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Effect of heat treatment on pervaporation separation of aqueous salt solution using hybrid PVA/MA/TEOS membrane

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Abstract

Heat treatment is believed to be an important step in controlling the morphology and properties of polymer based membranes. In this study, hybrid organic-inorganic membrane based on poly(vinyl alcohol) (PVA), maleic acid (MA) and tetraethyl orthosilicate (TEOS) was synthesised via a sol-gel route. The effects of heating temperature and heating time on pervaporation separation performance of aqueous salt solution were studied in relation to swelling and hydrophilic properties, the free volume, salt transport properties, and water diffusivity of the membrane. The free volume of the hybrid membrane under different heat treatment conditions were well correlated with the pervaporation testing results. With increasing heating temperature or time, the fractional free volume of the hybrid membrane was reduced due to a more compact structure by crosslinking among PVA, MA and TEOS. As a result, the water flux decreased and the salt rejection increased. The salt transport properties followed a similar trend as the water uptake, indicating the hydrated NaCl was solvated by water in the membrane phase.

Keywords: heat treatment; pervaporation; hybrid organic-inorganic membrane; PVA/MA/silica; desalination

Nomenclature

A	membrane area (m^2)
C	liquid concentration (g/cm^3)
D	apparent diffusion coefficient of water (cm^2/s)
Ds	sodium chloride diffusivity (cm^2/s)
FFV	fractional free volume (dimensionless)
I_3	intensity (%)
J	water flux ($kg/m^2.h$)
Ks	sodium chloride solubility (dimensionless)
l	membrane thickness (cm)
M	mass of sodium chloride in solution (g) or mass of permeate (kg)
Ps	sodium chloride permeability (cm^2/s)
R	free volume element size (nm)

R_s salt rejection (%)
R_{FVE} average radius of free volume elements (nm)
t   time (s) or (h)
τ_3 ortho-positronium lifetime (nm)
V_F average volume of the free volume elements (nm^3)
W   weight of membrane (kg)
ΔR electron layer thickness (nm)
δ membrane thickness (cm)

Subscripts
d   dried membrane
f   feed (NaCl)
p   permeate
s   wet membrane
t   time
w   water
∞   infinite time

1.   Introduction

Pervaporation is a promising membrane technology for many separation processes. It is able to separate mixtures by preferentially removing one component from the mixture due to its higher affinity with, and/or faster diffusion through a non-porous membrane. In the pervaporation process, mass transfer is driven by vapour pressure differences, and the liquid mixture is maintained at atmospheric pressure on the feed side of the membrane and the permeate is removed on the other side as a vapour due to the low pressure achieved by using a carrier gas or a vacuum pump [1]. Pervaporation has been extensively used for separation or concentration of mixtures of aqueous-organic or organic liquids. During the last decade, systematic studies on desalination using high-chemical-stability dense pervaporation membranes were conducted [2,3,4]. The pervaporation of an aqueous salt solution can be regarded as separation of a pseudo-liquid mixture containing free water molecules and bulkier hydrated ions formed in solution upon dissociation of the salt in water [2]. In desalination applications, pervaporation has the advantages of near 100% salt rejection and the energy need is independent of the salt concentration [4]. Additionally, the ability of pervaporation to operate at low temperatures means it may potentially be driven by low grade heat that would otherwise not be utilised.

Hybrid organic-inorganic membrane materials have been rapidly developing recently as a promising alternative to conventional organic or inorganic membrane materials [5,6]. More specifically, organic-inorganic hybrid membranes, in which the organic and inorganic components are linked together through strong ionic/covalent bonding, have attracted significant research interest due to better dispersion and stronger bonding of organic and inorganic moieties [1,5,6,7]. Among various polymers, poly(vinyl alcohol) (PVA) based hybrid organic-inorganic membranes have received significant interest as the inorganic moieties restrict swelling of the PVA but maintain their excellent film forming properties [8].

Poly(vinyl alcohol) has been studied extensively as a membrane material in pervaporation due to its high hydrophilicity, and excellent film forming properties [1]. The selection of PVA was also due to its low cost, commercial availability and chemical resistance. However, PVA has poor stability in water. To improve the performance and stability of PVA membranes in aqueous solutions it is necessary to insolublise or modify the membrane via crosslinking or crystallisation to achieve a stable membrane with good mechanical properties and selective permeability to water [9]. Incorporation of inorganic particles in PVA to form hybrid organic-inorganic membranes has been one of the most widely used techniques to improve the stability and separation performance of PVA membranes [1,5,6,8,10]. Many PVA/silica hybrid membranes have been reported. For example, PVA crosslinked with tetraethoxysilane (TEOS) via hydrolysis and condensation reactions has been widely studied for pervaporation dehydration of organic solutions [1,5]. Results showed an increased selectivity with decreased permeability due to crosslinking. PVA has also been crosslinked with glycidoxypropyltrimethoxysilane (GPTMS) to produce PVA-silica hybrid membranes, with the aim of improving both permeability and selectivity in pervaporation separation of benzene/cyclohexane [10]. With increasing annealing temperature and time, the permeation flux of benzene decreased and the separation factor towards benzene increased, which was ascribed to the changed free volume under different heat treatment conditions.

It is well known that heat treatment is an important step in controlling the structural morphology and swelling of the membranes which is central to the separation performance of hybrid organic-inorganic membranes [6]. For example, Ye et al. [8] studied the annealing conditions of PVA/PEG/TEOS membranes for pervaporation separation of an ethanol-water mixture. Increasing the heating temperature or time made the water permselectivity increase and the permeation flux decrease. Uragami et al. [5] prepared PVA/TEOS membranes for the pervaporation of aqueous ethanol, with the aim of minimising the swelling of the PVA. Heat treatment was needed to complete the condensation reaction that introduced bridging. The water permselectivity in the hybrid membrane increased significantly with annealing temperature and time. It was postulated that the crosslinking reaction took place in the non-crystalline parts of the PVA membrane, forming denser non-crystalline regions. The importance of heat treatment was also reported by Peng et al. [6] on pervaporation properties of hybrid PVA/γ-GPTMS membranes for separation of benzene/cycloheane mixtures. With higher annealing temperatures and longer heating times, the permeation flux of benzene decreased and the separation factor towards benzene increased, which was ascribed to the changed free volume under different heat treatment conditions.

