Robust organosilica membranes for high temperature reverse osmosis (RO) application:
Membrane preparation, separation characteristics of solutes and membrane regeneration.

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Abstract:

A pore network of bis(triethoxysilyl)ethane (BTESE) organosilica membranes was controlled by adjusting the molar ratios of BTESE/H₂O/acid=1/*x*/0.2 (*x*=3 and 240). The mechanisms for solute transport in the BTESE RO membrane were investigated using three different aqueous solutions of sodium chloride (NaCl), ethanol (EtOH) and isopropanol (IPA). The pressure and temperature were varied from 0.4 to 1 MPa and from 25 to 80 °C, respectively. Water flux and rejection increased for both alcohols and electrolyte with an increase in the applied pressure. It was noteworthy that the rejection of alcohols decreased with an increase in the RO operating temperature, while the electrolyte rejection remained almost constant. The BTESE membranes exhibited high thermal robustness under the long-term testing conditions, delivering salt rejections >98% until the end of the testing period (50 h). The BTESE membranes could also be regenerated after use in the gas and RO experiments, thus demonstrating robust properties.

Keywords:

Organosilica membranes, high-temperature, reverse osmosis, thermal stability, regeneration

1. Introduction

State-of-the-art silica membranes consist of a nanoporous SiO_2 top layer (SiO_4 tetrahedra) coated onto a ceramic support and normally exhibit molecular sieve-like properties. The potential application of this nanoporous SiO_2 is mainly dependent on material properties, such as pore size and pore size distribution, as well as on the surface chemistry of the pores, and the defects that are formed. Generally, silica membranes show a high permeability for small molecules and a low permeability for larger molecules. So it is reasonable to expect a high selectivity for He (2.6 Å) and H_2 (2.9 Å) in gas separation and for H_2O (2.6 Å) in a RO process. In gas separation, silica membranes have exhibited relatively high permeances and good stability in temperatures as high as 600 °C and in corrosive atmospheres [1, 2]. In the presence of water, however, SiO_2 has a low microstructural and hydrothermal stability [3, 4], even at temperatures as low as 60 °C [2-5]. Continuous exposure to water results in the release of silica moieties; as a result, dense particles or defects with large nonselective pores are formed [2]. Therefore, research on alternative materials to improve hydrothermal stability is needed to address these material-based limitations in water application.

Reverse osmosis (RO) membranes typically are pressure-driven membranes that are classified according to the characteristic pore size (0.3-0.6 nm) [6] and are used mostly for desalination, water reuse, and ultrapure water production. Besides important uses in desalination, RO membranes have also shown great potential for use in many industrial applications when operating temperatures reach > 60 °C [7-9]. For example, in the sugar industry temperatures in the range of 70-80 °C are needed to prevent biological contamination; in the textile industry, the operating temperatures sometimes reach 90 °C [8], which most commercially available polymeric RO membranes cannot withstand [9-11]. In addition to that, RO membranes have the potential to be applied in the Steam Assisted Gravity Drainage (SAGD) industry due to the capability of withstanding high temperatures. These can be used to purify and reuse high-temperature boiler feed water.

Polymer membranes have been used to evaluate permeation performance, such as permeate flux and the rejection of neutral and electrolyte solutes at temperatures that typically range from 5 to 65 °C [8]. To date, polyamide thin film composites (PA TFC) are widely used in commercial single-pass seawater desalination plants around the world [9, 12] due to a high water flux, the level of salt and organic matter rejection, and a wide pH range (1 to 11) [11]. However, PA TFC membranes have some drawbacks such as chlorine, fouling and limitations to the operating temperature (0-45 °C) [12].

Hence, the effect of temperatures higher than 60 °C has been investigated using ceramic and organosilica membranes, because these show thermal stability and chemical resistance, as mentioned above. Irrespective of the huge potential for high temperature applications, however, only a limited number of papers have focused on the development of inorganic-organic membranes. To date, nanoporous inorganic membranes such as zeolites [13-16] and organically bridged silica [17, 18] have been studied both theoretically and experimentally to reject ions in RO for the separation of salt from aqueous solutions. Organically bridged silica membranes that consist of an amorphous network with both organic Si-C_n-Si bridges and inorganic Si-O-Si bonds have attracted a considerable amount of recent attention because of their high performance in a variety of applications. In our previous study, we demonstrated that a bis(triethoxysilyl)ethane (BTESE) membrane could withstand temperatures as high as 90 °C in desalination applications with no obvious changes in filtration performance. We found that BTESE membranes also demonstrate excellent chlorine resistance during RO [17]. We also studied the performance of nanoporous titania membranes [19] and silica-zirconia (Si-Zr) membranes [20]. We found that the rejection of neutral solutes and alcohols decreased with temperature, whereas the rejection for electrolytes and alkanes remained approximately constant. In addition to these ceramic membranes, our group extended the RO research using varieties of organosilica membranes with ethane, ethylene and acetylene bridges [17, 21, 22] and triazine-based nitrogen-rich structures [18] on NaCl separation. All of these membranes exhibited the same trend whereby the salt rejection was almost constant (>98%) with increases in the operating temperature that ranged from 25 to 80 °C. However, when using organic solutes, the influence of temperature on these RO membranes has not yet been studied.

