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PVDF/Hyflon membrane applied to butanol dehydration
254x190mm (72 x 72 DPI)

Hydrophobic Hyflon[®] AD/PVDF membranes for butanol dehydration via pervaporation

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Abstract

Novel hydrophobic Hyflon[®] AD /PVDF membranes were developed and investigated for n-butanol dehydration via pervaporation. The coating protocols for thin defect-free Hyflon[®] AD selective layer on the PVDF support was optimized. Water and n-butanol transport was measured, analyzing the effect of operating conditions. The water flux through the newly developed membranes was higher than 150 g/m².h with selectivity for water higher than 99 wt %. The focus was on the use of Hyflon[®] AD as the selective layer for n-butanol dehydration. The membrane application can be extended to other solvents, supporting an effective and simple method for dehydration with hydrophobic membranes.

Keywords: Pervaporation, membrane, Hyflon[®] AD, butanol

1. Introduction

Perfluorinated polymers have been attractive to applications for which the most common polymers are not suitable due to their higher hydrophobic character and higher resistance towards most common solvents, acids, alkalis and strong oxidizing agents¹. While crystalline fluorinated Teflon[®] is opaque, amorphous polymers such as Teflon HF[®] and Cytop[®] are highly transparent to light from far UV to near infrared waves² increasing their potential for optical applications³, semiconductor industry⁴, and photocatalysis⁸. Hyflon[®] AD, Cytop[®] and Teflon[®] HF with high hydrophobicity and high free volume have attracted interest for membranes-based gas separation^{2,4,5,6} and contractor devices⁷. Perfluorinated/sulfonated polymers such as Hyflon[®] Ion and Nafion[®] are well explored for fuel cell⁸. Hyflon[®] AD was recently employed as a protective layer on a hydrophilic membrane for ethanol dehydration to enhance the membrane selectivity and control water-induced plasticization by preventing the hydrophilic membrane from the direct contact with the feed^{9,10}.

Other than Hyflon[®] AD, the perfluorinated polymer perfluoro-2,2-dimethyl-1,1,3-dioxole copolymerized with tetrafluoroethylene (PDD-TFE) has been used in pervaporation for separating different pharmaceutical solvents¹¹. Bhattacharyya et al.¹² were the first to employ PDD-TFE for water/solvent separation by pervaporation. They also proposed separation mechanism of water from ethanol, isopropanol, ethyl acetate and ethanol ethyl acetate. Tang and Sirkar¹³ found that the performance of PDD-TFE surpassed that of NaA zeolite for separating water from different aprotic solvents, such as dimethylformamide (DMF), dimethylsulfoxide (DMSO) and dimethylacetamide (DMAc). However, their large membrane thickness of 25µm-100µm may limit their application potential due to the high cost of perfluorinated polymers.

Butanol is considered as an alternative fuel for gasoline^{14,15}, diesel and kerosene¹⁶, which can be produced from the fermentation process^{14,15,17}. It is also used by the manufacture of urea resin, cleaning fluids, reaction with acids to form esters, etc¹⁸. Presence of water in such media is highly expected and hence it is essential to explore effective and energy-saving techniques to remove water from butanol. Membrane-based pervaporation has emerged as a potential technology for such separation because of its energy efficiency, small footprint, low maintenance cost, simple operation and ease of control¹⁹. Selection of appropriate membrane materials in pervaporation process can control the efficiency of the process²⁰.

For n-butanol dehydration, both ceramic and polymeric membranes have been studied²¹. Hybrid silica membranes with organic links were investigated for dehydration of 5/95% water/n-butanol solution. It displayed a high water flux and high permeate water content of about 98 wt% for a long test duration of 1000 days^{22,23}. By changing the operating temperature to 95°C, the permeate water content increased to 99.5 wt%²⁴. Paradis et al.²⁵ concluded that combination of bridging and terminating organic compounds increased the hydrophobicity leading to the decrease in permeate water content from ~99wt% to ~40wt%²⁵. On the other hand, polymeric membranes have been studied by Chung et al for butanol dehydration^{18,26-30}. They employed the commercial hydrophilic membrane Pervap®2510 and achieved the permeate water content of around 93wt% at 60°C¹⁸. Polyether block amide (PEBA), polydimethylsiloxane (PDMS), and polyurethane (polyether based, PUR) have been used for the dehydration of the 1/99 wt% water/n-butanol solution at 50°C and achieved the water fluxes of 222, 44, 78 g/m².h and the relatively low enrichment factors of 20, 37, 9, respectively³¹.

