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Separation of 1-butanol/2,3-butanediol using ZSM-5 zeolite-filled polydimethylsiloxane membranes[☆]

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ABSTRACT

Mixed matrix membranes were prepared by incorporating ZSM-5 zeolite particles into polydimethylsiloxane. A uniform dispersion of the zeolite in the membrane was obtained. The membranes were characterized with scanning electron microscopy, and the effects of zeolite loading on membrane performance were evaluated. It was found that 80 wt.% ZSM-5 loading was optimal for selectivity. Further increase in the zeolite loading either improved the selectivity slightly or even lowered the membrane selectivity while the membrane permeability was consistently reduced. The improved separating performance of the filled membranes was attributed to the filler–polymer interactions, and the mass transfer contribution of surface flow through the zeolite pores. The advantage of the improved membrane performance was demonstrated in a simulated continuous operation enriching 2,3-butanediol in a mixture with 1-butanol from 5 to 99.5 wt.% as a retentate using both the filled and un-filled PDMS membranes. Results showed that the filled PDMS membrane improved the recovery of 2,3-butanediol significantly while achieving the same product purity.

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1. Introduction

As an important intermediate for rubber synthesis, 2,3-butanediol manufactured from biomass conversion is recently attracting attentions from both industry and research [1,2]. Research interests in this green process are mainly focused on finding efficient methods for recovering 2,3-butanediol from its fermentation broth. Recovery of 2,3-butanediol poses many challenges due to intrinsic difficulties such as its high affinity with water and high boiling point. Therefore no single separating process was found to be energy-efficient [3,4]. We recently proposed an integrated process for dealing with this challenging separation [3]. In this approach, 2,3-butanediol would first be recovered from the fermentation broth using 1-butanol as the extracting solvent. The extract contains 1-butanol, 2,3-butanediol, and water, and the extracted 2,3-butanediol was further enriched with a pervaporation process using polydimethylsiloxane (PDMS) membrane. The membrane showed preferential permeation for both water and 1-butanol. The product 2,3-butanediol was finally enriched as a retentate in the feed stream. The feasibility of this process had been demonstrated by a batch operation, where 2,3-butanediol with purity up to 99.9 wt.% was obtained. This work is a continuation of

our previous efforts, and was mainly undertaken for improving the separating performance of the PDMS membrane for better process efficiency.

Various hydrophobic zeolites had been used as filler in enhancing membrane selectivity for gaseous separation [5–7], and for organic species removal [8–10] from aqueous streams by pervaporation. For removing relatively larger organic species (e.g., higher alcohols), zeolites with larger molecular sized pores are needed. It is known that ZSM-5 is a zeolite with a medium pore size of 0.55 nm [11] and it was shown that such ZSM-5 zeolite, when filled in PDMS membrane, could considerably improve the recovery of ethanol from the fermentation broth based on hydrophobic interactions [12]. It is thus expected that the ZSM-5 zeolite filled in the PDMS membrane can enhance the removal of 1-butanol from the 1-butanol/2,3-butanediol binary mixture due to the highly hydrophilic nature of 2,3-butanediol.

The focus of the present work is to evaluate the effects of ZSM-5 zeolite loading on membrane permeation and separation. The tradeoff between permeability and selectivity of the filled PDMS membranes with various ZSM-5 loadings was investigated, and an optimal ZSM-5 loading in the membrane was obtained. Based on the available permeability data, a continuous operation was simulated, in which 2,3-butanediol was enriched from 5.0 to 99.5 wt.% using both the filled and un-filled PDMS membrane. It was shown that the ZSM-5 filled membrane gives much better recovery for 2,3-butanediol than the pure PDMS membrane. ZSM-5 filled PDMS membrane was a good choice for the separation.

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2. Experimental

2.1. Materials

Pentane (99.7 wt.%) was purchased from Fisher Scientific, 2,3-butanediol (98.0 wt.%) and 1-butanol (99.7 wt.%) were purchased from Sigma–Aldrich, Canada. The silicone elastomeric base (dimethyl siloxane) and the corresponding curing agent (dimethyl, methylhydrogen siloxane) were obtained from Dow Corning, USA. ZSM-5 zeolite powder (0.3 μm) was obtained from Zeolyst, USA. Pure water (18.1 M Ω cm) used in this work was produced by a Milli-Q[®] water purification system. The pre-purified helium (99.999%) carrier gas for the SRI 8610G Gas Chromatograph was supplied by BOC Gases, Canada.

2.2. Preparation of ZSM-5 filled PDMS membranes

Pre-dried ZSM-5 powder was added to the prepared 10 wt.% silicone elastomeric base solution in pentane, the mass of the ZSM-5 added varied from 20, 40, 80 to 120 wt.% of the silicone elastomeric base. A sonicator (150D, VWR International) was used for 30 min to help disperse the ZSM-5 particles in the dope. A portion of 27 ml suspension was used for making each membrane coupon in a 3-dish (85 mm in diameter) Teflon plate. After pentane evaporation, the membrane formed in the dish was transferred to an oven at 90 °C to perform crosslinking for 12 h. The thickness (ℓ) of the membrane can be directly measured using a micrometer [3], and the mean thickness is 278, 306, and 367 μm for membranes having 20, 40, and 80 wt.% ZSM-5 loadings with deviation less than 5 μm in all the cases. Membrane thickness can also be estimated using the mean density ($\bar{\rho}$) of the zeolite-filled membrane by

$$\ell = \frac{1}{\pi r^2} \times \frac{w_1 + w_2}{\bar{\rho}} \quad (1)$$

$$\bar{\rho} = \frac{(w_1 + w_2)}{(w_1/\rho_1) + (w_2/\rho_2)} \quad (2)$$

where w represents the mass of the membrane constituents (1 and 2) in a membrane coupon, and r is the diameter of the Teflon dish. Considering that the membrane thicknesses determined by these two methods were comparable, and one is justified in using either of the approaches.