Mastering the practical application of BTESE membranes for RO requires a detailed understanding of the pressure-temperature influence on permeate volume flux and solute rejection for electrolyte and alcohol solutions. In addition, we also adjusted the molar ratios of BTESE/H₂O/acid= 1/*x*/0.2 (*x*=3 and 240) during the preparation of the BTESE sols to tune the pore sizes of the BTESE membranes. Furthermore, the membrane long-term stability and regeneration experiments of the BTESE membranes were carried out to further clarify the robustness of a BTESE membrane.

2. Experimental

2.1. Preparation of BTESE-derived sols and membranes

Bis(triethoxysilyl)ethane (BTESE) as a silica precursor was homogeneously dissolved in an ethanol (EtOH) solution. A mixture of water (H₂O) and hydrochloric acid (HCl) were then added dropwise to the solution under vigorous stirring, resulting in a final solution with molar ratios of BTESE/H₂O/HCl = 1/*x*/0.2 (*x*=3 and 240). The concentration of BTESE was kept at 5 wt% by adjusting the amount of EtOH added into the solutions. Then, the solution was kept in a closed system under continuous stirring at 25 °C for 6 h to allow the formation of silica sols.

2.2. Preparation of BTESE-derived sols and membranes

For membrane preparation, the same procedure was reported in our previous studies [17, 18]. Porous α -alumina tubes (porosity: 50%, average pore size: 1 μ m, outside diameter: 10 mm) were used as the supports for BTESE-derived silica membranes. At first, α -alumina particles (average particle diameter: 1.9 μ m) were coated onto the outer surface of a porous support using a silica-zirconia colloidal sol as the binder. Then the support was directly inserted in a furnace at a temperature 550 °C for 30 min to smooth the surface. After that, the membranes were coated with α -alumina particles (average particle diameter: 0.2 μ m) under the same firing conditions. These procedures were repeated several times to cover large pores that might have resulted in pinholes in the final membrane. Then, a SiO₂–ZrO₂ (Si/Zr = 1/1) solution (diluted to about 0.5 wt%) was coated onto the substrate to form an intermediate layer with pore sizes of several nm, followed by firing at 550 °C for approximately 30 min [17, 18]. Finally, the BTESE-derived silica layer was fabricated by the coating of a BTESE solution 2 times, followed by drying and firing at 300 °C in air for 30 min. In the regeneration process, the membrane was washed with water, dried overnight in an oven at 200 °C, and then fired again at 300 °C in air for 15 minutes.

2.3. Reverse osmosis performance test

By using experimental data, membrane performances such as solutes rejection, R_{solute} , water flux, J_v , and solute flux, J_s , were calculated directly. Solutes rejection, R_{solute} , was expressed as follows:

$$R_{\text{solute}} (\%) = (1 - C_p/C_f) \times 100 \quad (1)$$

where C_p and C_f are the concentration of permeate and feed, respectively. Meanwhile, the water flux, J_v , was calculated as follows:

$$J_v = W_p / \rho_p t A \quad (2)$$

where W_p is the mass of the permeate solutions (kg), ρ_p is the density of the permeate (kg/m³), t is the time for collecting the permeate (s), and A is the membrane area (m²). Solute flux, J_s , was obtained as follows:

$$J_s = C_p J_v \quad (3)$$

Membrane intrinsic parameters such as water permeability, L_p , and solute permeability, P , can be calculated using RO performance. The water permeability, L_p , was calculated using equation 4:

$$J_v = L_p (\Delta p - \Delta \pi) \quad (4)$$

where Δp and $\Delta \pi$ are the differences in applied pressure and osmotic pressure, respectively.

$$\text{The osmotic pressure was calculated using equation 5: } \pi = \phi C_s R T \quad (5)$$

where ϕ is the osmotic coefficient known as the van't Hoff equation. For dilute neutral solutions such as EtOH, IPA and glucose, ϕ was assumed to be unity. Meanwhile, for NaCl, ϕ is equal to 1.8 due to the ion pairing concept [23, 24]. C_s is the molar concentration of solutes, R is the gas constant and T is the absolute temperature. The solute permeability, P , through the membrane was calculated using equation 6:

$$J_s = P (C_f - C_p) \quad (6)$$

where $(C_f - C_p)$ is the concentration difference between the feed and the permeate.

