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Theoretical Studies on Structural and Electrical Properties of PES/SPEEK Blend Nanofiltration Membrane

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Polyethersulfone (PES) nanofiltration membranes were prepared using a simple dry-jet wet spinning technique with different contents of sulfonated poly(ether ether ketone) (SPEEK) ranging from 0 to 4 wt %. The structural parameters (r_p *and* $A_k/\Delta x$*) and electrostatic properties (*ξ *and* X*) of the blend membranes were deduced by employing the combination of irreversible thermodynamic model, steric hindrance pore (SHP) model, and Teorell-Meyer-Sievers (TMS) model. The modeling results obtained have been analyzed and discussed. The mean pore radius and pore size distribution of the blends were also determined based on the theoretical models. The results showed that pore radius increased with increasing the concentration of SPEEK from 0 to 2 wt % but decreased with a further increase in SPEEK content. The water flux, however, showed a systematically increase with increasing SPEEK content. The SPEEK also showed significant effect on membrane electrical properties. Both effective charge density and ratio of effective charge density to electrolyte solution increased with increasing concentration of SPEEK in the dope solution, reaching a value of* -21.02 *and* -2.29*, respectively. The pore radius which was determined by using different transport models has also been analyzed and discussed. It is found that the addition of SPEEK into dope solution is one of the paramount parameters in developing the negatively charged nanofiltration membrane with enhanced water flux while retaining the pore radius in the nanometer range.* *AIChE J,* 55: 2081–2093, 2009

Keywords: nanofiltration, steric-hindrance pore model, Teorell-Meyer-Sievers model, sulfonated poly (ether ether ketone), membrane separation

Introduction

Nanofiltration (NF) membranes which are positioned between ultrafiltration (UF) and reverse osmosis (RO) membranes have generated great interest in the field of process separations due to their excellent performances in the rejection of small molecular weight of neutral solutes (200–1000 Da) and divalent salts. Therefore, many describe NF membranes as a process with pores in the near- and subnanometer range (≤1 nm). Mostly, NF membranes are either negatively charged or positively charged. The fixed charges typically can be developed by the dissociation of appropriate chemical functional groups such as sulfonic acid (—SO_3H) or carboxylic acid group (—COOH). The presence of these ionic groups is able to improve salt rejection at a low operating pressure compared with RO.[1–5] In general, NF membranes

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with negatively fixed charge ions are preferentially applied as they show a higher salt rejection compared with neutral surface membranes. The negatively charged membranes can be prepared through the introduction of ionic groups on surface of polymeric membranes via interfacial polymerization technique[5–8] or single step fabrication by using charged polymeric material as the main membrane forming or as an additive.[9–11] To develop high performance membrane, additive or secondary polymer is frequently used in the membrane forming system as it offers a convenient and effective way to control the membrane structure.

Sulfonated poly(ether ether ketone) (SPEEK) is one of the charged polymeric materials that has been widely used for the development of proton conducting membranes due to its good thermal stability and adequate conductivity.[12–14] However, there are few studies on membrane fabrication for the purpose of separation processes using SPEEK as an additive. Therefore, it is of great theoretical and practical significance to study in detail the properties of NF membranes blended with SPEEK. Moreover, polymer blending is a proven tool to obtain new types of membranes with diversity of properties and possibly combined characteristics of the pure components.

Bowen et al.[15] noted the effect of small percent of SPEEK as an additive for improving the performances of polysulfone (PSf)/SPEEK blend membranes. The dope solutions were prepared by dissolving PSf and SPEEK into *N*-methly-2-pyrrolidine (NMP) blend solvent. SPEEK, however, is only miscible with PSf in NMP over a small range of SPEEK/PSf ratio. The increasing SPEEK content from 0.1 wt % to 1 wt % (total wt %) increased both the hydrophilicity and effective charge density of resulting membranes, causing the significant enhancement in the water flux and salt rejection. A small decrease in pore size and surface roughness was also followed by an increase in SPEEK content. The decreased pore size with the dope concentration is due to the higher viscosity of dope which hindered the diffusion exchange between solvent and nonsolvent during demixing process. On the contrary, Bowen et al.[15] observed that a further increase of SPEEK content to 2.5 wt % (or 10 wt % in the polymer blend) would produce many defects on the surface and consequently resulted in extremely high flux but low salt rejection. Thus, it is worthy of further investigation.

In a recent work, Arthanareeswaran et al.[16] investigated the effect of SPEEK content on the performance of PSf UF membranes by varying SPEEK content from 0 to 2.6 wt %. The results demonstrated that the flux, pore radius, and porosity of the membrane prepared increased with increasing SPEEK concentration in the casting solution. At higher SPEEK concentration, the precipitation is faster and demixing of dope solution is much easier to occur, leading to a more porous structure. This can be attributed to the fact that addition of large amount of hydrophilic polymer made the dope solution closer to the binodal line for phase separation. A similar phenomenon was also reported elsewhere.[17] The authors, however, did not take into account the effect of ionic charges introduced by SPEEK in the salt removal.[16,17] On the other hand, He et al.[18] developed PES NF membranes with a SPEEK as the top coating layer. The SPEEK coated membranes were found to have higher chemical resistance and higher ion exchange capacity compared with other sulfonated polymers. Moreover, the NF membranes with various properties are also possible to be developed using different sulfonation degree of SPEEK, which would result in different values of ion exchange capacity. The results proved that the salt rejection rates were increased by an increase in the coating thickness and SPEEK concentration in the coating solution.