In this study, our aim is to (1) explore hydrophobic Hyflon® AD coating on poly (vinylidene fluoride) (PVDF) membranes for dehydration; (2) optimize the coating protocols for

thin defect-free Hyflon[®] AD selective layer on the PVDF support; and (3) analyze the effects of the pervaporation operating conditions. By using a thin coating of Hyflon[®] AD on the lower-cost PVDF support, the composite membrane would be feasible for industrial application.

2. Experimental

2.1. Materials

Scheme 1. Chemical structure of Hyflon[®] AD60X.

Polyvinylidene fluoride (PVDF - HSV900) was kindly provided from Kynar[®]. The polyester non-woven support fabric (05TH-100) was purchased from Hirose. Hyflon[®] AD60X with an average molecular weight of 500,000 g/mol, density of 1.93g/cm³, and glass transition temperature of 125°C was provided by Solvay Plastics. Its chemical structure is shown in Scheme 1. N-methyl pyrrolidone (NMP) from Sigma-Aldrich was used as solvent for PVDF, while Galden[®] HT200 from Solvay-Solexis was employed as the solvent for Hyflon[®] AD. N-butanol (≥ 99.7% purity) was purchased from Sigma-Aldrich and Milli Q water was used for all experiments, generated using a Millipore unit.

2.2. Membrane preparation

The support was prepared by casting 10 wt% of PVDF in NMP on polyester non-woven support followed by phase inversion in water. Further, an ultra-thin layer of Hyflon[®] AD on the top support surface was obtained by dip coating, using 0.5, 2 and 4 wt % solutions. The layer was dried at room temperature overnight followed by vacuum drying at 130°C overnight.

2.3. Pervaporation experiment

A lab pervaporation system was built with effective membrane area of 3.14 cm². Downstream pressure was kept < 0.1 mbar by applying a vacuum pump. Permeate was collected in a cold trap, immersed in liquid nitrogen containing Dewar flask to condense its vapor to the liquid phase.

2.4. Characterizations

The membrane morphology was observed by scanning electron microscope (SEM) using a FEI Quanta 200 Field Emission Scanning Electron Microscope (FE-SEM).

The support pore size and the pore size distribution were estimated by using a Porolux[™] 1000 IB-FT instrument from Germany at the pressure range of 0–34.5 bar and using perfluoroether (Porofil) with the surface tension of 16 dynes cm⁻¹ as the pore filler. The hydrophobicity of the support and membrane surfaces was determined by measuring their contact angles using a KSV CAM200 equipment at ambient temperature. Sorption measurements for the support and membranes in pure water, pure n-butanol and 5wt% water/n-butanol solution were carried out at room temperature. The pre-dried support or membrane strips were weighed before immersed into sorption solutions, which were kept in a closed vessel for 30 days.

The swollen strips were then taken out, blotted with tissue paper and then weighed using the four digits balance (AND GH-202, Japan). The degree of sorption was calculated by using following equation:

$$DS = \frac{W_e - W_o}{W_o} \quad (1)$$

Where W_o and W_e refer to the weights of the strips before and after immersed in solution.

2.5. Membrane performance

The membrane performance was evaluated through flux and separation factor. Flux is the rate of mass transfer through the membrane in a unit of time as following equation:

$$J = \frac{W}{A.t} \quad (2)$$

Where W is the weight of permeate collected in g, A is the membrane surface area in m^2 , and t is the time in h.

Separation factor provides information on the quality of the permeate. It can be calculate from the following equation:

$$\text{Separation factor } \alpha = \frac{(y_1/y_2)}{(x_1/x_2)} \quad (3)$$

Where y_1 and y_2 are the water concentrations in permeate and feed respectively, x_1 and x_2 is the n-butanol concentrations in the permeate and in the feed, respectively. They are determined by using a chromatography (GC) instrument (Agilent 7890A) connected to a thermal conductivity detector (TCD) with a HP – INNOWAX column of 60 m in length, 0.320 mm in diameter.

To understand the membrane intrinsic properties, permeance (P_i/l) and selectivity (β) were analyzed^{32,33}. The permeance can be calculated from the following equation:

$$\frac{P_i}{l} = \frac{J}{x_i \gamma_i P_i^{Sat} - y_i P^p} \quad (4)$$

where $x_i \gamma_i p_i^{\text{sat}}$ is the feed fugacity.