The effect of concentration polarization was rationally ignored in this study due to the low permeate flux. The feed solution was vigorously agitated using a magnetic stirrer at 600 rpm to minimize the effect of concentration polarization [19, 25, 26]. Each of the feed and permeate solutions were sampled at a predetermined time interval for at least 5 hours to confirm a steady flux and rejection. Each of the experimental data points reported in this manuscript is the average value of 3 samples. The experimental error in water flux and observed rejection during each measurement was less than 5 and 1%, respectively. A schematic diagram of the RO experiment can be found in the Electronic Supporting Information (ESI-1) Fig.S1.

3. Results and Discussion

3.1. BTESE RO Membranes

The molecular weight cut-offs (MWCOs) of BTESE membranes were determined using neutral solutes, as shown in Fig. 1a and 1b. B-3 and B-240 denote BTESE membranes prepared at H₂O/BTESE molar ratios of 3 and 240, respectively. As shown, L_p was

approximately the same for all types of solutes because of low feed concentration. Rejection for all neutral solutes was increased with an increase in the molecular weight of the solutes. The molecular size was based on the Stokes diameters of EtOH, IPA and glucose and were reported to be 0.39, 0.48 and 0.76 nm [20], respectively, which confirmed that the separation mechanism was primarily the molecular sieving. The MWCOs were determined as a molecular weight, the rejection of which was 90%. The MWCO for the B-3 membrane was approximately 160 g/mol, while the MWCO for the B-240 membrane was smaller than 50 g/mol, which was due to the smaller pore size. The rejection curves, or molecular weight cut-off (MWCO) curves, can also be reflected by the effective pore size of a membrane, which can be controlled by varying the BTESE/H₂O molar ratio.

----- (Fig. 1) -----

Fig. 1. (a) Water permeability, L_p , and (b) rejection neutral solutes, $R_{\text{neutral solutes}}$, as a function of the molecular weight were measured at 1 MPa, 25 °C

In order to estimate the pore size of the membrane, a hindered transport model by Deen [27-29] was applied. According to Deen et al. [27-29], a sieving effect occurs within the nanopores, particularly when molecules are transported via diffusion in the nanopores. In this study, we used the rejection values of ethanol (EtOH), isopropanol (IPA) and glucose measured at 1 MPa and 25 °C. Pore size was best fitted to the Deen model as a function of the Stokes diameter of the solutes. Based on this model, the effective pore size for these membranes was estimated to be 0.53 nm for B-240 and 0.85 nm for B-3, as shown in Fig. 2a. Obviously, increasing the BTESE/H₂O molar ratio can stimulate the formation of a network of smaller pores in a BTESE membrane due to a higher degree of cross-linking [19, 30] as shown in Fig. 2b. When the BTESE/H₂O molar ratio increases, large numbers of BTESE ethoxide groups are fully hydrolyzed, and the density of silanol groups increases. Hence, Si-OH groups are condensed either with another silanol group or with an unreacted ethoxide group to form siloxane bonds [30]. The same phenomenon was presented and confirmed by all the characterizations including that from Fourier transform infrared spectroscopy (FTIR), Thermogravimetry - Mass Spectrometry (TG MASS), and Positron annihilation spectroscopy (PALS), all of which were basically similar to those in a previously published paper [17, 30].

------(Fig. 2)-----

Fig. 2. (a) Rejection of neutral solutes, $R_{\text{neutral solutes}}$ measured at 1 MPa, 25 °C, as a function of the Stokes diameter (curves in the figure are calculated using best-fitted pore sizes (0.85 nm (B-3) and 0.53 nm (B-240) to the Deen model); and (b) Schematic images of the pore networks of B-3 and B-240 of the BTESE membranes.

3.2. Pressure dependency of the BTESE reverse osmosis membranes

B-3 and B-240 membranes were used in order to study the effect of pressure on the