In our previous work [11,12], we have demonstrated that a new type of hybrid organic-inorganic membrane could be fabricated via a sol-gel route based on PVA, MA and TEOS. The hybrid membrane has shown significantly improved swelling and thermal properties. Incorporation of silica nanoparticles into the polymer matrix disrupted the polymer chains and enhanced the diffusion of water molecules through the membrane and consequently enhanced both the water flux and the salt rejection. A potential application of this membrane in pervaporation separation of aqueous salt solutions was demonstrated, and achieved high flux of 11.7 kg/m^2·hr and salt rejection up to 99.9% at 65°C and a 6 Torr vacuum.

In this study, the synthesised hybrid PVA/MA/TEOS membrane was subjected to various heat treatment conditions including different heating temperatures and heating times. Effects of heating temperature and heating time on pervaporation separation performance of aqueous salt solution was studied in relation to swelling and hydrophilic properties, the free volume characteristics, salt transport properties, and membrane water diffusivity. The pervaporation experiments were carried out at conditions of low temperature (21°C) and low feed concentration (0.2 wt% NaCl solution) to minimise temperature and concentration polarisation effects. Furthermore, the low flux (<6 L.m^{-2}.hr^{-1}) led to low loss of heat via evaporation of water into the permeate stream. The free volume of the hybrid membranes under different heat treatment conditions were characterised by Positron Annihilation Lifetime Spectroscopy (PALS), and were correlated with the pervaporation test results. In addition, the overall mass transfer coefficients of the hybrid membranes were also investigated based on the solution-diffusion model.

2. Experimental

2.1 Hybrid membrane synthesis

The hybrid PVA/MA/silica membranes containing 5 wt% MA and 10 wt% SiO$_2$ with respect to PVA were synthesised via an aqueous sol-gel route. Reagent grade chemicals including PVA (98-99% hydrolysed, average MW 160,000), tetraethyl orthosilicate (TEOS, 98%), maleic acid (MA), *p*-toluene sulfonic acid (98.5%, monohydrate) were obtained from Sigma-Aldrich and used without further purification.

PVA polymer powder (8.0 g) was first dissolved in 100 mL Milli-Q deionised water (18.1 M$\Omega \cdot$cm@25°C) at 95°C. The obtained 8 wt% PVA solution was left to cool to room temperature, followed by addition of 0.4 g of MA and 0.08 g of *p*-toluene sulfonic acid into the solution (pH 1.9±0.1). A premixed 2.78 g TEOS and 25.0 g ethanol mixture (weight ratio of TEOS:ethanol =1:9) was added drop wise to the above PVA solution under steady stirring and then was continuously stirred for another 2 hours. The resulting homogeneous mixture was cast on Perspex Petri dishes to the desired thickness and dried in air followed by either 2 hours of heating time at temperatures between 100 to 160°C or heat at 140°C for times between 2 to 24 hours. A membrane sample prepared at room temperature (21°C) without any heat treatment was prepared as a reference for comparison. The thickness of membranes was measured at different points across the membrane using a Fowler electronic digital micrometer (accuracy ±1 μm) and the membranes used in pervaporation testing each had an average thickness of 10 μm.

2.2 Water uptake and contact angle

The water uptake of PVA/MA/TEOS hybrid membranes was measured by the following procedures: (1) Immersing the dried membrane in deionised water at room temperature for 48 hours to reach the absorption equilibrium. (2) Blotting the surface of wet membranes with a tissue to remove surface water and quickly weighing the wet membrane within 10 sec (W$_s$). (3) Drying the membrane in a vacuum oven at 40°C

overnight and then weighing again to obtain the mass of dried membrane (W_d). The water uptake of membrane was then calculated according to:

Water uptake = $(W_s - W_d)/W_d \times 100\%$ (1)

The water contact angle of membrane samples were assessed by a KSV contact angle meter (CAM200) equipped with an image capturing system. Static water contact angles were measured by the sessile drop method. A 6 μL water drop was formed on the levelled surface of the membrane for contact angle measurements.

A minimum of three measurements were conducted for each sample with the experimental error of ±6% for water uptake and ±2° for contact angle.

2.3 Salt transport properties

Salt transport properties of membranes were determined for NaCl by the kinetic desorption method [13,14,15]. A membrane sample with thickness of 60μm was immersed in 50 mL of 5 wt% NaCl solution for 48 hours at room temperature. The membrane was then taken out of the NaCl solution and blotted dry with tissue paper. The membrane was then quickly transferred to a beaker containing 80 mL of deionised water which was stirred vigorously using a stirring bar to achieve a uniform distribution of NaCl in the solution during desorption. To minimise solution conductivity changes due to CO_2 absorption by the water, the water in the beaker was air-saturated before adding the film sample. Solution conductivity was measured as a function of time using an Oakton® Con 110 conductivity meter and the data were recorded at 5 s intervals. This was then converted to NaCl concentrations (mg/L) using a pre-established calibration chart of NaCl concentration Vs conductivity.

The desorption results were fit to the following Fickian diffusion model to calculate the NaCl diffusivity D_s in the membrane by plotting (M_t/M_∞) versus $t^{1/2}$ [13,14,15]:

$$D_s = \frac{\pi \cdot l^2}{16} \left[\frac{d(M_t / M_\infty)}{d(t^{1/2})} \right]^2$$ (2)

Where M_t is the amount of NaCl in the solution at time t and M_∞ is the total amount of NaCl desorbed from the membrane into the solution, and l is the thickness of the membrane. The NaCl solubility, K_s, is the ratio of NaCl absorbed into the membrane (M) per unit membrane volume to the concentration of NaCl in the original solution (i.e. 5 wt%). According to the solution-diffusion model, NaCl permeability, P_s, is the product of D_s and K_s [13,14,15].

$$P_s = D_s \cdot K_s$$ (3)

2.4 Positron annihilation lifetime spectroscopy (PALS)

PALS analysis of hybrid membrane samples was conducted using an automated EG&G Ortec fast-fast coincidence system at ambient temperature with a time resolution of 240 ps. Radioactive isotope [22]Na, which was sealed between thin Mylar

films, was used as the positron source. In this study, the free volume of wet films were analysed as it closely represents the actual condition of membranes used in pervaporation testing. Prior to the wet film measurement, the samples were immersed in a 0.2 wt% NaCl solution for 2 days which represented the feed solutions used in pervaporation testing prior to measurement. The ^{22}Na source was then sandwiched between stacks of wet films with 2 mm thickness. A minimum of 5 spectra were collected with each containing 1 x 10^6 integrated counts. The spectra were analysed using the LT v9 software. The longest lifetime, τ_3, and its intensity, I_3, were interpreted as the ortho-positronium (o-Ps) annihilation signature. The o-Ps components were used to characterise the sample's free volume [14]. Assuming that the o-Ps was localised in a spherical potential well surrounded by an electron layer of thickness ΔR of 0.166 nm, the free volume element size, R, can be calculated using the following equation [16,17]:

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \qquad (4)$$

The average volume of the free volume elements, V_{FVE} can be calculated by [16,17]:

$$V_F = \frac{4\pi}{3}R^3 \qquad (5)$$

The fractional free volume (*FFV*) was estimated from the following equation:

$$FFV = V_F I_3 \qquad (6)$$

2.5 Pervaporation testing

Pervaporation experiments were carried out at room temperature (21°C) on a laboratory scale pervaporation unit with details described previously [4]. The membrane was placed in the middle of a pervaporation cell with an effective surface area of 12.6 cm^2. The feed solution was circulated on the feed side of the membrane using a Masterflex$^®$ peristaltic pump with a feed flow rate of 30 mL/min. The feed flowrate was chosen such that further increases in velocity resulted in no change to the flux, indicating the hydrodynamic conditions were fully developed. The vacuum on the permeate side of the membrane was maintained at 6 Torr with a vacuum pump. The permeate was collected in a dry ice cold trap.

An aqueous salt solution containing 0.2 wt% (i.e. 2000 mg/L) NaCl was used as the feed solution, which is representative of brackish water (1500-5000 mg/L TDS). The salt concentration of the feed and permeate were derived from measured conductivity with an Oakton$^®$ Con 110 conductivity meter.

The pervaporation separation performance of aqueous salt solution of hybrid membranes were characterised by water flux and salt rejection. The water flux (J) was determined from the mass (M) of permeate collected in the cold trap, the effective membrane area (A) and the experimental time (t).

$$J = M / At \tag{7}$$

The salt rejection (R_s) was determined by the following equation:

$$R_s = 1 - \frac{C_p}{C_f} \times 100\% \tag{8}$$

where C_p and C_f are NaCl concentration in the permeate and feed respectively.

The apparent diffusion coefficient of water was calculated from the following equation based on Fick's law [18]:

$$D = \frac{J\delta}{C_w} \tag{9}$$

Where δ is the membrane thickness, and C_w is the water concentration on the membrane surface on the feed side.

It should be noted that, two independent methods adopted from other researchers [14, 15] have been used to estimate the diffusivity of NaCl (equation 2) and water (equation 9), respectively. NaCl diffusivity was derived from the kinetic desorption method and boundary layer effects did not influence the diffusivity results. On the other hand, apparent water diffusivity was calculated based on Fick's law by using the bulk feed water concentration and the measured water flux. In this case, the boundary layer effect is included. This implies that the diffusivity of NaCl and water derived from these two methods cannot be directly compared, and the absolute values of NaCl and water diffusivity were not directly compared. Rather, their relative changes following various heat treatment conditions were discussed in this study.

3. Results & Discussion

3.1 Swelling behaviour and contact angle analysis

The swelling behaviour of membranes is generally described by the water uptake results. Figure 1 shows the effect of heating temperature on water uptake and hydrophilic properties of PVA/MA/TEOS hybrid membranes. The heating time was kept constant at 2 h and the heating temperature was increased from room temperature (21°C) to 160°C. When compared with the un-heated membrane, heat treatment had a significant effect on water uptake. The water uptake decreased significantly from 154 to 43wt% when the temperature was increased from 21 to 100°C and then gradually decreased to 22 wt% when the temperature was further increased to 160°C. As explained in our previous study [11], in fabricating the hybrid PVA/MA/silica membranes, the hydroxyl groups in the repeating units of PVA and the carboxylic groups in MA were expected to produce strong secondary interactions with the residual silanol groups generated from acid catalysed hydrolysis and polycondensation of TEOS to form hydrogen and covalent bonds. In addition, PVA and MA went through an esterification reaction via grafting or crosslinking under heat

treatment to form ester groups. As a result, the hybrid PVA/MA/silica membranes formed a compact structure with network crosslinking due to above mentioned reactions among PVA, MA and TEOS. As heating temperature increases, it is expected that the crosslinking degree in the hybrid membrane will increase. Hypothetically, polycondensation of silanol groups resulting from hydrolysis of TEOS will also be favoured upon heating. Therefore, the swelling was suppressed.

The effect of heating temperature on the hydrophilic properties of hybrid membrane is less straight forward although the hybrid membrane remained hydrophilic upon the change of heating temperature. At heating temperatures less than 140°C, the water contact angle remained almost unchanged at about 45°. This could be explained by the contribution of hydrophilic –OH groups from silanol that resulted from hydrolysis reactions of TEOS and -COOH group from MA. At lower heating temperatures, the crosslinking reaction among PVA, MA and TEOS, and the polycondensation of TEOS may be incomplete. This will result in many free –OH and –COOH functional groups which contribute to the hydrophilic properties of membranes. As the heating temperature was further increased to 160°C, there was a significant increase in water contact angle, indicating that the hybrid membrane became less hydrophilic at the higher heating temperature. This could be due to crosslinking reactions among PVA, MA and TEOS, and the polycondensation of TEOS, being more complete at higher temperatures. This will lead to consumption of more hydrophilic groups, consequently increasing the hydrophobicity of the membrane.
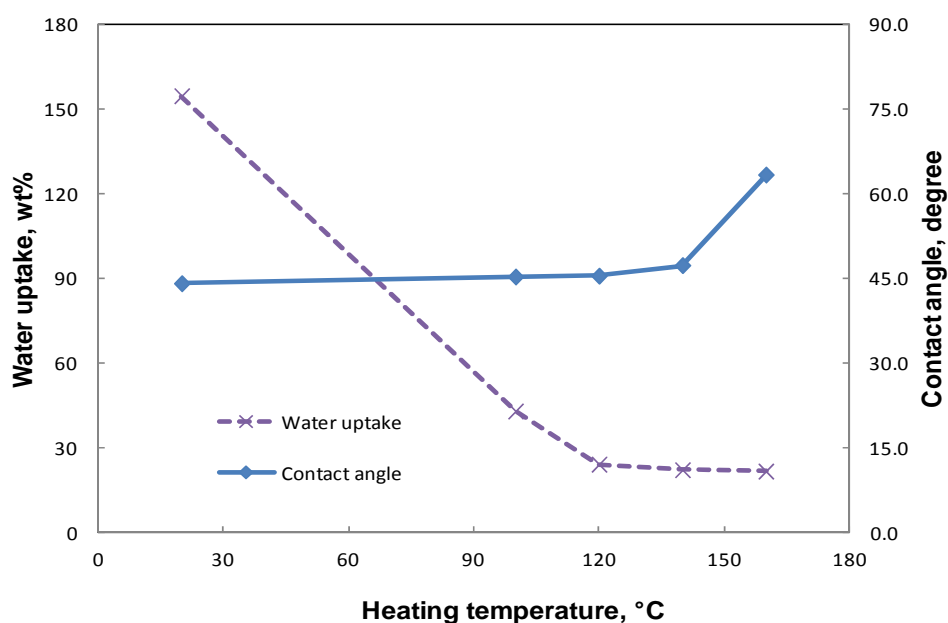