2.3. Scanning electron microscopy characterization of the membranes

Prepared membrane samples were immersed in liquid nitrogen for 30 s, and cut with scissors into strips. The dried strips were sputter coated with gold, and observed using a JEOL 840A scanning electron microscope (SEM) on the cross-sectional face.

2.4. Evaluation of the membrane performance

The pervaporation system used for membrane performance testing was specified in our previous work [3], and the feed used is the binary mixtures of 1-butanol/2,3-butanediol containing small quantities of water. During the pervaporation operation the downstream pressure of the membrane was maintained at 2 mmHg (267 Pa) using a vacuum pump, and permeate was collected in a glass tube submerged in liquid nitrogen as the membrane permeation reached a steady state. The mass of permeate was measured with an electronic balance, and the composition was analyzed using a SRI 8610G gas chromatograph fitted with a HAYESEP D column, and the temperatures of the oven, injector, and detector were all set at 270 °C.

The permeability (P), and selectivity (α) of the membrane are defined as follows:

$$P_i = \frac{W \cdot Y_i}{A \cdot t} \cdot \frac{\ell}{C_i} \quad (3)$$

$$C_i = \frac{X_i}{\sum (X_k/\rho_k)} \quad (4)$$

$$\alpha_j^i = \frac{P_i}{P_j} \quad (5)$$

where W is the total mass of the permeate collected in time interval t , A is the effective membrane area for the separation, C is the concentration of the species in the feed, which is the driving force for mass transport with the permeate concentration in the downstream ignored, X and Y represent the mass fractions of species in the feed and the permeate, respectively, and ρ is the density of the feed components.

3. Results and discussion

3.1. Distribution of ZSM-5 particles in the PDMS membranes

The SEM images of cross-sections of three filled PDMS membranes with different ZSM-5 loadings (20, 40, and 80 wt.%) was shown in Fig. 1. It can be seen that with sonication treatment a uniform dispersion of ZSM-5 particles in the PDMS membrane matrix was obtained. This can be attributed to the hydrophobic nature of the ZSM-5 particles, their favorable association with the prior dispersed silicone elastomeric base, and also the high volatility of the solvent (pentane) used for the membrane preparation. Note that the solvent in the dope for making the membrane coupon could be evaporated within 7–10 min, and thus the viscosity of the suspension increased sharply with the rapid loss of solvent. This excluded the possibility of particles deposition during the membrane formation although the ZSM-5 zeolite particles used in the work is relatively bigger, with a particle size of 0.3 μm . According to the literature [13,14], it is very important to get the particles well dispersed in mixed matrix structure. In case particles agglomerate, the “channel flow” would dominate the mass transport across the agglomerates region, where the inter-particle free channel space is generally too large to be molecularly selective. As a result, the highly discriminative surface flow, which takes place in the pore structure of the filled zeolite, would lose their chance in improving the overall membrane selectivity, depending upon the fraction of the particles formed in the agglomerates. On the other hand, it also had been noticed that good dispersion of the particles in a membrane matrix does not necessarily guarantee that the surface flow can exercise its highly selective performance. The dispersed particles need meanwhile to have a good interfacial compatibility with the polymer matrix [14] to exclude the non-selective “leaky flow” occurring in the so-called “sieve-in-cage” structure. Fortunately, Fig. 1 shows that the dispersed zeolite particles in the membranes are intimately enclosed by the surrounding PDMS phase, and it appears that the zeolite has a good interface compatibility with the hydrophobic PDMS material. Due to this structural integrity, the mixed matrix membrane can be viewed as the membrane consisting of single composite materials, and the performance of the membrane can thus be engineered by changing loading of the filler in the membrane matrix as long as a good inter-phase compatibility can be ensured.

3.2. Hydrophobic nature of the ZSM-5 zeolite and transport resistance of the filled membranes

The permeabilities of the PDMS membranes for water, 1-butanol, and 2,3-butanediol were determined using the feed mixture of 1-butanol/2,3-butanediol with presence of some water