permeation properties of alcohols and NaCl solutions, as shown in Fig. 3. The rejection of NaCl for both membranes increased with increasing operating pressure. The increased rejection with increased operating pressure is a typical tendency of polymeric reverse osmosis membranes [18]. As expected, rejection was higher for the tighter membrane, B-240. The rejection of the solutes for both membranes occurred in the following sequence order: NaCl>IPA>EtOH. J_v for all the solutions for both membranes increased proportionately with applied pressure, while the water permeability, L_p , remained constant. This can be explained according to Equation (4) as the $(\Delta p - \Delta \pi)$ was the driving force for the water transport across the membrane, and, hence, J_v increased linearly while L_p remained constant. Generally, the state of water molecules is unclear if they are permeating through a pore size that is less than 1 nm in diameter. If the water evaporates at the inlet of the pores and permeates as a vapor through a nanoporous membrane, the permeability is dependent on the vapor pressure of the water and not on the applied pressure. In this case, however, the constant L_p indicates that Δp is the single driving force for water permeation through BTESE membranes, confirming that water permeated through BTESE membranes in the liquid state. Again, the B-240 membrane showed a lower J_v than that of the B-3 membrane due to the smaller pore sizes, as mentioned in section (3.1). The high J_v of the alcohol solutions compared with that of the electrolyte solution—irrespective of the same L_p —was due to the differences in their osmotic pressure values (equation (4)). Meanwhile, the solute permeabilities, P , were almost constant with pressure at 25 °C, as obtained by equations (3), (4) and (6). Therefore, the permeation of water and solutes could be described by equations (4) and (6), which showed a similarity with the principles of the solution-diffusion (SD) model [31]. According to equation (6), the driving force for solute permeation, P , is dependent on differences in the concentration gradient and not on the operating pressure. Thus, NaCl exhibited the lowest solute permeability, which was consistent with its high rate of rejection. R_{solute} and J_v increased with an increase in the applied pressure, which was also observed in our previous studies on titania [19], triazine [18] and silica zirconia [20] and also MFI zeolite membranes [13-16,23]. The rejection behavior of the solutes in NF and RO is sometimes caused by both the charge effect and the sieving effect. If the charge effect plays a major role, an increase in the ion concentrations should result in a significant drop in salt rejection, which is often observed for many NF membranes. In our previous studies [25], the NaCl permeability, P_{NaCl} , remained approximately constant, which indicates that the influence of the charge effect between ions and the pores of a silica network has only a minor effect on the electrolyte rejection through

BTESE membranes. This is evidence that the transport mechanism for this membrane is based on molecular sieving.

------(Fig. 3)-----

Fig. 3. (a) Rejection, R , (b) water flux, J_v , (c) water permeability, L_p , and (d) solute permeability, P , as a function of pressure for RO experiments at 25 °C with 2,000 ppm NaCl, and 500 ppm EtOH and IPA.

3.3. Temperature dependency of the BTESE reverse osmosis membranes

The influence of the temperature-induced RO performance of BTESE membranes is shown in Fig. 4. It should be noted that in Fig. 4a, the rejection of alcohols decreased with increasing temperature, while NaCl showed a slightly increased rejection. Decreases in rejection for polymeric RO membranes were attributed mostly to an enlargement in the pore size due to thermal expansion at high-temperatures [12, 32-34]. However, in the present study an increase in pore size was not considered to be one of the reasons for the decreased rejection of alcohols, since the BTESE membranes were organic/inorganic hybrids prepared by firing at 300 °C, which makes them more thermally stable than polymeric membranes. In addition, the R_{NaCl} was constant, or even increased, which confirmed that the pore sizes of these membranes were not influenced by the thermal expansion in the present operating temperature range. A similar trend was observed in our previous studies [18-20].

It is well accepted that the interaction between solutes and membranes plays an important role in determining the temperature dependency of rejection. As shown in Fig. 4b to 4d, the J_v , L_p and P for both membranes increased as the operating temperature increased from 25 to 80 °C, which is characteristic of an activated process. It is noteworthy that L_p for both membranes increased approximately 10-fold without diminishing the rejection value of NaCl (R_{NaCl}). As the operating temperature increased from 25 to 80 °C, L_p and R_{NaCl} values of the B-3 membrane increased from 2×10^{-13} to 2×10^{-12} m³/(m² s Pa) and from 98.1 to 98.1%, respectively. Likewise, the L_p and R_{NaCl} for B-240 membrane increased from 3×10^{-14} to 2×10^{-13} m³/(m² s Pa) and 99.2 to 99.4%, respectively. It should be noted that the performance of the B-3 membrane at operating conditions of 1 MPa and 80 °C approximated that of the L_p and R_{NaCl} of a commercially polyamide RO membrane, SW30HR, (FilmTec) at an operating temperature of 25 °C with L_p and R_{NaCl} values of around 2.2×10^{-12} m³/(m² s Pa) and 98.5%, respectively [35] which confirmed the robustness of the hybrid organic/inorganic membrane when used in a high-temperature RO desalination process or to purify and reuse high-temperature production water.

----- (Fig. 4) -----

Fig. 4. (a) Rejection, R_{solute} , (b) water flux, J_v , (c) water permeability, L_p , and (d) solute permeability, P , as a function of temperature at 1 MPa, 500 ppm EtOH, IPA and 2,000 ppm NaCl.

3.3.1. Effect of temperature on the transport mechanism and activation energies of electrolyte and alcohol solutions

Fig. 5 shows the relationship between (a) viscosity-corrected water permeability, $L_p\mu$, and (b) solute permeabilities, P , as a function of temperature for both membranes. In order to determine the transport of a solvent (water) through the BTESE membrane, the Hagen-Poiseuille [26] (equation 7) value was conventionally employed to theoretically estimate the water permeability through porous membranes.

$$L_p\mu = \frac{r_p^2 A_k}{8\Delta x} = \text{constant} \quad (7)$$

where r_p is the effective pore size, Δx is the effective membrane thickness, A_k is the porosity, and μ is the viscosity of the solution in the pores.

