will facilitate water permeation through the membrane. The internal surface of silicalite is hydrophobic, and the silicalite fillers in the membrane do not affect water solubility in the membrane. Because of the dilute feed solutions, the water activity (as calculated by the NRTL method using the parameters suggested by Gmehling and Onken [21]) is virtually constant in the range of the low butanol concentrations investigated, and the observed increase in the water flux is primarily due to the increased permeability of the membrane. On the other hand, the permeation of butanol is expected to be affected by both the feed concentration and the membrane permeability. Silicalite is known to have a strong affinity to butanol [22,23]. Because of the organophilicity of silicalite fillers in the membrane, butanol sorption in the membrane will be enhanced, which is the rationale of using the fillers to improve the membrane permselectivity. However, as the butanol concentration increases, the active sorption “sites” in the silicalite available to sorb additional butanol molecules are gradually depleted, and as a result the enhancement in butanol permeability will become less significant, as shown in Fig. 4. This is in agreement with the results of sorption studies where butanol sorption from dilute aqueous solutions is shown to have reached the maximum capacity when the solution concentration is only 0.07–0.3 wt% butanol [22].

Since the silicalite fillers are dispersed in the membrane, it is thus foreseeable that there is a dual mode of sorption of butanol molecules: one is in the polymer, and the other on silicalite. The two populations of molecules may have different mobilities. Based on the activated state theory, there are four possibilities in the molecular diffusion jumps that can occur on the diffusion time scale: (1) within polymer, (2) from polymer to silicalite, (3) within silicalite, and (4) from silicalite to polymer. In principle, the mass transport of butanol in the silicalite-filled PDMS membranes could be formulated in analog to gas permeation in glassy polymers with dual mode sorption and diffusion [24]. Unfortunately, a quantitative description of the mass transfer mechanism is still difficult because butanol sorption on silicalite does not follow a simple Langmuir isotherm [22], and knowledge on butanol diffusivities in PDMS and silicalite is very limited. In addition, accurate information about the microstructure and sizes of the silicalite particles as well as their content in the membrane are unavailable for proprietary considerations; even the thickness of the selective layer reported in the literature is inconsistent (varying from 10 to 30.5 μm) [25–27]. This makes it difficult to quantify the contribution of the silicalite fillers and the PDMS matrix to the overall permeation separately. Nevertheless, for the sake of simplicity, assuming additive contribution of PDMS and silicalite to permeation, a semi-empirical equation of the form

$$J = aw + b \ln w + c \quad (4)$$

appears to be able to represent the concentration dependence of butanol flux, where J is the butanol flux ($\text{kg}/\text{m}^2 \text{ h}$), and a , b and c are empirical parameters that are related to sorption and diffusion properties, and w is butanol concentration in feed (kg/m^3). The first term on the right side of Eq. (4) represents permeation in PDMS with a constant permeability coefficient, and the remaining two terms represent permeation of silicalite-sorbed molecules based on Temkin equation of sorption (i.e., $q = B \ln(Ax)$) that takes into account the strong sorbent–sorbate interactions [28]. As shown in Fig. 4, the butanol flux data can be fitted with Eq. (4) satisfactorily with the parameters (shown in Table 1) obtained by nonlinear regression.

It appears clear that the curvature in Fig. 2 is due to the fact that although both permeation fluxes of water and butanol increase with an increase in the butanol concentration in the feed, the increase in butanol flux is more pronounced than the increase in water flux, but the increase in butanol flux gradually slows down

Table 1
Empirical parameters describing butanol flux.

Temperature ($^{\circ}\text{C}$)	$a \times 10^7$ (m/s)	$b \times 10^7$ ($\text{kg}/\text{m}^2 \text{ s}$)	$c \times 10^6$ ($\text{kg}/\text{m}^2 \text{ s}$)	R^2
25	2.2	3.1	0.5	0.976
35	2.1	7.6	1.3	0.953
45	1.9	8.9	1.9	0.965
55	1.3	10.2	2.6	0.969
65	0.7	11.6	3.2	0.983