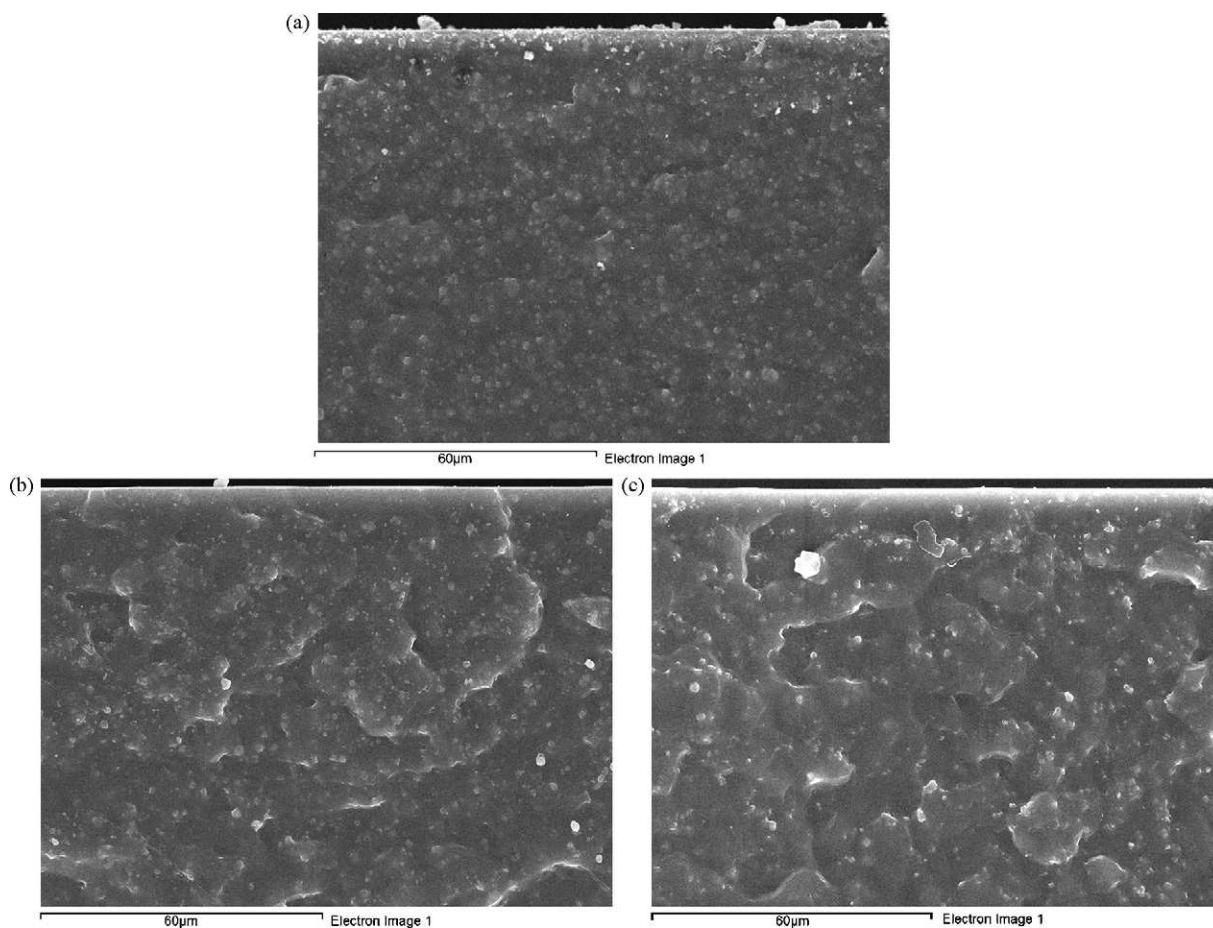


Fig. 1. SEM images of cross-sections of ZSM-5 zeolite-filled PDMS membranes, (a) 80 wt.%, (b) 40 wt.%, and (c) 20 wt.%.

(0.40–0.99 wt.%). The small quantity of water can serve as a probe molecule for testing the hydrophobicity of the ZSM-5 filled in the PDMS membrane. Fig. 2(a) indicates that among the three species, the un-filled PDMS membrane shows the highest permeability for water, followed by 1-butanol, and 2,3-butanediol. This characteristic permeation order had been interpreted [3] in terms of membrane/penetrants interactions and penetrants' kinetic diameters. For the ZSM-5 filled PDMS membrane, this permeation order was changed as shown in Fig. 2(b)–(d). The highest permeability of the filled membranes (20, 40, and 80 wt.%) is shifted to 1-butanol, which is known to be relatively hydrophobic among the three species. The hydrophobic nature of the filled ZSM-5 explains this change quite well. In order to clearly demonstrate the effect of fillers on the permeability of the three species, the permeability data (corresponding to 43 wt.% 1-butanol in the feed) in Fig. 2 is plotted against the mass percentage of ZSM-5 in Fig. 3, where the permeability of the un-filled PDMS membrane for the three species is also shown. It can be seen that due to the hydrophobicity of ZSM-5, the filled membranes showed decreased permeabilities for all the three species, including the relatively hydrophobic species, 1-butanol. This implies that for the separation of 1-butanol/2,3-butanediol system, improved selectivity of the PDMS membrane can only be obtained by sacrificing membrane permeability.

The ratio of permeabilities of the un-filled to a filled PDMS membrane is plotted against the mass percentage of ZSM-5 in the mixed matrix membrane as shown in Fig. 4. According to Eq. (6) below:

$$\frac{R^{\text{filled}}}{R^{\text{un-filled}}} = \frac{\ell/P}{\ell/P_0} = \frac{P_0}{P} \quad (6)$$

The ratio of permeabilities is equivalent to the ratio of transport resistances of the membranes with and without filler. Theoretically, as the mass percentage of ZSM-5 in the mixed matrix membrane approaches 0, the ratio of transport resistances should approach unity, and this trend is shown in Fig. 4. Compared with the more permeable species 1-butanol, the less permeable species 2,3-butanediol encounters much more permeation resistance due to the presence of the filler in the membrane, suggesting that the presence of ZSM-5 zeolite filler relatively improved the permeation of 1-butanol in the mixed matrix membranes. Fig. 4 also shows that in the feed of higher 1-butanol content (65 wt.%), the filler poses less permeation resistance for the transport of both species, and this probably result from the higher degree of membrane swelling due to the outstanding capability of 1-butanol in plasticizing PDMS membrane [3]. And in this situation, both the permeating species will automatically choose the pathway offering less transport resistance, namely, the much looser and as well swollen PDMS chain structure when diffusing through the mixed matrix membrane. Therefore, the membrane swelling should be minimized so that the filler particles can have better chance to influence the overall membrane performance with their own superior properties, and this is also the very reason zeolite is considered being used as filler in the membrane.

3.3. The effects of ZSM-5 loading on the membrane performance

The dependence of the membrane flux for 1-butanol, and 2,3-butanediol upon the content of 1-butanol in feed is illustrated in Fig. 5(a), where the ZSM-5 loading is listed as a parametric variable. As known previously, the zeolite-filled membranes