 Figure 1: Effect of heating temperature on water uptake and contact angle (heating time: 2 hours).

Figure 2 shows the effect of heating time on water uptake and hydrophilic properties of PVA/MA/TEOS hybrid membranes at a heating temperature 140°C. Compared with un-heated membrane, the water uptake decreased sharply from 154 to 24wt% when the membrane was heat treated for 2 hours. Further increases of heating time from 2 to 16 hours only had a marginal effect on the swelling properties of the membrane.

Unlike heating temperature, the heating time has more effect on the hydrophilic properties of the membrane. Although the membrane remained hydrophilic following the various heating periods, the water contact angle increased gradually with increasing treatment time possibly due to increased crosslinking and polycondensation of TEOS. This suggests that long heating times favour the completion of the crosslinking reactions among PVA, MA and TEOS, and polycondensation of TEOS.
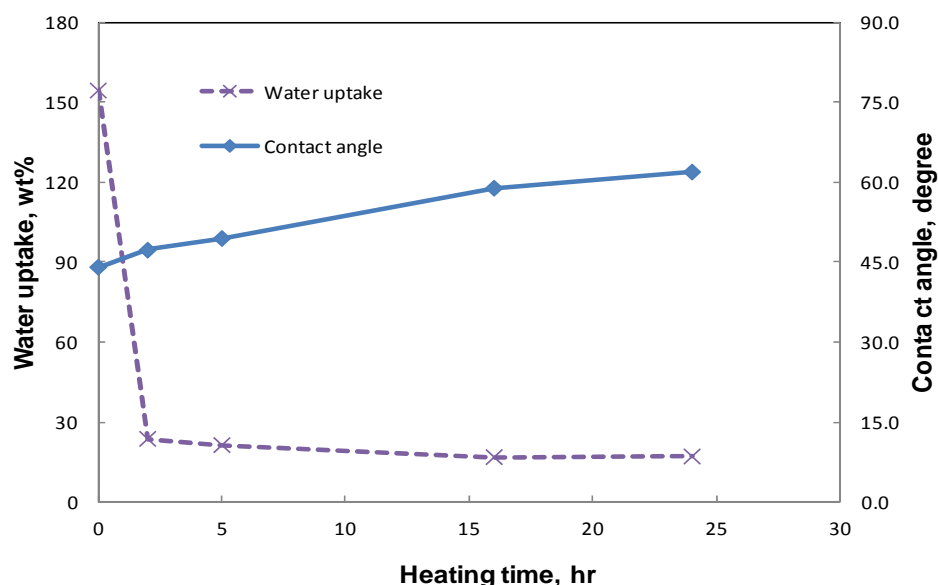

Figure 2: Effect of heating time on water uptake and contact angle (heating temperature:140°C).

3.2   Free volume analysis

Positron annihilation lifetime spectroscopy (PALS) has emerged as an advanced and relatively new approach to investigate the size and size distribution of free volume elements in polymers [19-20]. This method is based on the measurement of positron lifetime and lifetime intensity in a material. The annihilation of positrons in a polymer occurs via several pathways. One of the pathways, based on o-Ps in the triplet spin state, is typically sensitive to free volume elements in a polymer, including their size (characterised by o-Ps lifetime τ_3) and concentration (characterised by intensity I_3), respectively [20].

A defining feature of polymer nanocomposites is that the small size of the inorganic fillers leads to a dramatic increase in interfacial area as compared with traditional composites. This interfacial area creates a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings [21]. This is especially important for enhancing the permeation property of membranes in water separation applications. It is of most interest to understand how the PALS parameters change upon wetting and how the free volume correlates with transport properties.

Table 1 shows the PALS results of wet hybrid PVA/MA/TEOS membranes including o-Ps lifetime (τ_3) and intensity (I_3), average radius (R_{FVE}), volume of the free volume elements (V_F) and fractional free volume (FFV) as a function of heat treatment conditions. As can be seen, the average radius, R_{FVE} (~0.27-0.28 nm), are typical network pores which are in the range of 0.1-0.3 nm and represent the small cavities between polymer chains constituting the polymer aggregates. There was a slight decrease in the size of network pores (R_{FVE}) and the average volume of the free volume elements (V_F) upon more severe heat treatment conditions. In addition, the concentration of free volume elements as characterised by intensity, I_3, decreased significantly upon heating. Consequently, the fractional free volume FFV which is characterised by the product of V_F and I_3 changed significantly upon heat treatment. Generally, the fractional free volume decreased with either increasing heating temperature or heating time, indicating changes in the microstructure of the hybrid membrane upon heating potentially due to crosslinking reactions among PVA, MA and TEOS and the polycondensation reaction of TEOS.

It was also noted that the average radius (R_{FVE}) of the free volume elements (~0.27-0.28 nm) was bigger than the radius of water molecules (0.14 nm) [22] but smaller than the radius of the first hydration shell of sodium ions (0.34 nm) and chloride ions (0.38 nm) [23]. This assists in understanding how high salt rejection is achieved by the hybrid PVA/MA/silica membrane, as the pores are large enough to pass water molecules but too small to allow hydrated salt to pass.

Table 1: PALS results of wet hybrid membranes at different heat treatment conditions.