When the transport mechanism obeys the viscous flow mechanism, $L_p\mu$ should be constant irrespective of the permeation temperature and the types of solutions. As shown in Fig. 5a, the values for the $L_p\mu$ of both BTESE membranes were not constant and clearly increased with temperature, which confirmed that the transport mechanism through BTESE membranes deviates from the viscous flow mechanism. This is consistent with previous reports on the permeation mechanism of both aqueous [19] and nonaqueous solutions [20, 36, 37] via nanoporous membranes at high temperature. This is because the viscosity of water in small pores shows a temperature dependence that differs from that in bulk [26].

In terms of surface chemistry, Cohen-Tanugi and Grossman [38] reported that from their simulation study, OH-groups could hydrogen-bond with water and offer water molecules to traverse, thus allowing faster overall water flow. In fact, in our previous studies [18, 22], we also calculated the electrostatic potentials (ESPs), using a Gaussian09 program, which is related to the electron density distribution where negative potential represents electron rich-polar groups, and vice versa, for positive potentials. For BTESE, the ESPs showed that the negative potentials were mainly localized near oxygen atoms [22]. Indirectly, it provides additional evidence that the interaction between the membrane surface and the permeating molecules is thought to be responsible for the difference in the temperature dependence compared with that in the bulk.

$L_p\mu$ values (Fig. 5a) for the B-3 membrane that are larger than those for the B-240 membrane can be fully explained due to the larger pore size, which should continuously accommodate the transport of a greater volume of water molecules and solutes through the membrane. On the other hand, a smaller pore size should exert a strong blocking effect that

would inhibit water molecules and solutes from entering the membrane pores and would lower both the L_p and $L_p\mu$. The solute permeabilities, P , (Fig. 5b) for three different solutes also increased with temperature, which is characteristic of an activated process and can be explained as an increase in diffusion coupled with a decrease in viscosity. This is consistent with previous reports regarding the temperature dependence of electrolytes [19, 34, 39] and neutral solutes [19, 26, 32, 33, 40]. They have remarkably different permeances and sensitivities to temperature.

----- (Fig. 5) -----

Fig. 5. (a) Viscosity-corrected water permeability, $L_p\mu$, and (b) Solute permeabilities, P , as a function of temperature at 1 MPa, 500 ppm EtOH, IPA and 2,000 ppm NaCl.

The linearity of $L_p\mu$ and P in Fig. 5 (a and b) reveals a linear relationship with reciprocal temperature that validates the applicability of the Arrhenius relationship. As summarized in Table 1, the observed values for $\Delta E(L_p)$ and $\Delta E(L_p\mu)$ were larger for membranes with smaller MWCOs and pore sizes. The $\Delta E(L_p)$ and $\Delta E(L_p\mu)$ terms describe the interaction between permeating water molecules and the membrane pores. These interactions are formed and then broken during the process whereby water makes permeation “jumps” through the pore of the membrane. Since the average pore size of the B-240 membrane was smaller than that of the B-3 membrane, water molecules were expected to exert stronger friction against the pore walls of the B-240 membrane than against those of the B-3 membrane. As the temperature increased, a greater number of water molecules with sufficient energy can break through the energy barrier to be transported through the membrane micropores, which leads to an increased L_p and $L_p\mu$ with temperature. In addition to the interpretation based on the activation energy above, the temperature dependency could be explained as follows. The

thickness of adsorbed water on the pore wall decreases as temperature increases, which creates larger spaces for water molecules to permeate. Moreover, the viscosity of the water in these nanoporous networks might be higher than that of the bulk solution [26].