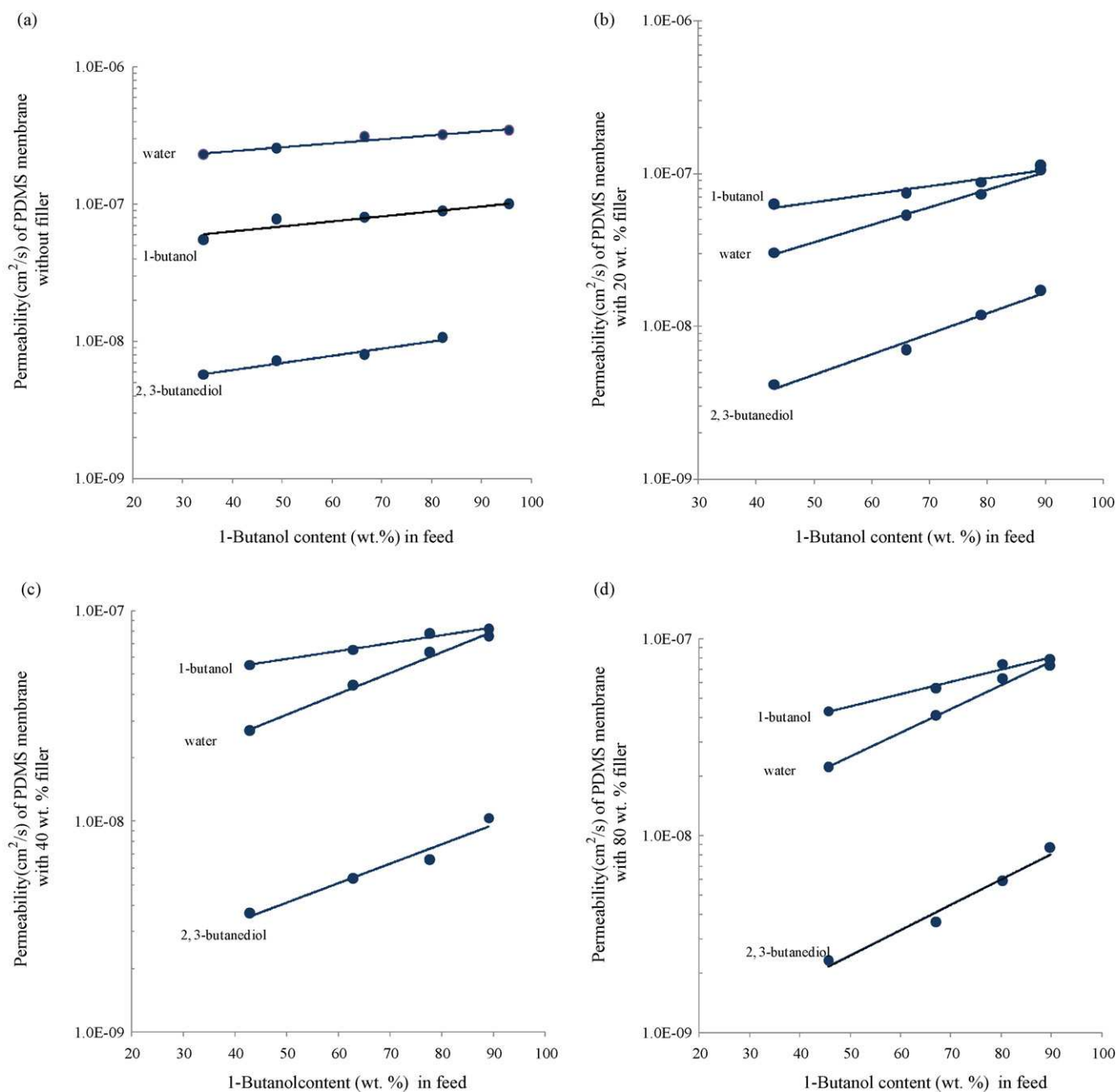


Fig. 2. Effects of ZSM-5 loading on the permeability of the PDMS membranes, (a) without ZSM-5, (b) 20 wt.%, (c) 40 wt.%, and (d) 80 wt.%.

display reduced permeability for all the permeating species, accordingly, the decreased membrane fluxes were observed for both 1-butanol and 2,3-butanediol with the increased ZSM-5 loading in the membrane. Fig. 5(a) indicates that the exponential increase in membrane flux for 1-butanol gets less remarkable as ZSM-5 loading in the PDMS membrane increases, implying that the membrane swelling was suppressed with more filler incorporated into the PDMS matrix. Two factors are responsible for this reduced membrane swelling. Firstly, the well-defined zeolite structure is usually not susceptible to the presence of interacting molecules therefore essentially no swelling occurs to the zeolite regions of the filled membrane [15]. Secondly, the PDMS polymer chains near the zeolite regions may be restrained by the interfacial interactions [16,17]. The filler particles therefore act as the physical cross-linker stations for the surrounding polymer chains.

The selectivity of the filled membrane was illustrated in Fig. 5(b). Like the typical response of polymeric membranes for pervaporative separations [18–21], the filled membranes displayed higher selectivity for the more permeable species as its content in feed is lower. This observation suggests that swelling occurred in the continuous phase (PDMS) of the filled membrane though it was effectively lowered by the presence of filler, which as discussed previously enhanced the membrane's capability in anti-swelling. It is difficult to evaluate this part of contribution since the selective surface flow through the zeolite pores [22–24] also played a part in enhanced membrane selectivity. Fig. 5(b) shows that membrane with 80 wt.% ZSM-5 loading gives the highest selectivity, followed by 40, and 20 wt.%. We also tried even higher ZSM-5 loading (e.g., 120 wt.%) in the PDMS membrane, anticipating for even better improvement. However the experimental results indicated that it was practically difficult to obtain thin yet defect-free PDMS

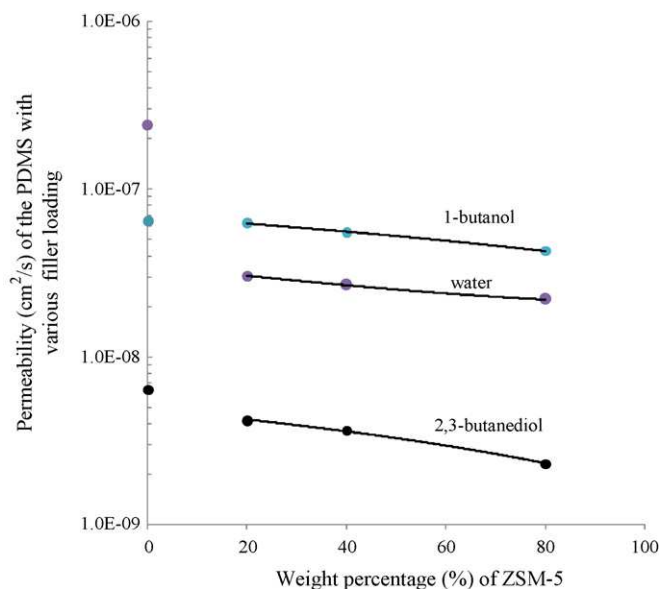


Fig. 3. Dependence of membrane permeability on the mass percentage of ZSM-5 in the mixed matrix membrane at 50 °C, and the 1-butanol content in feed is 43 wt.%.

membranes even though some higher loading membranes may occasionally show better selectivity. It suggested that the optimal ZSM-5 loading in the PDMS membrane is around 80 wt.% of the elastomeric component in the mixed matrix membrane.