Blends of PES with SPEEK could be an attractive alternative in developing membrane with a charged surface. It is generally agreed that by incorporating the SPEEK into the membrane, the membrane will possess negative charges and becomes more hydrophilic due to the presence of sulfonic acid group. As a consequence, these would enhance the membrane performances in terms of water flux and salt rejection. On the other hand, we also found that information given by the membrane manufacturers is too limited, commonly only the polymer material and separation efficiency on certain type of solutes and/or salts at specific conditions are mentioned. Therefore, it is an urgent need to study the relationships between the membrane characteristics and SPEEK content used.

Research works had been carried out to clarify theoretically the separation ability of a membrane and to investigate the rejection dependency on pore radius, ratios of membrane porosity to membrane thickness and charged density of membrane so that optimized and high performance membrane can be produced. The structural features and effective charged density of a membrane can be determined by means of diffusion experiments using aqueous solution of neutral solutes and strong electrolytes based on the theoretical models. These parameters play a main role in developing models and flux precision of different kinds of membranes.[19]

In the previous studies, we reported that the fine structural details of cellulose acetate (CA) NF membranes that could be deduced by employing the theoretical models.[20] The findings of this study demonstrated that the shear rate has a great influence on the structural and electrical properties due to the shear induced molecular orientation in the skin layer of the membrane. The data obtained also revealed that the NF membranes had achieved the standard of 29 commercial available NF membranes. Using the same approach, the effects of shear rate and polymer concentration on the structural properties and NF membrane performance were also investigated and reported elsewhere.[21]

Recently, investigation on the relationship between the additive concentration of polyvinylpyrrolidone K30 (PVP K30) on the membrane performance and structural properties was also reported by Ismail and Hassan.[22] It is found that the modeling results were able to provide valuable information of the morphological and electrostatic properties of the membranes prepared. Wang et al.[23] also evaluated the pore radii and fixed charge density of four commercial NF membranes from the permeation experiments based on the theoretical models and proposed a simple empirical equation to represent the dependency of fixed charge density on NaCl concentration for the membranes. Apart from pore radius and fixed charge density, characterization of membrane in terms of mean pore size and pore size distribution is also important. Wang et al.[24] applied the characterization method based on the separation of solutes of known sizes which is proposed by Michaels.[25] It is found that the correction between separation and the Einsten-Stokes radius of solute fits the log-normal distribution very well. The model proposed by Michaels, however, does not take into consideration the Donnan exclusion effect on the solute rejection.

The objective of the present article is to investigate the effect of SPEEK concentration on the fine morphological details and electrical properties of the NF membranes by employing the theoretical models. Based on the quantitative analysis of the experimental results and modeling data, it is expected that it would provide a better understanding for the relation of the SPEEK concentration to the membrane separation performances and membrane properties. To the best of our knowledge, the deduction of structural and electrical properties of PES NF membranes incorporating SPEEK is the first attempt in developing membrane material for low MW neutral solute and salt rejection.

Theoretical Background

The structural parameters (e.g., r_p and $A_k/\Delta x$) and electrical properties (e.g., ξ and X) play a vital role in developing models for rejection and flux previsions of membrane. Therefore, the experimental determination of these parameters is of prime importance. Because of the limitations of the available measurement techniques at the nanometers length scale, one has to carry out retention experiments using test solutes for the determination of the membrane parameters based on the theoretical models.

Irreversible Thermodynamic Model

In the pressure-driven NF processes, the transport phenomena in the process can be described by irreversible thermodynamics model. The solute flux, J_s through NF membrane was originally proposed by Kedem and Katchalsky[26] and can be expressed by the following equation:

$$J_s = P(C_m - C_p) + (1 - \sigma)J_v C \tag{1}$$

where P is the solute permeability, C_p is the concentration of solute in the permeate solution, C_m is the concentration of solute in the fluid at the feed/membrane interface, σ is the reflection coefficient, J_v is the volume flux, and C is the mean concentration over the thickness of membrane

The terms on the right hand side of Eq. 1 represent the transport of components due to diffusion and convection. The diffusion component is dependent of solute concentration whereas the convection component is proportional to the applied pressure. Based on the simple phenomenological transport model, it should be realized that retention is not only dependent on the flux but also on the solute concentration. Spiegler and Kedem[27] further expressed the flux of solute, J_s in a differential form when high concentration difference between the retentate and the permeate exists:

$$J_s = -P'\left(\frac{dc}{dx}\right) + (1 - \sigma)J_v C \tag{2}$$

where P' is the local solute permeability, defined as $P' = P{\cdot}\Delta x$. Spiegler-Kedem equation (SK) can be expressed as follows by integrating Eq. 2 across the membrane thickness:

$$R = 1 - \frac{C_p}{C_m} = \frac{\sigma(1 - F)}{(1 - \sigma F)} \tag{3}$$

where

$$F = \exp\left(-\frac{1 - \sigma}{P} J_v\right) \tag{4}$$

In this study, it is reasonable to assume that the real rejection is same as the observed rejection due to the low concentration of feed solution as well as the cross-flow filtration system applied. In general, osmotic pressure increases with increasing the solute concentration, leading to an increase in solute concentration at the membrane surface compared with the bulk solution.[28,29] The concentration polarization, however, is insignificant in this study because the cross-flow velocity tends to minimize the accumulation of rejected solutes and further reducing the boundary layer thickness at the feed/membrane interface causing the concentration polarization modulus close to be 1. Therefore, the solute concentration at the membrane surface, C_m is considered to be similar as in the bulk solution, C_b.