The observed $\Delta E(P)$ for the B-3 membrane ranged from 32 to 44 kJ/mol and from 34 to 57 kJ/mol for the B-240 membrane. For both membranes, the energies increased on the order $\Delta E(P_{\text{NaCl}}) < \Delta E(P_{\text{alcohols}})$. Although NaCl exhibited a smaller ΔE value, it has a higher rejection compared with other solutes for both membranes. The values for ΔE of NaCl permeation through both membranes ranged from 32 to 34 kJ/mol, which was much smaller than the hydration energy values of 371 and 374 kJ/mol that was reported for Na^+ and Cl^- ions, respectively [41]. The very large hydration energies of Na^+ and Cl^- ions meant that a large amount of energy was needed to remove the water molecules from the hydration shells of the Na^+ and Cl^- ions, thus lowering, or making less favorable, the permeation of Na^+ and Cl^- ions as a hydrated sphere. In general, ions permeate confined channels in either a hydrated, dehydrated or partially hydrated state. The crystal (d_{crystal}) and hydrated (d_{hydrated}) diameters are for Na^+ ion ($d_{\text{crystal Na}^+} = 0.19$ nm and $d_{\text{hydrated Na}^+} = 0.71$ nm) and Cl^- ion ($d_{\text{crystal Cl}^-} = 0.36$ nm and $d_{\text{hydrated Cl}^-} = 0.66$ nm) [41, 42], respectively. Based on MWCOs and NaCl rejection (Fig. 1b and Fig. 3a), almost 99.9% of glucose and NaCl was rejected by the B-240 membrane, whereas the B-3 membrane rejected only 92% of the glucose and 98% of the NaCl. Hence, it is reasonable to suggest that the size of the hydrated sphere of NaCl is at least similar to and possible larger than 0.76 nm, which is the Stokes diameter of glucose. NaCl permeated through only a limited number of large pores for both membranes, thus exhibiting a lower ΔE value due to a weak interaction between the ions and the membrane pore wall. On the other hand, we assumed EtOH and IPA would permeate through pore sizes that were smaller than their own Stokes diameters (Stokes diameter for EtOH = 0.39 nm and IPA = 0.48 nm, respectively) hence contributing larger ΔE values for both membranes (Please refer ESI-2; Fig. S2). In our previous paper [43], we reported that the activation energies of He and H_2 were below 10 kJ/mol for BTESE membranes with variations in water ratio (6, 120 and 240). This was due to the smaller kinetic diameter and lighter weight; hence, these gases easily diffused through the pore network. On the other hand, the activation energy for water depends on the viscosity of water. It should be noted that even macroporous membranes such as microfiltration (MF) and ultrafiltration (UF) follow the viscous flow, and the activation energy of water permeation is 15 kJ/mol.

------(Table 1)-----

Table 1. Summary of the pore sizes and activation energies of L_p , $L_p\mu$, and P for B-3 and B-240 membranes

	Membranes	
	B-3	B-240
MWCO	160	<50
Average pore size, H-D model (nm)	0.85	0.53
$\Delta E (L_p)$ (kJ/mol) ^a	30.3	36.6
$\Delta E (L_p\mu)$ (kJ/mol) ^b	15.7	22.0
$\Delta E (P_{NaCl})$ (kJ/mol) ^c	32	34
$\Delta E (P_{EtOH})$ (kJ/mol) ^c	39	57
$\Delta E (P_{IPA})$ (kJ/mol) ^c	44	54

^a Activation energies $\Delta E (L_p)$ were calculated using $L_p=(L_p)_o\exp(-\Delta E(L_p)/RT)$

^b Activation energies $\Delta E (L_p\mu)$ were calculated using viscosity in bulk $L_p\mu=(L_p\mu)_o\exp(-\Delta E(L_p\mu)/RT)$

^c Activation energies $\Delta E (P_{solute})$ (solute = NaCl, EtOH and IPA) were obtained using $P_{solute}=(P_{solute})_o\exp(-\Delta E(P_{solute})/RT)$

Note (1): The experimental error in activation energies of water and solutes during each measurement was less than 5%.

Note (2): The activation energies of viscous flow were calculated based on the temperature dependence of the water viscosity, μ , in the bulk assuming a constant $L_p\mu$; $\Delta E (L_p)=15.4$ and $\Delta E (L_p\mu)=0$ kJ/mol.

Hence, in order to distinguish the mechanisms governing the transport between NaCl and alcohols through the BTESE membrane in terms of diffusivity, two of the main transport parameters (P and L_p) from our experimental analysis, were plotted as normalized P/L_p over an operating temperature at 1 MPa, as shown in Fig. 6. P can be expressed as the effective diffusivity of solutes divided by the membrane thickness, as shown by equation 8 [19]:

$$P = \frac{D_m A_k}{\Delta x_m} \quad (8)$$

where D_m is the diffusivity, A_k is the surface porosity, and Δx_m is the membrane thickness. According to the Wilke-Chang equation [20] shown below, the diffusivity, D_{bulk} , of the dilute concentration of a solute in liquid is expressed as the inverse of the solvent viscosity in equation 9:

$$D_{\text{bulk}} = 7.4 \times 10^{-12} \frac{(\varphi M_B)^{1/2} T}{\mu_B V_A^{0.6}} \quad (9)$$