3.4. The tradeoff between membrane permeability and selectivity

The tradeoff between permeability and selectivity of the filled and un-filled PDMS membranes were described in Fig. 6. The four data points in each series represent the data-pair of a membrane tested in four feeds of different 1-butanol contents. And all the tested membranes agree on the fact that they show lower selectivity and higher 1-butanol permeability when tested in feeds having higher 1-butanol contents. Compared with the un-filled PDMS membrane, Fig. 6 shows that the selectivity of the filled membranes (e.g., 80 wt.% loading) is almost doubled while the membrane permeability for 1-butanol is nearly reduced by half. This is the typical tradeoff of the mixed matrix membrane consisting of a highly permeable rubbery polymer and zeolite powders. Unlike the mixed matrix membrane based on the tight glassy polymer and zeolite which shows relatively good permeability, it is generally impossible for this type of filled membranes (rubbery polymer plus relatively less permeable zeolite) to demonstrate simultaneously both the enhanced permeability and selectivity.

This tradeoff between permeability and selectivity is valuable for membrane separation. Since for separation, the selectivity of a membrane is of foremost importance, and the productivity of a membrane can, in the long run, always be made satisfactory through the advance of technology for fabricating composite membranes with a thin or ultrathin film. With the availability of even fine ZSM-5 powders (e.g., ZSM-5 nanoparticles), the lower limit on the thickness of the thin film supported on a substrate can be brought down further. So optimistically speaking, the tradeoff-resulting lower permeability of the membrane should not be a problem.

On the other hand, for this particular separation, where 2,3-butanediol is to be enriched as the product in the retentate stream, the reduced membrane capability for 1-butanol removal can yet be compensated by the larger mass transport driving force for 1-butanol as 2,3-butanediol content is lower in the feed stream. As 2,3-butanediol content in the feed is getting higher, the loss of

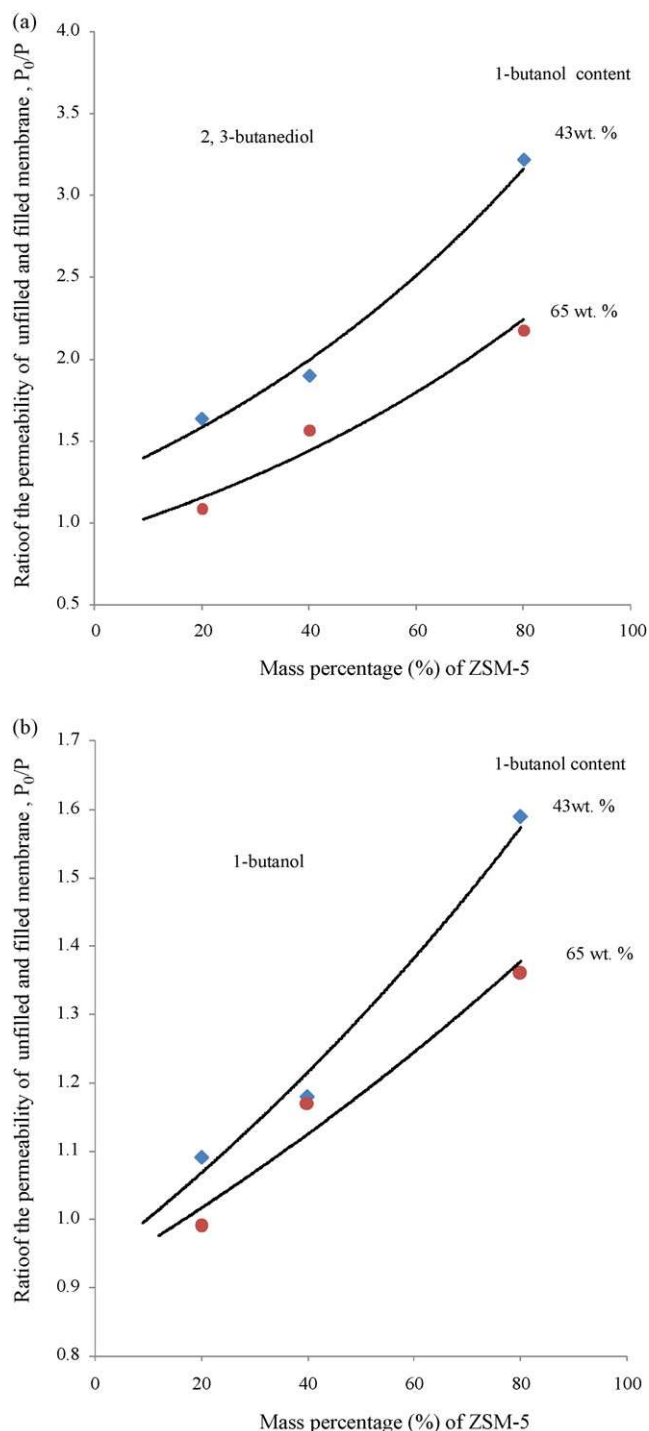


Fig. 4. Dependence of mass transport resistance on the mass percentage of ZSM-5 in the membrane matrix, (a) for 2,3-butanediol, and (b) for 1-butanol.

2,3-butanediol can thus be effectively inhibited by the increased membrane selectivity. An increase of membrane selectivity by a factor of 2 can be significant for this challenging organic–organic mixture separation, and the details on how the tradeoff works for improved 2,3-butanediol recovery has been revealed in the following text with a simulation.