By substituting Eq. 4 into Eq. 3, a well-known SK equation can be rearranged and described by the following equation.

$$R = \frac{\sigma(1 - \exp(-\frac{1-\sigma}{P} J_v))}{1 - \sigma \exp(-\frac{1-\sigma}{P} J_v)} \tag{5}$$

Referring to the above equation, the retention, R increases with an increase of the solvent flux. Therefore, one can assume that the retention, R becomes equal to the reflection coefficient, σ (maximum solute rejection) when the volume flux, J_v is infinite as the filtration flow overtakes solution diffusion. σ and P can be determined directly from the experimental data of R as a function of $1/J_v$ using one of the best-fitting methods. Based on the irreversible thermodynamic model, membrane is treated as a black box because no information about the membrane properties can be obtained from it. To further evaluate the membrane properties, theoretical models such as steric-hindrance pore model and Teorell-Meyer-Sievers (TMS) model are considered.

Steric-Hindrance Pore Model

Nakao and Kimura[30] proposed that steric-hindrance pore (SHP) model can be used to determine the pore radius r_p and ratio of porosity to thickness of a membrane $A_k/\Delta x$ if the system only consists of single neutral solute. These parameters can be written as follows:

$$\sigma_s = 1 - H_F S_F \tag{6}$$

$$P_s = H_D S_D D_s (A_k/\Delta x) \tag{7}$$

where H_F and H_D are the steric parameter related to wall correction factors in convection coefficient and diffusion coefficient, respectively, and S_F and S_D are the distribution coefficient of solute in convection condition and diffusion condition, respectively. The H_F, H_D, S_F, and S_D parameters as expressed in the SHP model can be calculated from the following equations:

Table 1. The Diffusion Coefficient and Stokes Radius of Neutral Solutes and Sodium Chloride

Solute	AW/MW	D_s (10^{-9} m^2 s^{-1})	r_s (10^{-9} m)
PEG 200	200	0.537	0.376
PEG 400	400	0.389	0.518
PEG 600	600	0.323	0.624
PEG 1000	1000	0.255	0.790
Na^+	23	1.33	0.184
Cl^-	35.5	2.03	0.121
NaCl	58.5	1.61	0.152

$$H_F = 1 + \frac{16}{9}\lambda^2 \tag{8}$$

$$H_D = 1 \tag{9}$$

$$S_F = (1-\lambda)^2\left[2-(1-\lambda)^2\right] \tag{10}$$

$$S_D = (1-\lambda)^2 \tag{11}$$

where λ is ratio of solute radius (r_s) to pore radius (r_p).

Teorell-Meyer-Sievers Model

Teorell-Meyer-Sievers (TMS) model is a rigorous approach that has been widely used to describe quantitatively the electrical properties of NF by assuming uniform radial distribution of fixed charges and mobile species on membrane surface.[20–23] By combining the extended Nernst-Planck model and the Donnan equilibrium theory, the parameters σ_{salt} and P_{salt} of a membrane can be determined using a mono–mono type electrolyte (NaCl) as feed solution.

$$\sigma_{salt} = 1 - \frac{2}{(2\alpha - 1)\xi + \sqrt{(\xi^2 + 4)}} \tag{12}$$

$$P_{salt} = D_s(1-\sigma_s)(A_k/\Delta x) \tag{13}$$

where α is the transport number of cation in free solution defined as $D_{cation}/(D_{cation} + D_{anion})$ and ξ is the effective volume charge density of membrane to the electrolyte concentration of feed solution defined as X/C.

Apart from σ_{salt} and P_{salt}, the diffusion coefficients of the cation and anion of the salt are also required for the electrical properties characterization. These coefficients as shown in Table 1 can be determined by the Stokes-Einstein equation, as in Eq. 14.

$$D_i = \frac{kT}{6\pi\mu r_i} \tag{14}$$

where k, T, μ, and r_i are Boltzmann's constant, temperature, solvent viscosity, and ion radius, respectively.

Mean Pore Size and Pore Size Distribution

Many methods have been used for pore size determination. One of the simplest and direct methods is through the field emission scanning electron microscope. However, in fact, the result is not reliable as the heavy metal that is coated on the sample during coating process may induce some damage to the surface. Because of this reason, the measurement of the mean pore size is generally conducted by means of solute transport method. The method has been carried out by doing filtration experiments with aqueous solution of different neutral solutes. As reported by Micheals,[25] a linear relationship can be yielded when the solute rejection of UF membrane is expressed by a log-normal probability function of known solute diameter.

$$F(R) = A(ln\, d_s) + B \tag{15}$$

where A and B are the slope and the intercept, respectively. Employing the solute transport method, the mean pore size (μ_p) and the geometric standard deviation of membrane (σ_p) can be considered to be same as the solute mean size (μ_s) and solute geometric standard distribution of the membrane (σ_g) by neglecting the effect of both steric and hydrodynamic interaction between solute and pore.[31] The relationship of the solute rejection as a function of known solute diameter can be expressed as:

$$R = erf(y) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{y} e^{(-u^2/2)}du, \quad \text{where } y = \frac{ln r_s - ln \mu_s}{ln \sigma_g} \tag{16}$$

where r_s is the solute radius, μ_s the geometric mean radius of solute molecule at $R = 50\%$, and σ_g is the geometric standard deviation about the mean radius determined from the ratio of r_s at $R = 84.13\%$ and at 50%. In this article, the solute radiuses as shown in Table 1 were determined using Eq. 17 as described by Bowen and Mohammad.[32]

$$\log r_s = -1.4854 + 0.461 \log \text{MW} \tag{17}$$

where r_s and MW are Stokes radius ($\times 10^{-9}$ m) and molecular weight (kg/kmol), respectively. Based on these experimental data obtained from the above equations, the pore size distribution of a membrane can be calculated based on the probability density function as described in the following equation:

$$\frac{dR(r_p)}{dr_p} = \frac{1}{r_p ln\, \sigma_p \sqrt{2\pi}} exp\left[-\frac{(ln\, r_p - ln\, \mu_p)^2}{2(ln\, \sigma_p)^2}\right] \tag{18}$$

where r_p is the pore radius. Compared with the Gaussian distribution, the log-normal probability density function holds the distinct advantage as only the pore radius in the range of 0 to ∞ be integrated.