Heating temperature, °C	τ_3(ns)	I_3(%)	R_{FVE} (nm)	V_F (nm^3)	FFV
			± 0.002	± 0.008	± 0.03
Un-heated	1.925 ± 0.016	19.5 ± 0.3	0.278	0.090	1.77
100	1.947 ± 0.004	18.9 ± 0.2	0.280	0.092	1.75
120	1.925 ± 0.017	17.8 ± 0.3	0.278	0.090	1.61
140	1.910 ± 0.010	17.0 ± 0.2	0.277	0.089	1.52
160	1.875 ± 0.013	14.9 ± 0.1	0.274	0.086	1.26
Heating time, hour	τ_3(ns)	I_3(%)	R_{FVE} (nm)	V_F (nm^3)	FFV
			± 0.002	± 0.008	± 0.3
Un-heated	1.925 ± 0.016	19.5 ± 0.3	0.278	0.090	1.77
2	1.910 ± 0.010	17.0 ± 0.2	0.277	0.089	1.52
5	1.876 ± 0.005	15.4 ± 0.2	0.274	0.086	1.32
16	1.878 ± 0.017	14.3 ± 0.3	0.274	0.086	1.23
24	1.872 ± 0.017	13.2 ± 0.1	0.273	0.086	1.13

3.3 Salt transport properties

The kinetic desorption method is well established for characterising the salt transport properties of polymer membranes [12,13,14,15]. A typical NaCl desorption curve

from the kinetic desorption experiments in this study is shown in Figure 3. Similar to the study of PEG-based hydrogel membrane coating by Ju et al.[14], the NaCl diffusion coefficient, Ds, for each membrane was calculated from the slope of the linear portion of the desorption curve using Eq.(2). Table 2 presents the salt transport properties of hybrid membranes as a function of heat treatment conditions. NaCl solubility decreased with increasing heating temperature or time. The results agree well with the water uptake data (Figs. 1&2). In theory, no salt (NaCl) is expected to dissolve in a pure polymer matrix, so any NaCl in the membrane phase is assumed to be solvated by the water within the membrane [13]. Therefore, the amount of NaCl in the membrane will be closely connected to the amount of water in the membrane. With increasing heating temperature or time, the swelling degree in the membrane decreases, and as a result, there is a tendency to accommodate less NaCl along with water in the membrane. It is expected that this low NaCl solubility would lead to low permeability and subsequent high rejection of NaCl through this membrane.
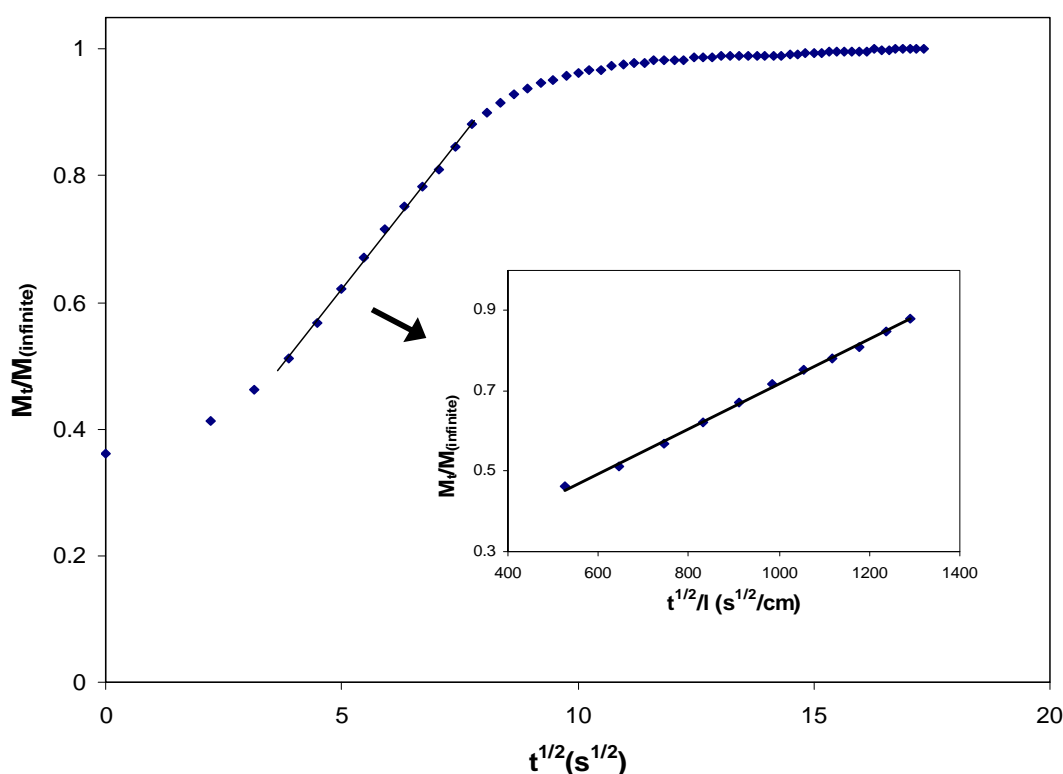

Figure 3: Typical NaCl desorption curve for PVA/MA/TEOS membrane (membrane containing 5 wt% MA and 10 wt% silica)

Table 2: Transport properties of NaCl as a function of heat treatment conditions.

Heat treatment temperature, °C (2 hours)	NaCl diffusivity $(x10^{-6}\ cm^2/s)$	NaCl solubility (dimensionless)	NaCl permeability $(x10^{-6}\ cm^2/s)$
Unheated	4.96	1.93	9.54
100	2.88	1.82	5.23

120	2.32	1.74	4.03
140	1.91	0.99	1.90
160	1.04	0.67	0.70
Heat treatment time, hour (140°C)	NaCl diffusivity ($\times 10^{-6}$ cm^2/s)	NaCl solubility (dimensionless)	NaCl permeability ($\times 10^{-6}$ cm^2/s)
Unheated	4.96	1.93	9.54
2	1.91	0.99	1.90
5	1.21	0.97	1.17
16	0.70	0.74	0.52
24	0.45	0.43	0.19