Fugacity is the driving force for the component i transferring through the membrane, when the permeate pressure P^p is negligible. The fugacity is independent of the membrane properties. The saturated vapor pressure (p^{sat}) can be calculated from the Antoine equation:

$$\log P^{\text{sat}} = A - \frac{B}{C+T} \tag{5}$$

where A , B and C can be obtained from Lange’s handbook of chemistry³⁴. The values are listed in Table 1.

Table 1. A , B , C parameters of Antoine equation for water and n-butanol.

	A	B	C
Water	16.4	3886	230
n-Butanol	15.3	3212	183

The activity coefficient γ_i can be determined by applying the Wilson equation:

$$\ln \gamma_i = -\ln(x_i + A_{ij} x_j) + x_j \left(\frac{A_{ij}}{x_i + A_{ij} x_j} - \frac{A_{ji}}{A_{ji} x_i + x_j} \right) \tag{6}$$

Hence x_i and x_j are the mole fractions of water and butanol, respectively, while A_{ij} , A_{ji} can be determined by using the Aspen plus V.8.6 software. , The values $A_{ij} = 1.1$ and $A_{ji} = 22.7$ were obtained in this way. The selectivity of water over butanol is defined as the ratio of their respective permeance:

$$\beta = \frac{P_i}{P_j} \tag{7}$$

3. Results and discussion

3.1. Membrane characterizations:

3.1.1. Pore size distribution

Figure 1 shows the SEM image of the support surface and its pore size distribution. It can be seen that the support has relatively large pores with an average diameter of 111 nm, which was measured by Capillary Flow Porometry. This method detects the active permeating pores. SEM gives a good estimation of pore size and distribution, however depicts only the surface and not necessarily distinguishes impermeable closed pores from continuous open pores. A relative low concentration of PVDF in NMP as casting solution and water as a non-solvent led to supports with large pores. The high porosity reduces the resistance for vapor transport under pervaporation operation. In addition, the pore size distribution is sharp, convenient for a homogeneous Hyflon[®] AD coating layer on the support surface.

Figure 1. Pore size distribution of PVDF support measured using Porolux, Inset: SEM image of the PVDF support surface.

3.1.2. Support and composite membrane morphologies

Figure 2 shows the SEM images of the PVDF support coated with Hyflon[®] AD under different procedures. The surface of the membrane prepared with 2 wt % coating solution was not fully covered by Hyflon[®] AD with large open pores still evident. The surfaces of the membranes coated twice with a 2 wt % solution or with a single coating using 4 wt % solution are dense and no obvious pores can be observed anymore. The latter is smoother and therefore the subsequent results were obtained with coatings using 4 wt % Hyflon[®] AD solution.

Figure 2. SEM surface images of porous PVDF support coated with (a) 2 wt%, (b) 2 wt% (twice) and (c) 4 wt% Hyflon[®] AD solutions.

3.1.3. Contact angle measurement

The PVDF support has a contact angle of $91.7^{\circ} \pm 0.8^{\circ}$, which indicates an inherently hydrophobic nature. After coating with Hyflon[®] AD, the hydrophobicity of the resultant membrane increased, reflected by an increment in contact angle to $119.6^{\circ} \pm 0.8^{\circ}$.

3.1.4. Sorption

The sorption behavior reflects the affinity between water and n-butanol and the membrane material. The sorption data in Figure 3 show that both the support and the coated membrane have much higher affinity towards n-butanol than water. The n-butanol sorption degrees are 44 % and 34 % for the support and the coated membrane, respectively, while those for water sorption are negligible. This result is consistent with the contact angle data, both of which confirm the hydrophobicity of PVDF and Hyflon[®] AD. Compared to the support, the sorption of the coated

membranes is lower. This should be more a consequence of the higher support porosity than of thermodynamic interaction or solubility.

Figure 3. Sorption of PVDF support and membrane coated with 4 wt% Hyflon[®] AD during 4 min.

3.1.5. Thermal stability

The thermal stability of the support and coated membrane was determined by TGA analysis. The results in Figure 4 show that the polyester non-woven, PVDF support and Hyflon[®] AD coated membrane have high degradation temperatures of around 340°C. Although this indicated high chemical stability, the operation at high temperatures is limited by the PVDF melting temperature, which is around 177°C.