Experimental

Materials

The membrane material, polyethersulfone (PES Radel A300) was purchased from Amoco Chemicals. Poly(vinyl) pyrrolidone (PVP K15, average MW 10,000) and NMP purchased from Fluka were used as the blend polymer and

Table 2. Dope Formulations of Hollow Fiber Blend Membranes

Components	Dope Formulation (wt %)				
	PES	PES/SPEEK 1	PES/SPEEK 2	PES/SPEEK 3	PES/SPEEK 4
Polyethersulfone	20	20	20	20	20
N-methyl-2-pyrrolidone	70	70	70	70	70
Polyvinylpyrrolidone	10	9	8	7	6
Sulfonated poly(ether ether ketone)	–	1	2	3	4

solvent. Poly(ether ether ketone) (PEEK) obtained from Victrex US Inc. Ltd in powder form was used as additive to enhance the electrical properties of the membranes. Neutral solutes, poly(ethylene glycol)s (PEGs) from Aldrich and inorganic salt, sodium chloride (NaCl) from Merck, were used to characterize membrane structural and electrical properties. All the chemicals used in the experiments were analytical grade and were used as received without further purification. The solutions used in all experiments were prepared using distilled water.

Sulfonation of PEEK

The sulfonation procedures of PEEK were similar as reported previously.[33] PEEK is sulfonated in solution using a sulfonating acid solvent to produce ion-containing polymer bearing HSO_3^- groups. In this study, the SPEEK solution was prepared by dissolving 45×10^{-3} kg of PEEK in 1×10^{-3} m^3 of concentrated H_2SO_4. After completing the dissolution of PEEK, the temperature was controlled at 328 K (±2 K) and was stirred thoroughly for 3 h before the acid solution was poured into large excess of ice water where the SPEEK would be precipitated. The precipitate was then washed with distilled water until the pH was nearly 7. To remove residual water completely, SPEEK was then dried in an oven at 343 K for at least 2 days before it was ready to be used.

Dope solution and hollow fiber membrane preparation

In the preparation of the dope solutions, five different batches of dope formulations were prepared (See Table 2 for details). SPEEK was first dissolved into the mixture of NMP and PVP in a flange reaction flask and stirred continuously. The dried PES was then added slowly into the mixture once SPEEK was completely dissolved in the solvent. The solution was stirred continuously overnight to obtain a homogeneous dope solution. At last, the solution was degassed at room temperature to remove any microbubbles that might exist.

Table 3 summarizes the experimental parameters of spinning hollow fiber membranes. The membranes were spun according to the well-known dry-jet wet spinning method, using a setup in which the take-up velocity of the fibers was nearly the same as the falling velocity of fibers in the external coagulation bath (water). The detailed description for hollow fiber spinning can be found in the previous work.[34] The as-spun membranes were stored in water bath at room temperature for 1 day to remove the residual NMP and then post-treated by immersing in a glycerol aqueous solution of 10 wt % for another 1 day. The membranes were then air-dried at room temperature before they were used for making test modules.

Fourier transform infrared and nuclear magnetic resonance

Fourier transform infrared (FTIR) studies for the PEEK and SPEEK samples were conducted using Nicolet-Magna 560 IR spectrometer in the wave number between 500 cm^{-1} and 4000 cm^{-1}. To determine the degree of sulfonation of SPEEK polymer, hydrogen nuclear magnetic resonance analysis (^{1}H NMR) was conducted using Bruker Avance 300 NMR spectrometer at a resonance frequency of 300 MHz for ^{1}H. Before the test, approximately 3 wt % SPEEK polymer was dissolved in the deuterated dimethy sulfoxide (DMSO-d_6) for the purpose of analysis. The chemical shift of tetramethylsilance was used as the internal standard reference.

Membrane performance evaluation

All the permeation tests were carried out using laboratory-scale cross-flow filtration unit. The hollow fibers were potted into bundles consisting of 50 fibers of approximately 20 cm long. The feed was permeated through the shell-side of the hollow fibers, and permeate was collected from the lumen side. The pressure was controlled to the desired trans-membrane pressure by adjusting the back-pressure regulator. The feed concentration was assumed to remain constant during permeation test as small amount of permeate was collected for TOC analysis. The neutral solute concentration in the feed and in the permeate was determined using TOC-$V_{CSH/CSN}$ analyzer (Shimadzu, Japan). To realize the separation efficiency of NaCl, the retention *R* was calculated according to the formula:

$$R_{\text{salt}}(\%) = \left(1 - \frac{C_{\text{p}}}{C_{\text{f}}}\right) \times 100 \qquad (19)$$

Table 3. Spinning Conditions of Hollow Fiber Blend Membranes

Parameter	Value for Spun Fiber
Dope flow rate (m^3 s^{-1})	5.83×10^{-8}
Bore fluid composition	Water
Bore fluid rate (m^3 s^{-1})	1.95×10^{-8}
Bore fluid temperature (K)	300
Air gap distance (m)	0.1
External coagulant	Water
Coagulant temperature (K)	300
Take-up speed (m s^{-1})	0.24
Dimension of spinneret (10^{-6} m)	i.d./o.d. 290/600
Humidity (%)	60