Compared with the un-heated membrane, both NaCl diffusivity and permeability decreased significantly upon heating. With increasing heating temperature or time, NaCl diffusivity and permeability decreased due to the changes in free volume potentially resulting from increased crosslinking degree upon heating. Figure 4 shows NaCl permeability as a function of free volume under different heat treatment conditions. NaCl permeability data correlated well with the free volume. In general, NaCl permeability increased exponentially with increasing fractional free volume, indicating the salt transport properties of the membrane is strongly influenced by the microstructure of the hybrid membrane.
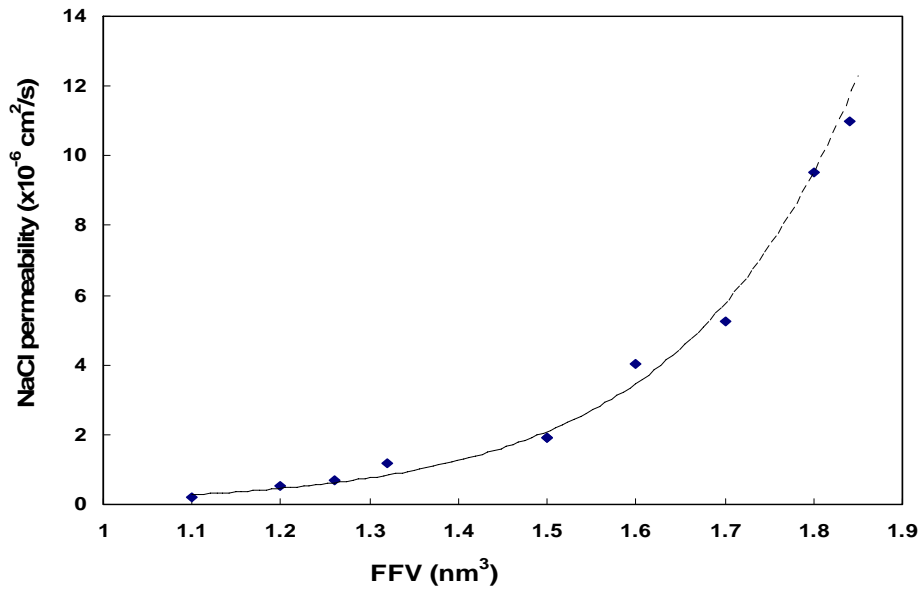

Figure 4: NaCl permeability versus fractional free volume (*FFV*) of hybrid PVA/MA/silica membranes (membranes containing 5 wt% MA and 10 wt% silica)

The diffusion coefficients of NaCl in this study were in the range of 0.45-4.96$\times 10^{-6}$ cm^2/s. These are significantly lower than the diffusion coefficient of NaCl in pure water, 1.47$\times 10^{-5}$ cm^2/s [13]. As explained by Yasuda et al. [13], this could be due to the effect of concentration polarisation at the interface of the membrane sample and the extraction water during the desorption measurement. A similar finding was also reported by Ju et al. (1968) in a study of crosslinked poly(ethylene oxide) hydrogels [14], and they reported NaCl diffusivities in a similar range of 0.3 to 4.4$\times 10^{-6}$ cm^2/s.

3.4   Pervaporation testing

In pervaporation, flux is generally low and corresponding flux is lower than RO. Therefore, the expected boudary layer effect at the membrane interface is lesser of a problem. In addition, the permeate stream is often drawn into a high vacuum on the vapour side, and therefore conductive heat losses to the permeate are negligible because of the low heat transfer coefficent from the membrane to a gas phase. The effect of concentration polarisation also becomes negligible in pervaporation process, as mass transfer is driven by vapour pressure differences rather than concentration differences. Vapour pressure is a weak function of salt concentration, particularly for low salt concentration solutions. Therefore, even large concentration changes at the surface do not alter the mass transfer because the vapour pressure difference remains unaffected.

However, temperature polarization can be a serious problem, especially when operating the system at high feed temperatures where the vapour pressure is an exponential function of temperature. As water is transported through the membrane, the feed side temperature lowers as water evaporates at the membrane surface adiabatically. As a result, a relatively thick stagnant layer will be formed, which severely reduces water transport from the bulk to the membrane surface. Due to increased water vapour pressure at higher feed temperatures and consequently higher water flux, the temperature difference from the bulk feed to the permeate are also high due to higher evaporation rates at high feed temperatures. On the other hand, at low feed temperatures (e.g, 21°c as used in this study) and low salt concentrations (low compared to saturation concentrations), salt concentration has negligible influence on water flux. The water flux was also low, resulting in low water evaporation rate. As a result, the temperature difference across the membrane was small. During the experiment, thermocouples installed at the feed side and permeate side of the membrane indicated that there was no noticeable measured temperature difference between the feed and permeate. This indicates the bulk temperature drop from feed side to permeate side was small, the temperature polarisation effect could be negligible under the studied room temperature conditions, and is supported by the low operating temperatures and low flux.

Figure 5 and 6 show the effect of heating temperature and time on pervaporation separation performance of aqueous salt solution through hybrid PVA/MA/TEOS membranes. The salt rejection of un-heated membrane achieved 95.5% due to the non-volatile nature of NaCl and the size exclusion mechanism of the hybrid membranes. Upon heat treatment, the salt rejection increased to >99.5%. The relatively low salt rejection (95.5%) of un-heated membrane could be explained by the high swelling of the membrane (Figs. 1&2). Without heat treatment, the crosslinking reactions among PVA, MA and TEOS, and also the polycondensation of TEOS are most likely incomplete. Especially, the esterification reactions between PVA and MA in the aqueous phase, since they are generally favoured by heating [12]. As a result, the unheated membranes tended to swell due to their less compact structure and consequently, hydrated NaCl was solvated by the water in the membrane and the salt rejection was lower. Introducing heat treatment to the hybrid