Figure 4. Thermogravimetric analysis

3.1.6. Pure water and n-butanol properties

Besides the membrane properties, the thermodynamics of the penetrating molecules significantly affect their transport³⁵. Figure 5 demonstrates the diagram of the vapor liquid equilibrium for water/n-butanol mixtures at 21°C by using the Aspen NRTL-RK method. It shows broad positive deviation from the Raoult's law at low water compositions. When the water concentration in n-butanol is lower than 18 wt %, the slope of the curve is sharper, which implies higher water vapor fractions in the vapor mixture and hence higher separation efficiency towards water. From 18 to 76 wt % of water in n-butanol, the vapor pressure is constant which implies a two-phase system, and hence it is not necessary to conduct pervaporation on this region.

Figure 5. The diagram of the vapor liquid equilibrium for water/n-butanol mixtures at 21°C.

Table 2 lists the activity coefficient, saturated vapor pressure, fugacity and flux of water and n-butanol at 21°C. These values of water are much higher than those of n-butanol, which indicates higher driving force for water permeation. When the temperature increases, the increment in saturated vapor pressure of water is much higher (Figure 6), which suggests that high temperatures may be beneficial for the separation.

Table 2. Characteristics of pure components

	Water	n-Butanol
Activity coefficient	0.475	0.042
Fugacity	1.188	0.012
Saturated vapor pressure	2.5	0.26
Flux ($\text{g m}^{-2} \text{h}^{-1}$)	710 ± 157	222 ± 69

Figure 6. Saturated vapor pressure of water and n-butanol in different temperatures.

3.2. Effect of different coating procedures on the membrane performance

Different coating protocols with various coating solution concentrations and coating time have been tested, starting from 0.5 wt% Hyflon[®] AD for 1 min. The resultant membrane did not have

an adequately dense layer of Hyflon[®] AD, and consequently the pervaporation process was not satisfactory, with the feed solution leaking to the permeate side. Although the pervaporation process was feasible with a membrane coated with 2 wt% solution for 4 min, it has insufficient mechanical stability under vacuum. The membrane can resist the vacuum only for 30-40 min with high flux but very low separation factor as shown in Table 3. This result is consistent with its SEM image, which displayed the support partially covered by Hyflon[®] AD. Double coating with the same condition decreases the flux significantly and did not enhance the separation factor. Although double coating is able to fill the large pores as its SEM image verified, it may not efficiently seal minor defects while increasing transport resistance due to the formation of the thicker coating layer. Increasing the coating concentration to 4 wt % was the best option, which enhances the separation factor to more than 1550 with a reasonably high flux of 156 g/m².h. Hence coating with 4 wt % concentration was used for further investigation with respect to coating time.

These results indicate the dehydration capability of the Hyflon[®] AD /PVDF membranes although both materials are hydrophobic as confirmed by contact angle measurement and sorption data.

The separation efficiency is attributed to the occurrence of at least two simultaneous conditions, a high driving force for water permeation (as discussed in the section 3.1.6) and a low, but not negligible, water selectivity. As well-known, the transport mechanism of pervaporation is governed by the solution-diffusion model, where the performance is determined by the affinity of membrane materials towards the permeate molecules (solubility) and their diffusion across the membrane (diffusivity). Although the Hyflon[®] AD /PVDF membranes have higher affinity towards n-butanol, Hyflon[®] AD is known for its high free volume. The diffusivity is critical for the selectivity in this case because of high driving force of water comparing to n-butanol. Water

has also much smaller kinetic diameter than n-butanol (2.6 vs. 5.1 Å)^{36, 37}. Dehydration with the high free volume hydrophobic membrane with small degree of swelling with water is then very effective.

Table 3. Pervaporation performance for membranes coated by different procedures

Coating solution concentration (wt %)	Time (min)	Total flux (g m ⁻² h ⁻¹)	Water in the permeate (wt %)	Separation factor
2	4	12758 ± 146	27 ± 5	7
2	4 (twice)	500 ± 64	30 ± 7	8
4	2	149 ± 2	82 ± 1	87
4	4	156 ± 3	98.8 ± 0.3	1564
4	6	156 ± 17	95 ± 4	361
Feed composition: 5 (wt):95 (wt) water:n-butanol				

3.3. Effect of different coating time on membrane performance

In order to further optimize the coating procedure, different coating times, varying from 2 to 6 min, have been tested. Figure 5 shows that the total flux is similar for all the membranes coated with three different coating times, but the water permeate concentration increases from 80 wt % to 99 wt %. These results imply that no much change in the performance occurs after 4 min coating with 4 wt %, which was then adopted for all further membrane preparations.