3.5. The effects of operating temperature

The mixed matrix membranes also displayed the typical Arrhenius relation between the membrane flux and reciprocal tem-

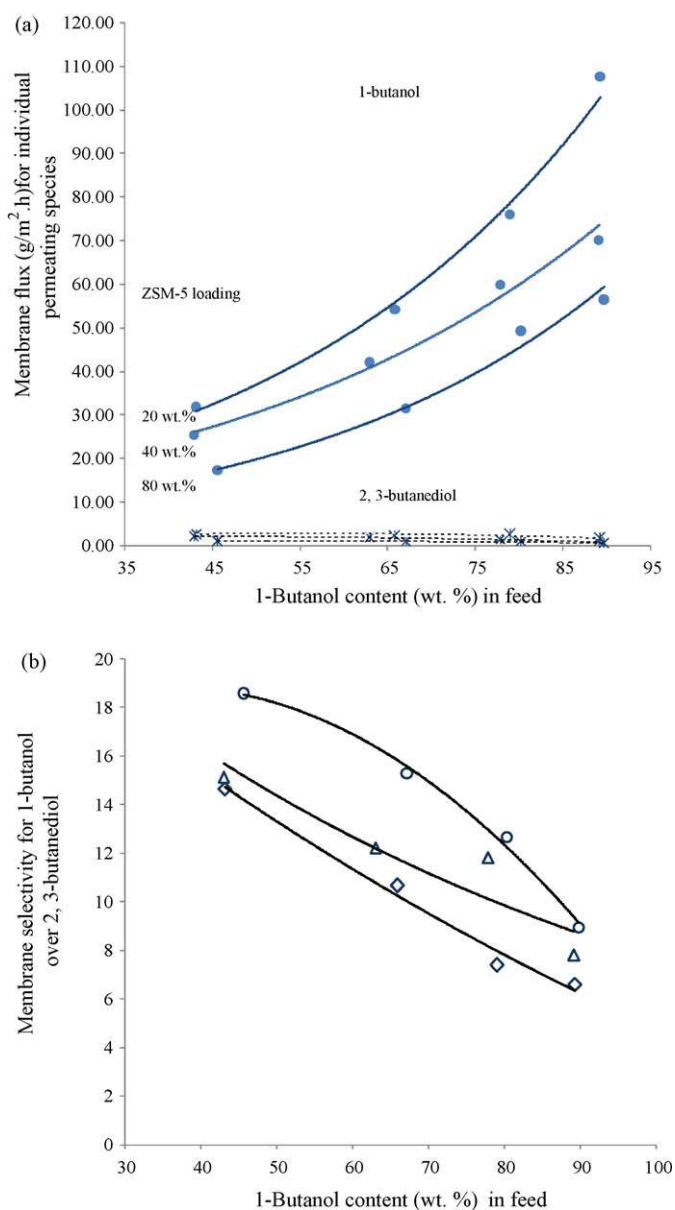


Fig. 5. Effects of ZSM-5 loading on membrane performance, (a) the membrane flux and (b) the membrane selectivity. For (b) (○) 80 wt.% ZSM-5 loading, (△) 40 wt.% ZSM-5 loading, and (◇) 20 wt.% ZSM-5 loading.

perature as expressed in Eq. (7) and shown in Fig. 7(a).

$$\ln Q_i = -\frac{(Ea)_i}{RT} + \ln \frac{(P_0)_i}{\ell} + \ln \Delta C_i \quad (7)$$

where Q is the membrane flux, ΔC is the trans-membrane concentration difference as the driving force, which is usually a very weak function of the feed temperature [3]. According to Fig. 7(a), a permeating species, i.e., 1-butanol needs to overcome a larger permeation activation energy (Ea) (27.1, 31.2, and 43.4 kJ/mol for 20, 40, and 80 wt.% ZSM-5 loading membrane, respectively) as it permeates in the membrane with higher filler contents. This in part results from the fact that the permeation activation energy of the species in the zeolite pores is much higher than that in the PDMS polymer, which is known to be one of the few flexible polymers possessing a very high fractional free volume [15,25]. The robust dependence of the permeation activation energy of the filled membrane on the loading of filler implies that the filler dispersed in the membrane matrix did involve in, and contribute to the separation.

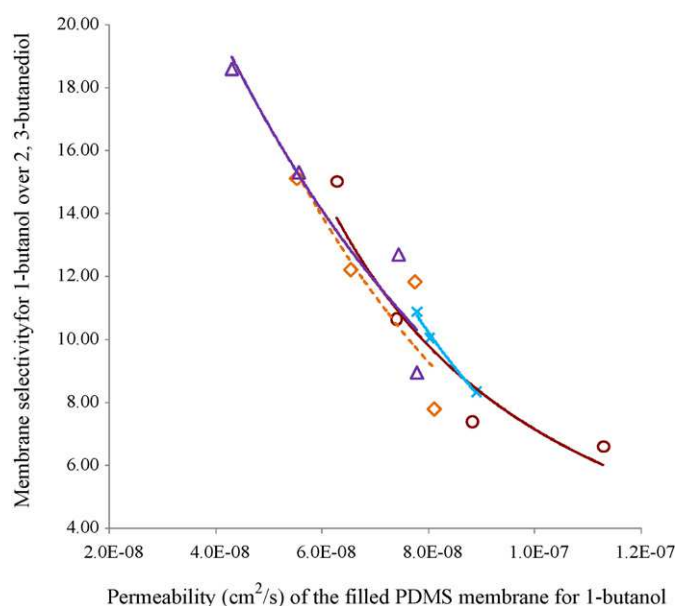


Fig. 6. Tradeoff between membrane permeability and selectivity, (×) without filler, (○) 20 wt.% ZSM-5 loading, and (◇) 40 wt.% ZSM-5 loading, and (△) 80 wt.% ZSM-5 loading, tested in feeds of different 1-butanol contents.

Accordingly, the temperature-dependence of membrane selectivity also agrees with the Arrhenius relation as shown in Eq. (8),

$$\ln \frac{P_i}{P_j} = \frac{(Ea)_j - (Ea)_i}{RT} + \ln \frac{(P_0)_i}{(P_0)_j} \quad (8)$$

Generally speaking, the less permeable species has higher permeation activation energy than the more permeable one, and this is true for both the polymeric and zeolite membranes [26–28]. Similar to the single material membrane, the zeolite-filled PDMS membrane demonstrated a decreased selectivity at a higher temperature. And it seems that the mixed matrix membrane behaves more like the zeolite membrane as the zeolite loading in the membrane increases, and its selectivity decreases more sharply as the feed temperature increases.