membrane tended to form a more compact structure with reduced swelling (Figs. 1&2). Therefore, the salt rejection increased upon heating.
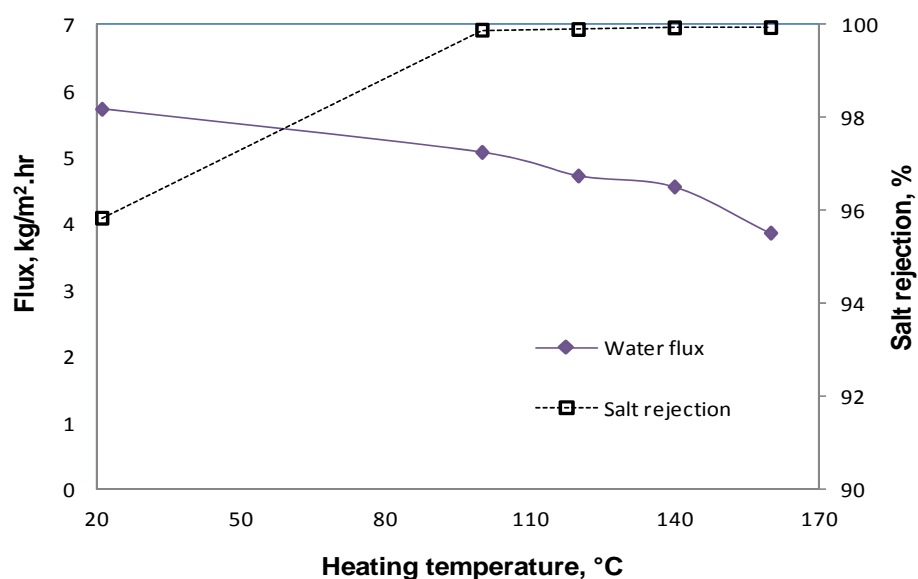

Figure 5: Effect of heating temperature on water flux and salt rejection (heating time 2 hours, membrane thickness 10 μm, feed temperature 21°C, feed flowrate 30 mL/min, vacuum 6 Torr).
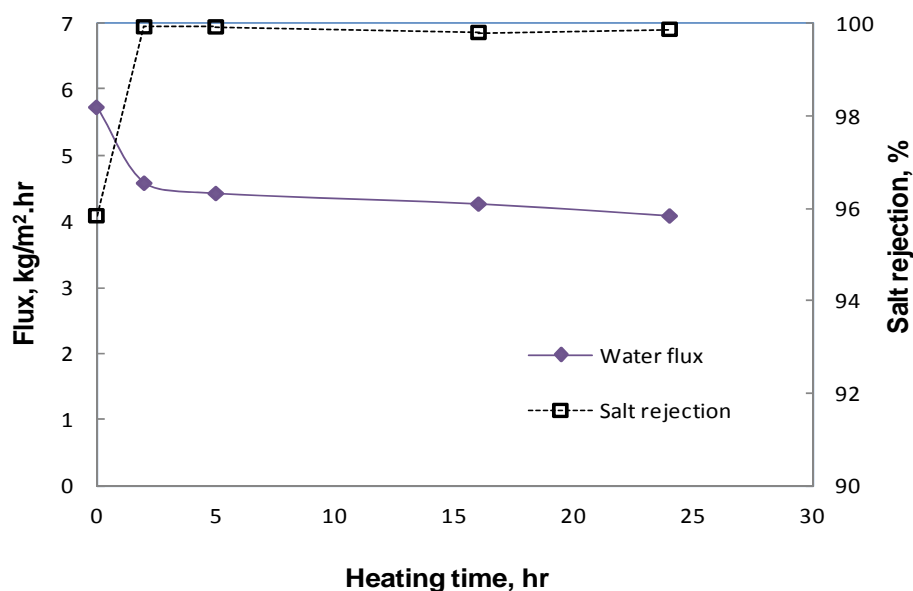

Figure 6: Effect of heating time on water flux and salt rejection at 140˚C. (Membrane thickness 10 μm, feed temperature 21°C, feed flowrate 30 mL/min, vacuum 6 Torr).

The water flux generally decreased with increasing heating temperature and time. This could be explained by the solution-diffusion model and free volume theory. There are three steps in the pervaporation transport mechanism: sorption at the

membrane surface, diffusion through the dense membrane and desorption into the vacuum [24]. Under the high vacuum used in the study, the desorption step on the permeate side of the membrane is believed to be a fast step. Sorption at the membrane surface and diffusion through membrane are more likely to be the controlling steps. For the sorption step, selectivity is more dependent on the affinity between the membrane and the permeants [5]. Increasing heating temperature or time will likely increase the degree of crosslinking among PVA, MA and TEOS, and consequently increased the hydrophobicity of hybrid membranes upon depletion of hydrophilic – OH and -COOH groups (Figs. 1&2). The increased hydrophobicity will result in less sorption of water at the membrane surface.
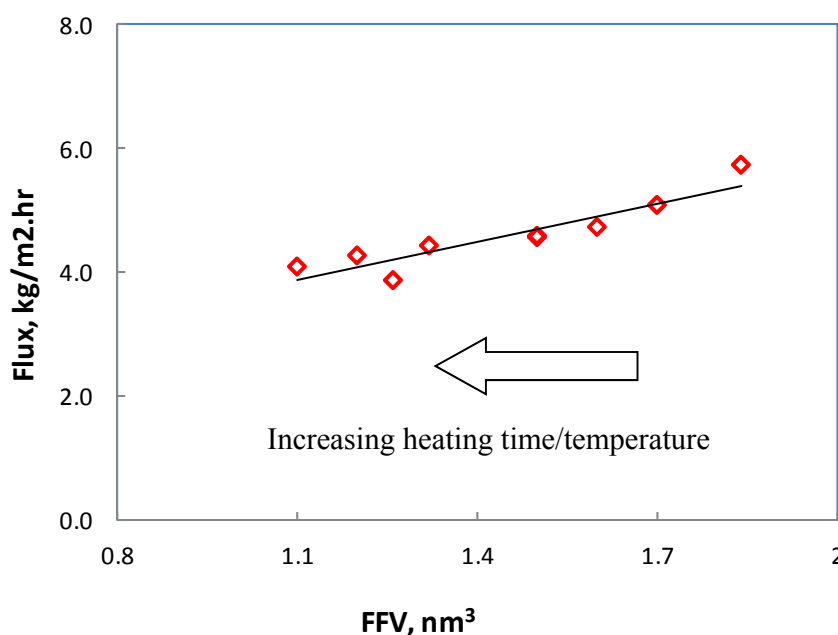

Figure 7: The water flux versus the fractional free volume (*FFV*) of hybrid PVA/MA/TEOS membranes (membrane containing 5 wt% MA and 10 wt% silica)

In addition, decreasing water flux with increasing heating temperature or time is fully supported by the free volume results analysed by PALS (Table 1). Figure 7 shows the relationship of water flux versus the fractional free volume. Water flux increased linearly with increasing FFV by means of controlling heat treatment time/temperature. In the diffusion step, the transport of molecules through the dense membrane is limited by the fractional free volume available in the membrane. At higher fractional free volumes, more water could be accommodated and consequenly diffused through the membrane, therfore enhanced water flux and overall mass transfer. Similar results were reported by Peng et al. [6] for a study of pervaporation properties of PVA-GPTMS hybrid membrane through PALS. As the free volume is closely related to the diffusion of molecules through the membrane, this close correlation of pervaporation properties of membrane and fractional free volumes confirms that the diffusion through membrane is the most likely controlling step of the pervaporation separation of aqueous salt solution.