3.4. Effect of feed water concentration on pervaporation performance

Different feed water concentrations varying from 5 wt % to 17.5 wt % have been investigated. The maximum solubility of water in n-butanol is about 20.1 wt % at 20 °C³⁸. Figure 7 shows how the flux of each component changes with increasing feed water concentration. From Eq. 4, flux is determined by the intrinsic membrane permeance and the external driving force, which is feed-

concentration dependent. Table 4 shows the activity coefficients and feed fugacity as a function of mole fraction. A higher mole fraction of water leads to a lower activity coefficient, but the corresponding feed fugacity for water increases sharply with increasing feed water concentration. The decrease in n-butanol mole fraction and its activity coefficient with the increase in feed water concentration leads to the sharp decline in its fugacity. However, both water and n-butanol fluxes do not follow the trends of their fugacity. To better understand the reasons behind the flux variation with feed concentration, we calculate the membrane permeance and selectivity according to Eqs. 4 and 7.

Figure 7. Effect of feed water concentration on flux.

Table 4. Mole fraction, activity coefficient, saturated vapor pressure and fugacity of water and n-butanol with different feed water concentration

Water / n-Butanol in feed (wt %/wt %)	Mole fraction (mol %)		Activity coefficient		Saturated vapor pressure (kPa)		Feed fugacity (kPa)	
	Water	n-Butanol	Water	n-Butanol	Water	n-Butanol	Water	n-Butanol
5.0/95.0	0.18	0.82	1.61	0.39			0.71	0.08
7.5/92.5	0.25	0.75	1.35	0.29	2.5	0.26	0.84	0.06
13.5/86.5	0.39	0.61	1.15	0.18			1.12	0.03
17.5/84.5	0.47	0.53	1.10	0.14			1.27	0.02

Figure 8. Effect of feed water concentration on water and n-butanol permeance.

Figure 8 shows the water and n-butanol permeances of the membranes as a function of feed concentration. The water permeance decreases slightly while that of n-butanol increases sharply with feed water concentration. These observations may be attributed to the change in interaction among water, n-butanol and the membrane. When the feed water concentration increases, the internal interaction among water molecules is enhanced. The formation of water–water clusters with the aid of hydrogen bonds might contribute to a decline in their transport³⁹. On the other hand, the dilution of the butanol-butanol interaction with the increase in feed water concentration might facilitate the transport across the membrane.

Figure 8 also indicates that n-butanol permeance is much higher than water permeance, expressing that the intrinsic property of the membranes is still butanol-selective because of their high hydrophobicity. But higher driving force and higher diffusivity of water lead to its preferential permeation. Figure 9 shows that both separation factor and selectivity decrease with an increase in feed water concentration. However, the separation factor still remains high (> 200), leading to a permeate water concentration > 90 wt%.

Figure 9. Effect of feed water concentration on separation factor and selectivity.

3.5. Effect of feed temperature on membrane performance

Figure 10 presents the water, n-butanol, and total fluxes through Hyflon[®] AD /PVDF membranes as a function of feed temperature. The results indicate that all the permeation fluxes increase with feed temperature. The temperature dependence of the flux can be analyzed by the Arrhenius equation⁴⁰:

$$J = J_o \exp\left(\frac{-E_J}{RT}\right) \quad (8)$$

where J_o is the pre-exponential factor, R is the universal gas constant, T is the operating temperature in K, and E_J is the apparent activation energy of the flux, which determines the overall temperature dependence on flux. The plot of the logarithmic permeation flux versus the reciprocal of feed temperature is shown in Figure 11. From this plot, the activation energies can

be calculated and listed in Table 5, as 6.6 and 85.7 kJ/mol for water and n-butanol, respectively. Their positive values reflect permeation fluxes increasing with temperature as shown in Figure 10. For other polymeric membranes it has been explained by the enhancement in thermal motion of polymer chains, leading to more accessible free volume in the polymer matrix and improved diffusion coefficients of the permeating molecules^{41, 42}.