as the feed butanol concentration increases. Consequently, the corresponding separation factor initially increases and then decreases when the butanol concentration is sufficiently high, resulting in a maximum at a certain concentration, as shown in Fig. 5. Interestingly, a variation in temperature may increase or decrease the membrane selectivity, depending on the butanol concentration. This is important to determination of suitable operating conditions for instantaneous removal of butanol from fermentation broth. Although a detailed analysis is beyond the scope of this work, it is expected that during the early period of the reaction, the bio-conversion rate is relatively fast and the butanol concentration is low, and so is the rate of butanol removal because of the relatively low driving force for permeation. As a result, butanol concentration will increase until butanol formation rate and removal rate become equal, reaching a quasi-steady state. It is thus preferred to choose appropriate membrane design and operating parameters (i.e., membrane area, temperature) such that the resulting butanol concentration at quasi-steady state will be equal to the concentration at which the membrane exhibits maximum selectivity.

The above research findings are particularly important for potential use of the membrane for simultaneous removal of butanol from fermentation processes, where butanol becomes inhibitory at a concentration of as low as 4–6 g/L, and the cell growth would be completely inhibited at a butanol concentration of 17 g/L [29]. Clearly, the membrane performance data for dilute butanol solutions (i.e., 0.01–0.4 wt%) reported in this study cannot

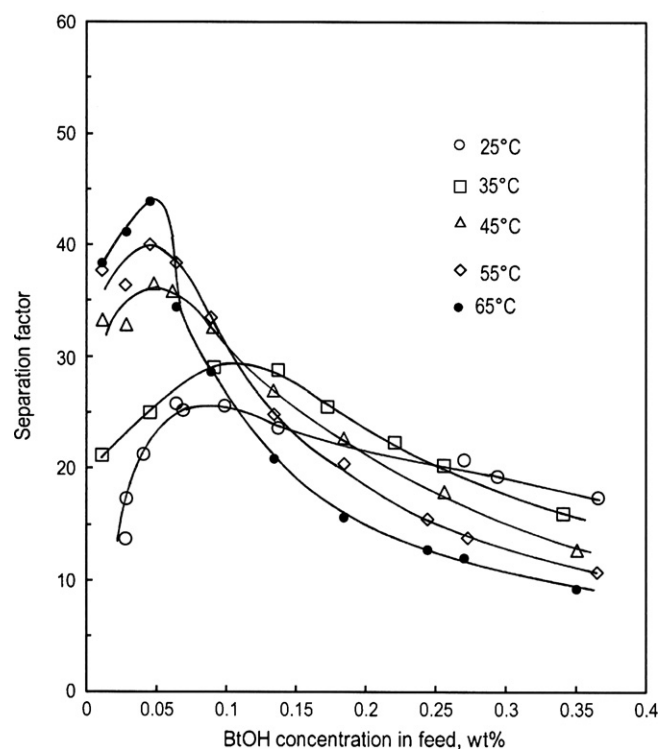


Fig. 5. Separation factor as a function of feed butanol concentration at different temperatures.

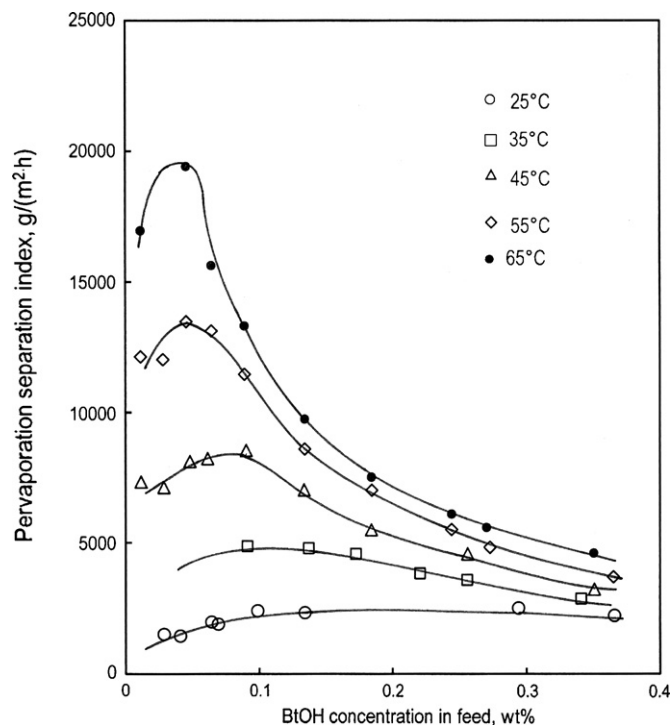


Fig. 6. Pervaporation separation index versus feed butanol concentration at different temperatures.

be obtained by extrapolation of the performance data reported in the literature with relatively high butanol concentrations (i.e., at 1, 2.5 and 5 wt%) [19].