Table 3 lists water transport properties of hybrid PVA/MA/TEOS membrane at different heat treatment conditions. As expected, both water solubility and water diffusivity generally decreased with increasing heating temperature or heating time.

This is mainly due to the reduced free volume that resulted from increased crosslinking and the compacted structure upon heat treatment (Table 1).

Table 3: Transport properties of water through hybrid membranes as a function of heat treatment conditions (membrane containing 5 wt% MA and 10 wt% silica).

Heat treatment temp, °C (2 hours)	Water solubility (dimensionless)	Water diffusivity $(x10^{-7} cm^2/s)$
Un-heated	382	1.59
100	105	1.41
120	58	1.30
140	54	1.27
160	49	1.11
Heat treatment time, hour (140°C)	Water solubility (dimensionless)	Water diffusivity $(x10^{-7} cm^2/s)$
Un-heated	382	1.59
2	58	1.27
5	52	1.21
16	41	1.19
24	40	1.14

Yasuda et al. [13] have proposed that the free volume theory of diffusion to interpret the water and salt diffusion through hydrogel. Based on Yasuda's version of free volume theory, water or salt diffusion coefficients vary exponentially as reciprocal free volume varies. Figure 8 shows the NaCl and water diffusivity as a function of fractional free volume. In this study, two independent methods adopted by other researchers [14, 15] have been used for estimating diffusivity of NaCl and H_2O respectively. For this reason, no absolute values of NaCl and H_2O diffusivity were compared. Rather, only relative changes under various heat treatment conditions were compared. As can be seen, both water and NaCl diffusivity increased exponentially with decreasing 1/*FFV*. When 1/*FFV* increased from 0.54 to 0.91, water diffusivity decreased about 30% while NaCl diffusivity decreased about 10 times. This indicates that changing free volume has more pronounced effect on NaCl diffusivity than water diffusivity. A similar finding was also reported by Ju et al. [14]. These results agree well with the free volume theory for which the transport properties of the larger penetrant are more sensitive to changes in free volume than those of smaller penetrant. In our study, hydrated NaCl is the larger penetrant and water is the smaller penetrant. Therefore, it is expected that increasing free volume will increase the water flux but decrease water/NaCl selectivity (i.e. salt rejection).
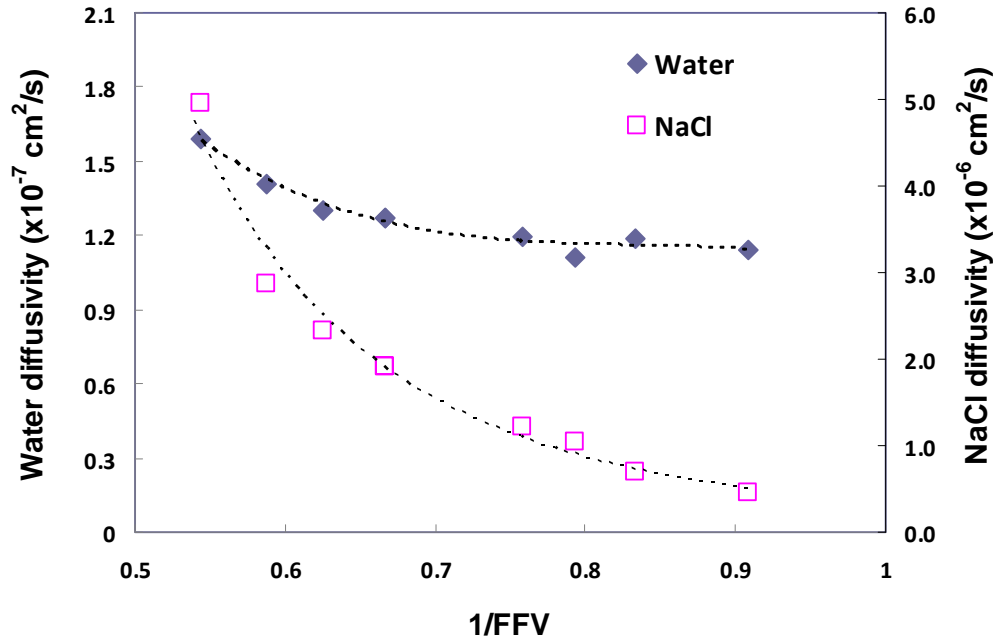
Figure 8: NaCl and water diffusivity of hybrid PVA/MA/silica membranes as a function of 1/*FFV* (membrane containing 5 wt% MA and 10 wt% silica).

4. Conclusions

Hybrid organic-inorganic membranes based on PVA, MA and TEOS were synthesised via a sol-gel route. The synthesised hybrid membranes underwent different heat treatment conditions and were tested for pervaporation separation of aqueous salt solution. Heating temperature and heating time were found to strongly affect the microstructure and pervaporation performance of membranes. It was proposed that increasing heating temperature or time favoured the completion of the crosslinking reactions among PVA, MA and TEOS, and also favoured the polycondensation reaction of TEOS. This resulted in a less hydrophilic membrane with reduced swelling and smaller fractional free volume. NaCl diffusivity and permeability decreased with increasing heating temperature or time. This was in agreement with the water uptake results, supporting the hypothesis of hydrated NaCl being solvated by the water in the membrane phase. Upon increasing heating temperature or time, the water flux reduced but the salt rejection increased. The pervaporation properties of hybrid membranes upon heating were attributed to the free volume change characterised by PALS. There were strong correlations between water flux and fractional free volume, and mass transfer coefficient and fractional free volume of the membrane. Increasing heating temperature or time changed the microstructure of PVA/MA/TEOS membrane and consequently reduced the free volume of the membrane. Therefore, there was less water accommodated in the membrane for water transport during the diffusion step. Consequently, the water flux decreased. Both NaCl and water diffusivity increased exponential with decreasing 1/FFV, and NaCl diffusivity was more sensitive to the change of FFV than water diffusivity, in agreement with free volume theory.

Acknowledgements

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