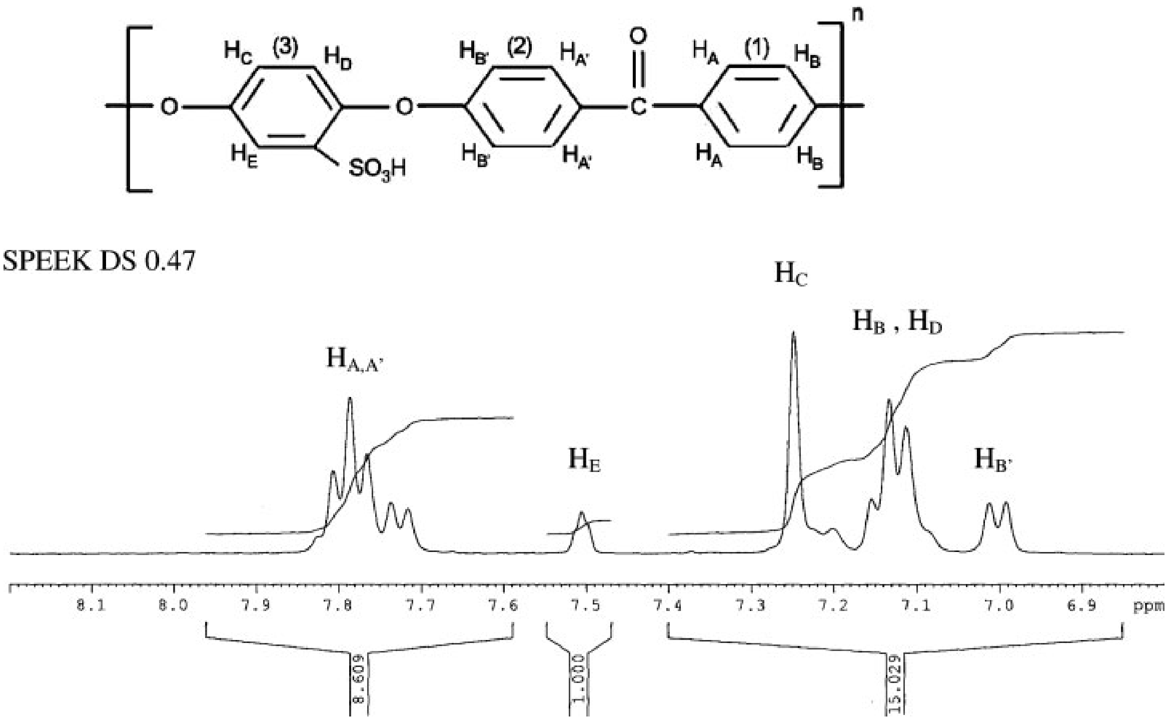

Figure 1. Nomenclature of the aromatic protons for the SPEEK repeat unit and its ^{1}H NMR spectrum.

where C_p is the concentration of permeate and C_f is the feed concentration. The concentration of the solutions was measured with a conductivity meter (EC300, YSI Inc).

Results and Discussion

^{1}H NMR calculation

The presence of the SO_3H group resulted in a distinct signal of protons H_E at 7.5 ppm as shown in Figure 1. The intensity of H_E signal may be used for determination of the H_E content which is equivalent to the DS of SPEEK per repeat unit. The DS of SPEEK can be estimated from the ratio between the peak area of the distinct H_E signal (A_{H_E}) and the integrated peak area of all the other aromatic hydrogens ($A_{H_{A,A',B,B',C,D}}$) as shown on the bottom of Figure 1 using the following mathematical expression.[35–37]

$$\frac{DS}{12-2DS}=\frac{A_{H_E}}{\sum A_{H_{A,A',B,B',C,D}}} \qquad (0 \le DS \le 1) \qquad (20)$$

At low DS of SPEEK (~0.4), the H_C and H_D of the unsubstituted hydroquinone ring of PEEK repeat units in the SPEEK polymer appeared as a characteristic singlet at 7.25 ppm and 7.11 ppm, respectively.[36] The two $H_{B'}$ protons were a doublet at 7.00 ppm whereas the remaining H_B protons absorbed at 7.15 ppm. Based on Eq. 20, it is found that the DS of the SPEEK prepared under given experimental conditions was 0.47. This indicated that the SPEEK has little chance to be leached out of the blend membranes prepared during permeation test due to its insolubility in water at room temperature.[38,39] Huang et al.[38] reported that only highly sulfonated SPEEK (DS > 0.99) could dissolve perfectly in hot water.

FTIR analysis of the SPEEK

FTIR spectra were performed on PEEK and sulfonated PEEK polymer to confirm the chemical structures of the SPEEK polymer. As shown in Figure 2, the presence of two absorption peaks of SPEEK at 1021 cm^{-1} and 1078 cm^{-1} shows the characteristic peak for aromatic symmetric and asymmetric stretching vibration of O=S=O group present in the sulfonic acid group of SPEEK. These bands were in close agreement with the results reported by Jaafar et al.[33] The peak identified at approximately 1221 cm^{-1} and 1486 cm^{-1} confirmed the presence of aromatic C—O—C structure