Fig. 6 shows the pervaporation separation index as a function of feed butanol concentration at various temperatures. At a given temperature, an increase in the feed butanol concentration tends to increase the PSI in a low concentration range, and thereafter a further increase in butanol concentration in the feed will lower the PSI. Nonetheless, at a given feed concentration, an increase in temperature will always increase the PSI, and the temperature dependency of the PSI is more significant at lower feed butanol concentrations. It should be pointed out that PSI is a composite parameter accounting for permeation flux and separation factor. While it is convenient to use for evaluation and comparison of membrane performance, but its use should not be taken for granted as the membranes with same PSI values may perform quite differently.

The effects of temperature on the membrane performances have been illustrated qualitatively in the above figures discussed. However, it is interesting to note that the effects of temperature on the permeation of both butanol and water follow the typical Arrhenius relation, as shown in Fig. 7, where the partial permeation fluxes are plotted versus reciprocal temperature. The apparent activation energies for the permeation of butanol and water, which were determined from the slopes of the plots, are presented in Fig. 8. The activation energy for both water and butanol permeation tends to decrease as the feed butanol concentration increases, and the temperature dependence of butanol flux is more significant at feed butanol concentrations below 0.15 wt%. As butanol concentration increases, the amount of butanol sorbed in the polymer and silicalite will increase, making the sorptive sites in silicalite more saturated with butanol molecules and the polymer chains more flexible. As a result, the energy barrier that needs to be overcome by the permeant molecules for permeation to occur will be lowered. In pervaporation, temperature affects the permeation flux in three aspects: the solubility, diffusivity, and the driving force for permeation (i.e., vapor pressure). The apparent activation energy

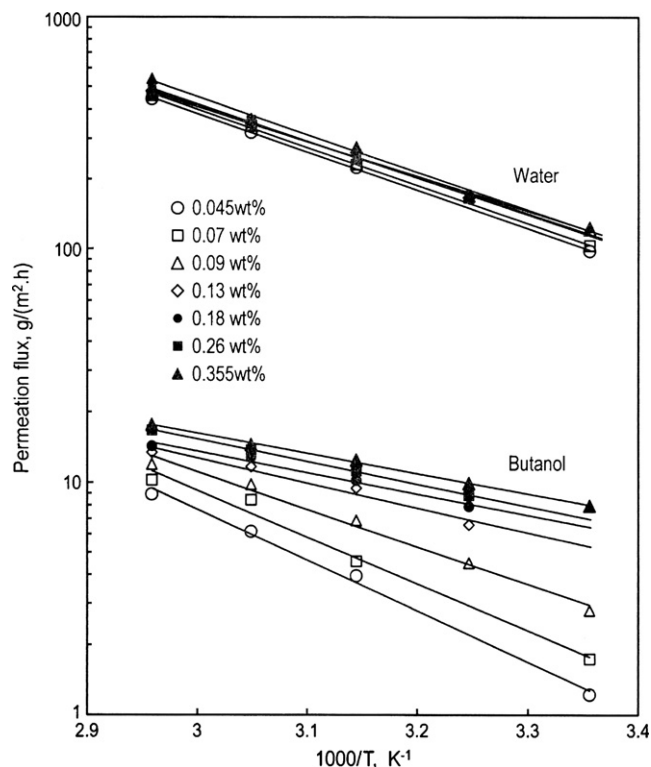


Fig. 7. Arrhenius plot showing the temperature dependence of the permeation fluxes of water and butanol at given feed concentrations.