where φ is the association factor of a solvent (2.6 for water), M_B is the molecular weight of a solvent B (kg/mol), T is the absolute temperature in K, μ_B is the solvent viscosity in (Pa s), and V_A is the molar volume of solute A in (m^3/mol) at its normal boiling temperature. Under the assumption that the diffusivity inside the nanopores shows a dependency on viscosity that is similar to that in bulk, then by dividing the solute permeability, P , by the water permeability, L_p (equation 7), it is possible to discuss the temperature dependence of the solute permeability in nanosized pores by eliminating the effect of the viscosity of the solvents. As shown in Fig. 6, $P/L_{p(\text{alcohols})}$ increased by a larger rate, indicating that the solute flux increased with temperature more rapidly than it did with water flux, compared with $P/L_{p(\text{NaCl})}$. Indirectly, this supports a decrease in the rejection of EtOH and IPA when temperatures and rejection values are high for NaCl. Water permeability increased faster than the diffusion of NaCl, leading to a $(P/L_p)/(P/L_p)_{25^\circ\text{C}}$ that was either $\cong 1$ or < 1 . The normalized value for the P/L_p of NaCl solutes was either approximately 1 or less than 1, which indicates that NaCl permeability in membrane pores was increased with an increase in temperature in the same manner as with the inverse of water viscosity in membrane pores. This suggests that there was no activated process in the NaCl diffusion through either of these BTESE membranes. Rejection, therefore, was independent of permeation temperatures or could possibly have even increased due to the activated permeation of water. On the other hand, the normalized P/L_p of EtOH and IPA solutes increased with temperature for both membranes, indicating that permeability of EtOH and IPA increased with temperature more rapidly than the inverse of viscosity through the membranes, hence exhibiting a molecular sieving mechanism.

----- (Fig. 6) -----

Fig. 6. Normalized P/L_p as a function of temperature at 1 MPa, 500 ppm EtOH, IPA and 2,000 ppm NaCl.

3.4. Thermal stability and regeneration of BTESE reverse osmosis membranes

Fig. 7 demonstrates the stability of the B-3 membrane at temperatures that were elevated from 25 to 80 °C at 1 MPa with 2,000 ppm NaCl. No flux decrease was observed. It should be noted that the water permeabilities for the B-3 membrane were more than $1 \times 10^{-12} \text{ m}^3/(\text{m}^2 \text{ s Pa})$ and showed an excellent salt rejection of >98% at 60 and 80 °C. The water permeabilities increased as the operating temperature increased. It was noteworthy that the rejection remained unchanged for as long as 50 hours at temperatures as high as 80 °C. When the feed temperature was decreased gradually back to the starting temperature (25 °C), the water permeability returned to approximately the initial value, while the rejection remained the same. These results also show that no alteration of the effective pore diameters and structures had occurred.

The excellent hydrothermal stability can be attributed to the main body of the BTESE structure that consists of chemically strong bonds such as Si-C and Si-O-Si. This contrasts with other silica membranes. According to Yazawa et al. [44], after reflux for 48 hours in water, a porous glass membrane (pure silica) showed about 60% of SiO_2 elution by dissolving into water. It is clear that the porous glass (pure silica) membranes used in that study exhibited no thermal stability in aqueous solutions. Another study [45] found that a pure silica membrane with ordered pores was tested for desalination via membrane distillation at an

operating temperature of 60 °C for 30 minutes. The water flux dropped approximately 50% after 30 minutes and salt rejection decreased from 96.4 to 70.3%. The decrease in rejection was ascribed to the hydrophilic surface of the pure silica membrane while the drop in flux was probably because of the build-up of salt within the membrane pores due to pore wetting and subsequent evaporation [44].

However, only a limited number of papers have reported on the hydrothermal stability of zeolite during RO. Li et al. [13] found that for a 0.1 M NaCl solution, a silicalite membrane showed transient (time dependent) water flux and Na⁺ rejections at 2.07 MPa, 25 °C. After a RO time of 50 h, the water flux and Na⁺ rejections were stabilized at 0.112 kg/m² h and 76.7%. By incorporating aluminum ions into the zeolite framework, both water flux and ion rejection was increased from 0.112 to 1.129 kg/ m² h and from 90.6 to 92.9%, respectively [14]. Another recent study on MFI membranes reported desalination performance of the prepared silicalite membrane of a seawater solution (0.3 wt% TDS (total dissolved solids)) for as long as 180 days at a constant pressure of 700 kPa and at various temperatures. The prepared silicalite membrane achieved a high rate of rejection (>93%) for all major seawater ions, including Na⁺ (except for K⁺, 83%) at an applied pressure of 700 kPa and at room temperature (22 °C), but showed a continuous decrease in ion rejection when the temperature was increased from 22 to 90 °C. However, the permeation flux was significantly increased with an increase in temperature [15]. Therefore, these results suggest that BTESE membranes can provide a unique solution for hot water desalination. In addition, these membranes provide a feasible way to improve water flux by increasing the operating temperature with no drop in salt rejection.

----- (Fig. 7) -----

Fig. 7. Salt rejection, R , and water permeability, L_p , for a B-3 membrane as a function of temperature and time at 1 MPa and 2,000 ppm NaCl.