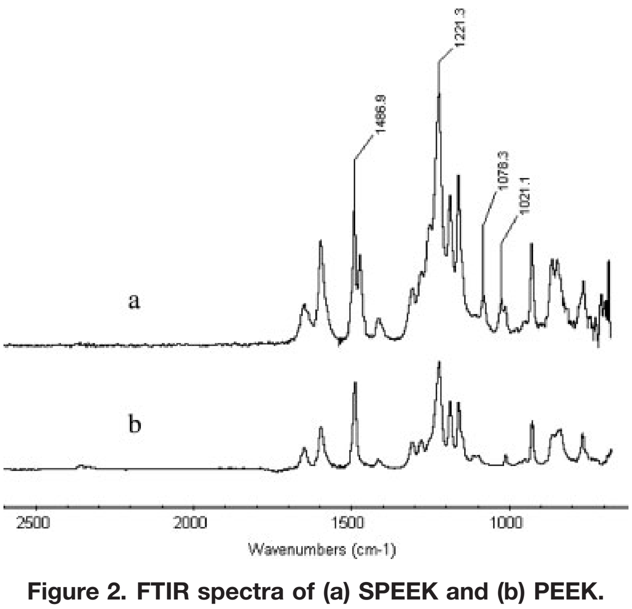

Figure 2. FTIR spectra of (a) SPEEK and (b) PEEK.

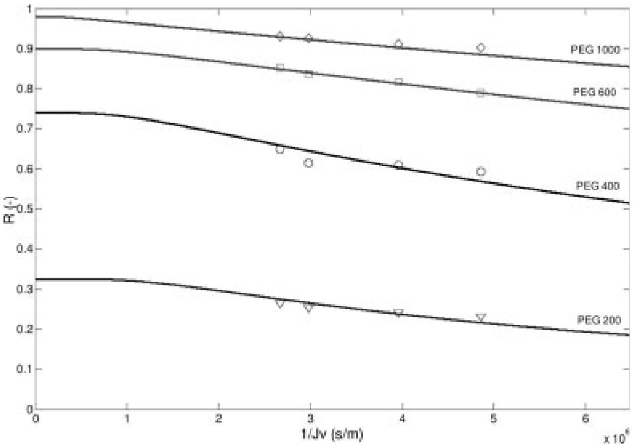

Figure 3. The neutral solute rejection of PES membrane as a function of volume flux.

and C—C aromatic ring, respectively, in the PEEK and SPEEK polymer.

Effect of SPEEK content on membrane structural parameters

To evaluate the effect of SPEEK content on the membrane performance, the pure water flux was first investigated. The experimental data show that at operating pressure of 6 bar, the membrane fluxes were increased from 3.75×10^{-7} m s^{-1} to 7.84×10^{-7} m s^{-1} as the SPEEK concentration was gradually increased from 0 to 4 wt %. This can be attributed to the change in the hydrophilic nature of the blend membrane upon the addition of higher concentration of SPEEK. A similar observation was also reported by Bowen et al.[15] that the increasing SPEEK content in membrane formation has systematically increased the water permeability of the PSf membranes. To determine the membrane pore radius, studies were conducted to obtain the membrane rejection rates and fluxes at various operating pressures using different MWs of PEG at a feed concentration of 200 ppm. Figure 3 shows the relationship between rejections of neutral solutes and volume fluxes of PES membrane. Higher rejection was obtained when higher MW of solute was used. The membrane parameters (P and σ) of other membranes which were determined by SK equation based on a best fit method are listed in Table 4. Based on the results obtained, the pore radius was estimated through reverse calculating of Eq. 6. The change in the structural details can be clearly viewed by plotting the membrane pore radius vs. the SPEEK content as shown in Figure 4. The graph shows that there was an increase in the membrane pore radius with increasing the SPEEK content up to 2 wt %. However, a further increase in the SPEEK concentration to 3 wt % and 4 wt % in the blends caused the membrane pore radius to decrease from 0.99 nm to 0.89 nm and 0.79 nm, respectively. The slight

Table 4. σ and P of Neutral Solutes and r_p and $A_k/\Delta x$ of Membranes Determined From Spiegler Kedem Equation and SHP Model, Respectively

Membrane	Neutral Solute	σ	P (10^{-7} m s^{-1})	λ	$A_k/\Delta x$ (m^{-1})	r_p (10^{-9} m)
PES	PEG 200	0.33	1.63	0.46	1058	0.81
	PEG 400	0.74	0.85	0.74	3209	0.70
	PEG 600	0.90	0.38	0.85	5321	0.73
	PEG 1000	0.98	0.24	0.94	24,017[a]	0.84
					3196 (av.)	0.77 (± 0.07)[b]
PES/SPEEK 1	PEG 200	0.30	2.25	0.45	1378	0.84
	PEG 400	0.51	1.75	0.60	2748	0.87
	PEG 600	0.75	1.03	0.74	4891	0.84
	PEG 1000	0.93	0.65	0.87	14,786[a]	0.91
					3006 (av.)	0.86 (± 0.03)[b]
PES/SPEEK 2	PEG 200	0.23	2.60	0.39	1299	0.97
	PEG 400	0.37	1.77	0.49	1778	1.05
	PEG 600	0.53	1.40	0.61	2822	1.03
	PEG 1000	0.93	1.00	0.87	22,747[a]	0.91
					1986 (av.)	0.99 (± 0.06)[b]
PES/SPEEK 3	PEG 200	0.31	2.80	0.46	1765	0.82
	PEG 400	0.46	2.40	0.56	3231	0.92
	PEG 600	0.70	1.30	0.71	4890	0.88
	PEG 1000	0.87	0.91	0.83	11,953[a]	0.95
					3295 (av.)	0.89 (± 0.06)[b]
PES/SPEEK 4	PEG 200	0.42	3.07	0.54	2651	0.70
	PEG 400	0.66	2.00	0.69	5302	0.75
	PEG 600	0.79	1.30	0.77	7675	0.81
	PEG 1000	0.93	1.00	0.88	26,348[a]	0.90
					5209 (av.)	0.79 (± 0.08)[b]