has accounted for the effect of temperature on the driving force for permeation, which can roughly be measured by heat of evaporation. In principle, the temperature effects on driving force and membrane permeance can be separated on the basis of solution-diffusion model using partial vapor pressure difference across the

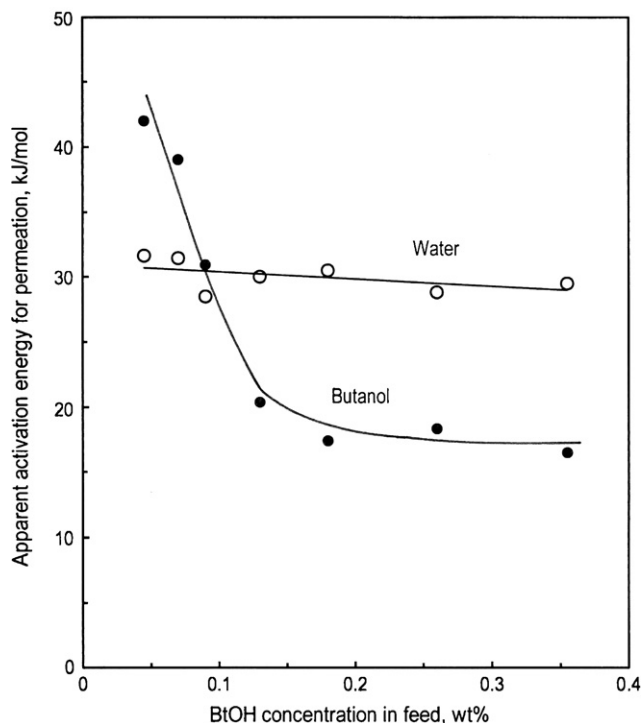


Fig. 8. Apparent activation energy for permeation at different feed butanol concentrations.

membrane as the driving force [30]. However, there is a lack of agreement in the data published or predicted by various models on the activity coefficient of butanol at the low concentration studied, and this will directly affect the evaluation of the permeance. On the other hand, as a first approximation, the activation energy (E_p) that characterizes temperature dependence of membrane permeability can be estimated by extracting the heat of evaporation from the apparent activation energy (E_j) [31]. Comparing the E_j values with the heat of evaporation (which is 52.4 kJ/mol at 25 °C for butanol and 44.0 kJ/mol for water [32]) one will find that the E_p for butanol and water permeation in the membrane is negative, indicating that an increase in temperature will lower the membrane permeability. Since E_p consists of the activation energy for diffusion (which is always positive) and the heat of dissolution (which is often negative due to exothermic mixing process), a negative E_p suggests that the sorption aspect is dominant. This is in agreement with the fact that the permselectivity of the membrane for butanol/water separation derives from the solubility selectivity of the membrane due to the affinity between butanol and the polymer/silicalite membrane. In spite of the larger sizes of butanol molecules, they permeate through the membrane preferentially over water molecules because of their favorable solubility in the membrane. The use of silicalite fillers in the membrane is to enhance the selective solubility of butanol in the membrane.

4. Conclusions

The pervaporative separation of *n*-butanol from dilute aqueous solutions (0.01–0.5 wt%) using silicalite-filled poly(dimethyl siloxane) membranes was studied. At a given temperature, an increase in feed butanol concentration was shown to increase water flux almost linearly, while the butanol flux increased in a concave fashion due to silicalite fillers that have a strong affinity to butanol molecules. Based on dual mode sorption, an empirical equation was proposed to represent the concentration dependence of butanol flux. With an increase in feed butanol concentration, the butanol concentration in the permeate initially increased and then gradually leveled off when the feed butanol concentration was high enough, and the leveling off in permeate butanol concentration started to occur at a lower butanol concentration when the temperature increased. The membrane selectivity as measured by the separation factor initially increased and then started to decrease when the butanol concentration was sufficiently high, reaching a maximum at a certain concentration. A variation in temperature would increase or decrease the membrane selectivity, depending on the butanol concentration. These results are especially important for potential application of the membrane for in situ butanol extraction from fermentation as the membrane performance at low concentrations (0.01–0.4 wt%) that are relevant to fermentation cannot be obtained simply by extrapolation of the literature data obtained at high butanol concentrations.

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