3.6. A case for the continuous operation

In order to demonstrate the advantage of the filled PDMS membrane (with 80 wt.% filler) in recovering 2,3-butanediol over the PDMS membrane, a continuous operation for the 1-butanol/2,3-butanediol separation was simulated. The parameters involved in the simulation are listed in Table 1, where the permeability is the regressed result of the data in Fig. 2, and a typical thin film thickness of 5 μm was selected. The initial feed flow rate of 360 kg/h with the initial mass fraction of 2,3-butanediol of 0.05, and an operating temperature of 50 °C were considered.

By ensuring a high enough tangential feed velocity, the diffusion layer resistance in the feed side can be reasonably ignored. There-

Table 1
Parameters used for the continuous operation simulation.

Membrane	Thickness ^c (μm)	Permeability ^b (cm^2/s)
PDMS	5	p1-butanol = $4.5 \times 10^{-8} \text{ EXP}(0.84X)^a$ p2, 3-butanediol = $3.8 \times 10^{-9} \text{ EXP}(1.2X)$
Filled PDMS (80 wt. % ZSM-5)	5	p1-butanol = $2.2 \times 10^{-8} \text{ EXP}(1.4X)$ p2, 3-butanediol = $5.6 \times 10^{-10} \text{ EXP}(3.0X)$

^a X in the function represents the mass fraction of 1-butanol in the feed.

^b Permeability values refer to those at 50 °C.

^c Assumed thickness of the thin film of the thin-film-composite membrane.

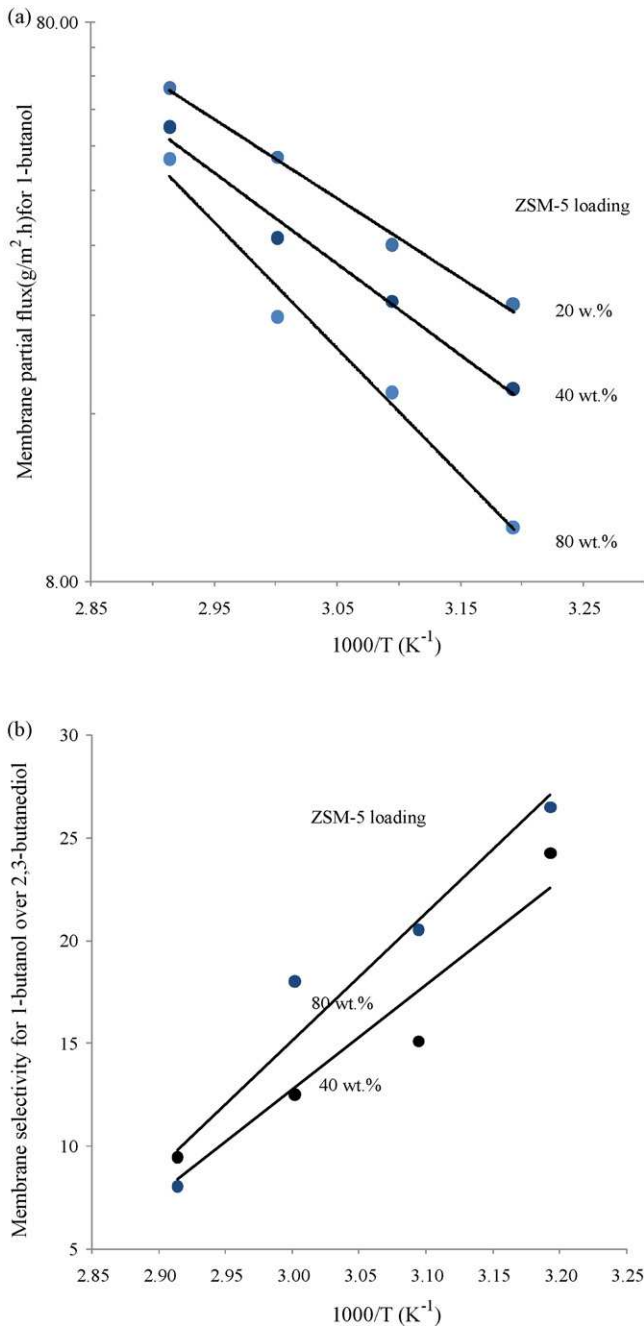


Fig. 7. Temperature-dependence of the flux (a) and selectivity (b) of the ZSM-5 zeolite-filled PDMS membrane. The feed composition is 56 wt.% 2,3-butanediol, and 44 wt.% 1-butanol.

fore, the difference equation as shown in Eq. (9) can be used for implementing the numerical simulation,

$$\frac{F_i^{(n+1)} - F_i^{(n)}}{A^{(n)}} = -\frac{P_i(X^{(n)})}{\ell} \cdot \frac{F_i^{(n)}}{\sum_{i=1}^2 (F_i^{(n)}/\rho_i)} \quad (9)$$

$$Y_i^{(n+1)} = \frac{P_i(X^{(n)}) \cdot F_i^{(n)}}{\sum_{i=1}^2 P_i(X^{(n)}) \cdot F_i^{(n)}} \quad (10)$$

$$X^{(n)} = \frac{F_{1\text{-butanol}}^{(n)}}{F_{1\text{-butanol}}^{(n)} + F_{2,3\text{-butanediol}}^{(n)}} \quad (11)$$