[a] These data were excluded for the average value of $A_k/\Delta x$.
[b] These data were the average value of r_p together with their standard deviation

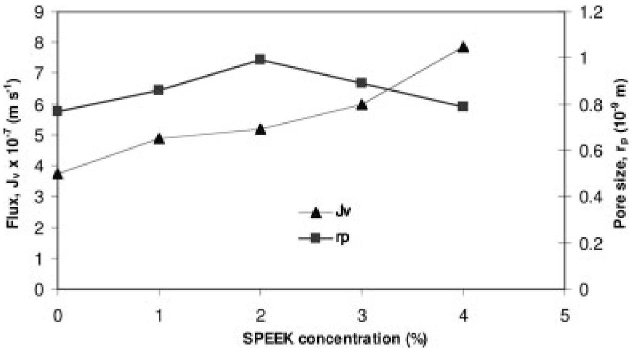

Figure 4. Fluxes and pore size of membranes at different SPEEK concentrations.

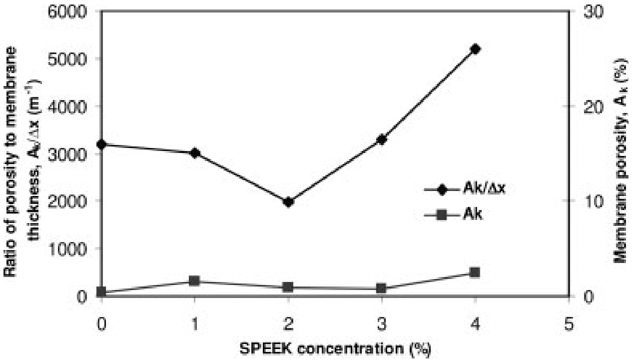

Figure 5. Ratio of membrane porosity to thickness and porosity at different SPEEK concentrations.

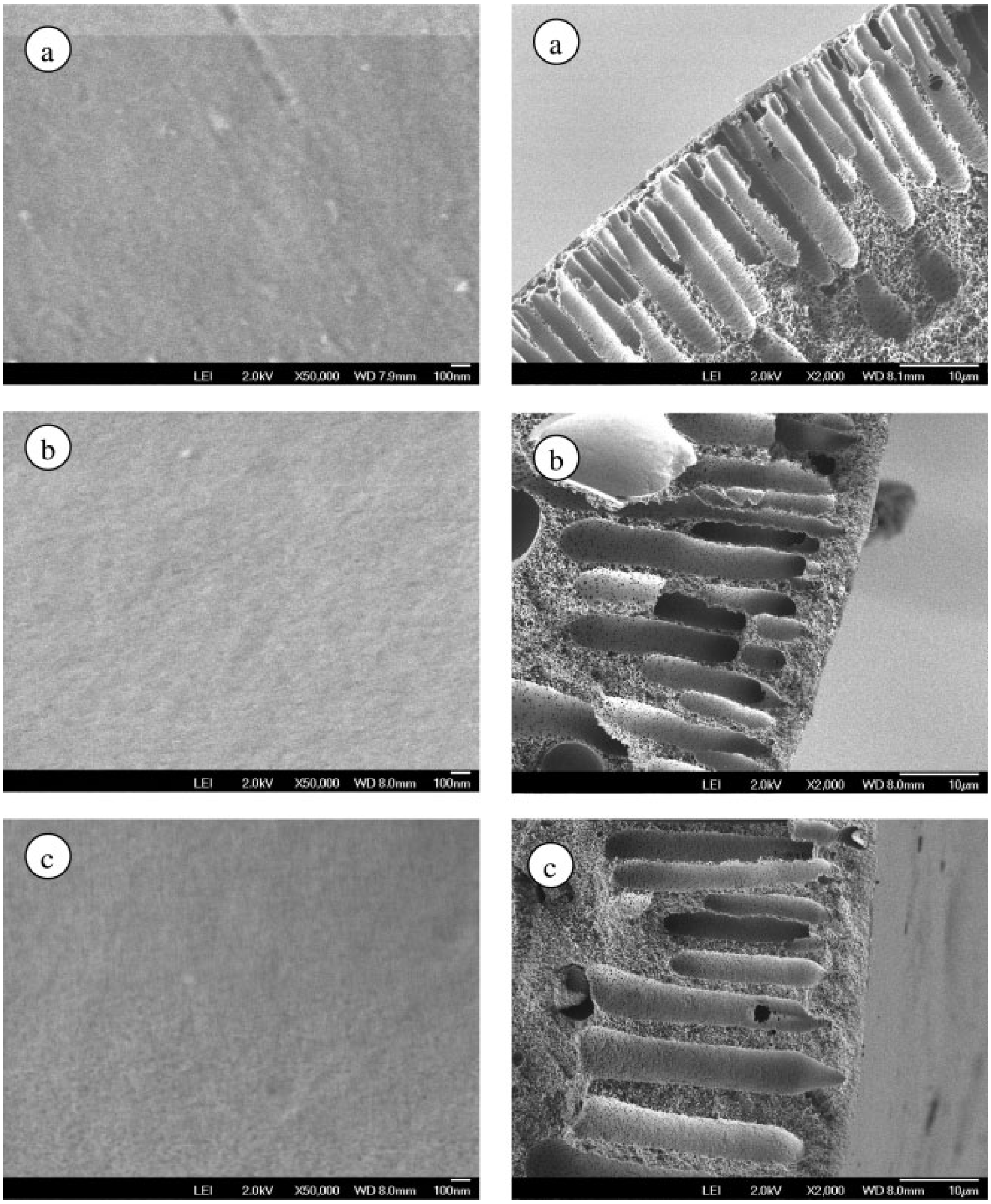

Figure 6. FESEM images of the outer membrane surface and near outer layer of (a) PES, (b) PES/SPEEK 2, and (c) PES/SPEEK 4 membrane.