Table 5. Activation energies of water and n-butanol fluxes and permeances for Hyflon® AD /PVDF membranes

	E _J	P _J
	(kJ/mol)	(kJ/mol)
Water	6.6	-29.6
n-Butanol	85.7	-9.5

However in order to thoroughly understand the reason behind, the effects of feed temperature on membrane intrinsic property and external driving force have to be analyzed separately. According to Eq. 4, the driving force for each component depends on its feed fugacity if the permeate pressure is negligible. Table 6 shows that the driving forces of both water and n-butanol increase remarkably with increasing temperature due to the rapid increase in their saturated vapor pressures. On the other hand, the trends of permeance vs. temperature as shown in Figure 12 are opposite to those of fluxes, where water and n-butanol permeance decrease with increasing feed temperature. Therefore, the increase in their fluxes is mainly attributed to the increase in driving force (saturated vapor pressures), rather than any intrinsic change in membrane property.

Figure 10. Effect of feed temperature on flux.

Figure 11. Plot of the logarithmic flux versus the reciprocal of feed temperature.

Figure 12. Effect of feed temperature on permeance.

Figure 13. Effect of feed temperature on separation factor and selectivity.

Similarly the permeance dependence on temperature follows the Arrhenius relationship and its activation energies E_P are also listed in Table 5 as -29.6 and -6.9 kJ/mol for water and n-butanol, respectively. By definition, E_P is the combination of the activation energy of diffusion (E_D) and the enthalpy of dissolution (ΔH_S). E_D generally has a positive value, while ΔH_S is negative because of exothermic sorption. Since typically diffusion enhances but sorption declines with increasing temperature, the negative values of E_P express that a more decrease in solubility than the increment in diffusivity for the permeating molecules at high temperatures. Similar observations have also been reported in previous studies^{18, 43}.

Table 6. Mole fraction, activity coefficient, saturated vapor pressure and fugacity of water and n-butanol at different feed temperatures (T).

T (°C)	Mole fraction (mol%)		Activity coefficient		Saturated vapor pressure (kPa)		Feed fugacity (kPa)	
	Water	n-Butanol	Water	n-Butanol	Water	n-Butanol	Water	n-Butanol
21					2.5	0.26	0.71	0.083
35	0.18	0.82	1.6	0.4	5.6	0.40	1.60	0.13
45					9.6	0.54	2.73	0.17
55					15.7	0.69	4.49	0.22

Figure 13 illustrates the temperature effects on separation factor and membrane selectivity and indicates that by increasing the temperature both separation factor and selectivity decrease. The membrane selectivity comprises diffusivity selectivity and solubility selectivity, and their values change with increasing temperature. As afore mentioned, Hyflon[®] AD membranes is characterized by diffusion selectivity towards water and sorption selectivity towards n-butanol. Increasing temperature enhances the mobility of polymeric chains, creating more and larger free volume available for both water and n-butanol, so the diffusion selectivity towards the smaller-sized molecule, i.e. water, decreases. On the other hand, both Hyflon[®] AD and PVDF are hydrophobic, which means the membrane displays solubility selectivity towards n-butanol. A temperature increase may increase solubility selectivity towards n-butanol. The combined effects contribute to decrease in both separation factor and membrane selectivity

4. Conclusion

In this study, Hyflon[®] AD /PVDF membranes have been developed for n-butanol dehydration. The following conclusions can be made:

1. The large and uniform pores of the PVDF support reduce the resistance for vapor transport and enable a homogeneous coating of the Hyflon[®] AD layer on its surface.

2. Water has higher driving force than n-butanol, which is the main contribution to its higher flux.
3. The coating condition of 4 wt% for 4 min was the most suitable to form a defect-free Hyflon[®] AD layer on the PVDF support.
4. The resultant membrane has a comparably high performance in terms of both flux and separation factor.
5. The partial fluxes and total flux follow a Λ -shape with increasing feed water concentration, which was attributed to the combination of the change in fugacity and the increase in permeability. In addition, increasing the water content in the feed results in lower separation factor and lower selectivity.
6. An increase in feed temperature leads to an increase in driving force and flux. However, both water and n-butanol permeance decrease with increasing temperature due to the decrease in permeants' sorption. By increasing the temperature, the membrane separation factor and selectivity also decrease, due to the lower diffusion selectivity associated to the enhanced polymer chain mobility, free volume and solubility selectivity in the polymeric matrix.

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