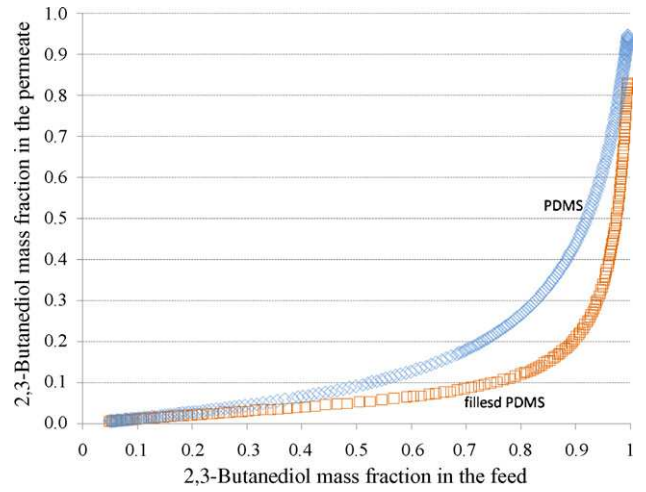


Fig. 8. Plot of mass fraction of 2,3-butanediol in feed versus that in permeate in a continuous pervaporation operation for enriching 2,3-butanediol at 50 °C.

$$R = \frac{F_{2,3\text{-butanediol}}^{(N)}}{F_{2,3\text{-butanediol}}^{(0)}} \quad (12)$$

where F is the partial flow rate of species, $X^{(n)}$ is the mass fraction of 1-butanol in each of the membrane sections divided for simulation, the subscript i ($i = 1, 2$) stands for the species in the feed mixtures, the superscript n ($n = 0, 1, 2, \dots, N$) represents the sequential number of the membrane sections (N , in total), and $n = 0$, refers to the initial conditions, P is the permeability, A is the membrane area in each of the divided sections, and Y in Eq. (10) is a mass fraction of a species in the permeate. By running iterations based on Eqs. (9)–(11), the flow rate and mass fraction of the species in both permeate and feed sides can be determined in each of the divided membrane sections, and the final recovery (R) of 2,3-butanediol can be obtained by using Eq. (12).

The dependence of mass fraction of 2,3-butanediol in permeate on that of feed is depicted in Fig. 8. At the initial stage of concentration, where the mass fraction of 2,3-butanediol in the feed is below 0.2, no significant difference was observed between the two membranes. The filled PDMS membrane started showing a big difference as the feed mass fraction of 2,3-butanediol is over 0.6, particularly in the range of 0.7–0.95, the mass fraction of 2,3-butanediol in the permeate of the un-filled PDMS membrane is more than two times

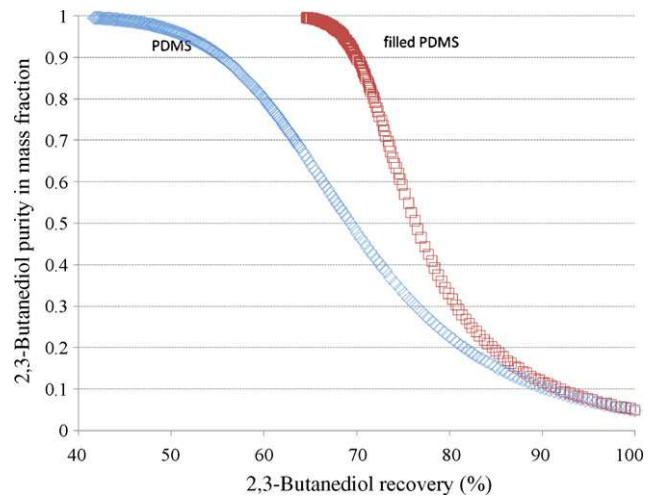


Fig. 9. Interdependence between 2,3-butanediol recovery and its purity in a continuous pervaporation operation for enriching 2,3-butanediol at 50 °C.

higher than that of the filled PDMS membrane. This high content of the product in permeate coupled with its high flux due to the larger mass transport driving force constituted a big loss of 2,3-butanediol. Although, in real operation permeates of high contents of 2,3-butanediol can be recycled, the energy efficiency of the pervaporation process would be lowered for this repeated processing, suggesting the importance of the membrane selectivity.

The interdependence of 2,3-butanediol product purity and its recovery is illustrated in Fig. 9. Naturally, the high purity of 2,3-butanediol can only be obtained by sacrificing its recovery. Again, the filled and un-filled PDMS membranes made essentially no difference in recovery when the purity of 2,3-butanediol is below 0.2 (mass fraction). This can be attributed to the fact that permeation flux of both the membranes for 2,3-butanediol are so low that no significant difference could be demonstrated. However, as the purity of 2,3-butanediol becomes higher than 0.4, the mass transport of 2,3-butanediol through the membranes is getting increasingly significant, and it can be seen that the better separating performance of the filled PDMS membrane starts taking effect. For the same product purity, the filled PDMS membrane gives a higher product recovery. The difference is particularly remarkable as the purity of 2,3-butanediol is higher. For example at the purity of commercial 2,3-butanediol (98.0 wt.%), the recoveries of the filled and un-filled PDMS membranes are at 66.8, and 47.4%, respectively, which represents a rise of 19.4%. As indicated in Fig. 8, this improvement would be even better when the purity of 2,3-butanediol required is even higher, e.g., for the production of ultra-pure product: 99.9 wt.%, an increase of 25.8% could be achieved. Indicating that better selectivity of the ZSM-5 filled membrane really helps improve the process efficiency for recovering 2,3-butanediol.

4. Conclusions

It was shown that the ZSM-5 particles could be uniformly dispersed in the PDMS membrane and incorporation of ZSM-5 particles into the PDMS membrane improved the membrane selectivity for 1-butanol, but decreased membrane permeability for all the species. It was found that the optimal ZSM-5 loading in the membrane matrix is around 80 wt.% of the silicone rubber and above this limit, the membrane selectivity tended to drop down. It appears that higher loading of ZSM-5 particles in the membrane matrix could induce defects in the membrane. A simulated continuous operation for enriching 2,3-butanediol from a binary mixture 1-butanol/2,3-butanediol showed that the 80 wt.% ZSM-5 zeolite-filled PDMS membrane can increase the recovery of 2,3-butanediol from 47.4 to 62.8% for producing 98.0 wt.% 2,3-butanediol. And this improvement can be even better when the required product purity is higher.

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