Another challenge was to demonstrate the possibility for the regeneration of a BTESE membrane after its use under conditions of temperature-variation (25-80 °C) in a hot-water desalination RO experiment with alcohols and electrolytes. A B-3 membrane was chosen for thermal stability and regeneration study since B-3 membranes have shown a higher water permeability than the B-240 and a similar R_{NaCl} . Following the regeneration process, the regenerated membrane was used for the gas permeation experiment at a permeation temperature of 200 °C using He, H₂, N₂, CH₄, and SF₆ (Please refer ESI-3 Fig.S3). Fig. 8a shows the gas permeation performance for the B-3 membrane just after membrane fabrication (before the RO experiment) and after the regeneration process. These results show that the gas performances before the RO experiment and after the regeneration process were approximately the same. In order to verify the robust properties, we also conducted a RO experiment with the B-3 membrane using neutral solutes at 1 MPa and 25 °C and a NaCl solution at 1 MPa and 25 and 80 °C, as shown in Fig. 8b. The L_p and $R_{\text{neutral solutes}}$ for the B-3 membrane before RO and after the regeneration process were confirmed to be approximately the same, which showed that the MWCOs for B-3 membranes before RO and after the regeneration process remained unchanged at approximately 160. The capability to regenerate the membrane would depend on the decomposition of foulants such as proteins in order to prevent biofouling. Generally speaking, based on all the experimentation such as the hydrothermal stability studies, regeneration studies, and chlorine-resistant testing [17], we

concluded that the robust properties of BTESE membranes make them a good choice for innovative water desalination.

----- (Fig. 8) -----

Fig. 8. (a) Gas permeation properties at a permeation temperature of 200 °C as a function of molecular size and (b) Water permeability, L_p , and rejection, R , as a function of the molecular weights of 500 ppm neutral solutes (EtOH, IPA and Glucose) and 2,000 ppm NaCl at 1 MPa and 25 and 80 °C for B-3 membranes calcined at 300 °C.

4. Conclusions

In the present study, we demonstrated that as the BTESE/H₂O molar ratio was increased from 3 to 240, the pore sizes decreased from 0.85 to 0.53 nm. Both membranes exhibited high degrees of water flux and rejection for both alcohols and an electrolyte with an increase in the applied pressure. As the operating temperature increased from 25 to 80 °C, L_p and R_{NaCl} values of B-3 membrane increased from 2×10^{-13} to 2×10^{-12} m³/(m² s Pa) and from 98.1 to 98.1%, respectively. Likewise, the L_p and R_{NaCl} for a B-240 membrane increased from 3×10^{-14} to 2×10^{-13} m³/(m² s Pa) and 99.2 to 99.4%, respectively. The transport mechanisms for water and alcohols were predominantly influenced by activated diffusion. In the case of NaCl, which showed the highest rejection, we concluded that only a limited number of large pores were available for NaCl permeation. As compared with other silica membranes such as pure silica and zeolites, BTESE membrane also showed a thermal stability in a hot desalination experiment with improved water flux by increasing the operating temperature with no drop in salt rejection, as well as exhibiting the capability to be regenerated after being used in a hot

1 desalination experiment.

2

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6

1 **Nomenclature**

2 A = membrane area, m^2

3 A_k = porosity, dimensionless

4 C_f = concentration of feed, mol/m^3

5 C_p = concentration of permeate, mol/m^3

6 C_s = molar concentration of solutes, mol/m^3

7 D_m = diffusivity, m^2/s

8 D_{bulk} = diffusivity in bulk, m^2/s

9 J_s = solute flux, $\text{mol}/(\text{m}^2 \text{ s})$

10 J_v = water flux, $\text{m}^3/(\text{m}^2 \text{ s})$

11 L_p = water permeability, $\text{m}^3/(\text{m}^2 \text{ s Pa})$

12 M_B = molecular weight of a solvent, kg/mol

13 P = solute permeability, m/s

14 R = gas constant, $\text{m}^3 \text{ Pa}/(\text{mol K})$, $\text{J}/(\text{mol K})$

15 R_{solute} = solutes rejection, %

16 r_p = effective pore size, m

17 T = absolute temperature, K

18 t = time for collecting the permeate, s

19 V_A = molar volume of solute A, m^3/mol

20 W_p = mass of the permeate solutions, kg

21 x = water molar ratio

22 ΔE = observed activation energy, kJ/mol

23 Δp = differences in applied pressure, Pa

24 Δx = effective membrane thickness, m

25

26 **Greek letters**

27 ρ = density of the permeate, kg/m^3

28 σ = reflection coefficient, dimensionless

29 $\Delta \pi$ = osmotic pressure, Pa

30 ϕ = osmotic coefficient, dimensionless

31 μ = viscosity, Pa s

32 μ_B = solvent viscosity, Pa s

33 φ = association factor of a solvent, dimensionless

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