decrease in the pore radius can be explained by the interactions between components in the dope solution and phase inversion kinetics. When the composition of SPEEK in the solution increased to higher than 2 wt %, a solution with higher viscosity is formed. The increase in viscosity hinders the diffusion exchange between solvent (NMP) and nonsolvent (water) from the coagulation bath and leads to a higher polymer concentration at the interface between polymer solution and nonsolvent. As a consequence, it leads to the formation of membrane with smaller pore radius on top surface which is in good agreement with the modeling results. Although there was a decrease in the membrane pore radius when high content of SPEEK was added, the membranes still gave systematic increase in the water fluxes. Thus, it is strongly believed that pore radius is not the only factor affecting the membrane flux, the highly hydrophilic characteristic of SPEEK in the blends may also contribute to the water transport mechanism. On the other hand, it is found that the fabricated NF membranes are in the range of pore radius of 29 commercial NF reported by Bowen and Mohammad,[40] indicating the fabricated NF has achieved a commercial standard.

Besides membrane pore radius, another structural property of membrane, $A_k/\Delta x$ can also be determined by employing SHP model. Based on SHP model, when r_p is known, parameters H_D and S_D can be calculated as they are the

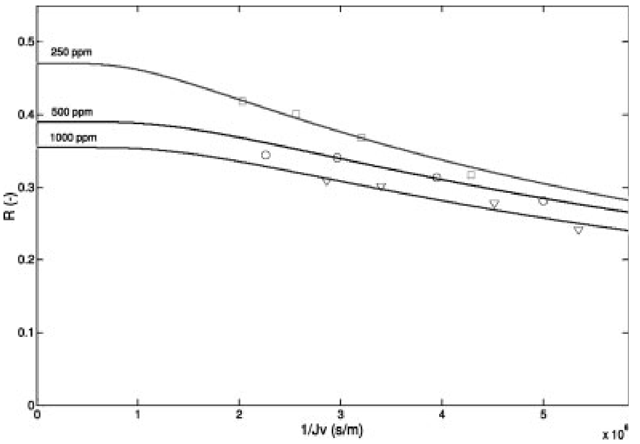

Figure 7. NaCl rejection of PES/SPEEK 2 blend membrane as a function of volume flux.

function of the ratio of solute radius to pore radius (r_s/r_p). The structural parameter, $A_k/\Delta x$ of all the studied membranes was then estimated in reverse by Eq. 7 and the results are summarized in Table 4. It can be seen that $A_k/\Delta x$ increased with increasing neutral solute size regardless of the membrane compositions.[11,23,41] As there was great deviation of the value $A_k/\Delta x$ between PEG 1000 with other low MWs of neutral solutes for all the membranes, therefore the data were excluded for calculation of the average values of $A_k/\Delta x$. It is because SHP model is not suitable to be applied for calculating $A_k/\Delta x$ when the reflection coefficient, σ is more than 0.90 due to highly restricted permeation.[23] Figure 5 shows the membranes $A_k/\Delta x$ were in the range of 1986 m^{-1} to 5209 m^{-1} and PES/SPEEK 4 blend membrane exhibited the highest value among the studied membranes. To increase confidence in the veracity of the modeling results, it is worth noting that porosity of membranes can be predicted based on the membrane top active layer thickness determined from the FESEM micrographs. The calculated porosity seems to be reasonably accurate for NF membranes which typically show very low porosity value due to the formation of dense skin layer. The results were further confirmed by studying the surface skin of membrane using FESEM, as shown in Figure 6. Clearly, no pores can be visually observed on the membrane surface even up to magnification of 50,000×, indicating the membranes prepared are in line with the performance of NF which exhibiting small pore size and low porosity. Overall, in this case, it can be concluded that pore size and porosity may not be the main factor influencing permeated flux as the enhancement in water flux is strongly influenced by the addition of SPEEK due to the enhanced hydrophilicity characteristic of the blend membranes.[3,15–17]

Effect of SPEEK content on membrane electrical parameters

Figure 7 shows the dependency of the salt rejection of PES/SPEEK 2 blend membrane on volume flux. It can be clearly seen that the higher the NaCl concentration, the lower the salt rejection was. The decrease in NaCl retention at high concentration is attributed to the Donnan exclusion effect. The Donnan exclusion effect becomes weaker with increasing electrolyte concentration due to a greater screening of the surface charge. According to Eq. 5, the salt rejection would reach the maximum value, which corresponding the reflection equation when the volume flux is infinite. Because of the limitation of SHP model in describing the effect of electrostatic properties on membrane, TMS model was applied to allow the evaluation of membrane electrostatic properties. Single electrolyte solution with a fixed NaCl concentration was used for evaluating the membrane performance as TMS model considers only electrostatic effect during the permeation. NaCl aqueous solutions with concentrations of 250 × 10^{-3} kg m^{-3}, 500 × 10^{-3} kg m^{-3} and 1000 × 10^{-3} kg m^{-3} were prepared individually for the evaluation. Based on Eq. 12, the electrical properties of the

Table 5. σ_{salt} and P_{salt} of Neutral Solutes and ξ and X of Membranes Determined From Spiegler-Kedem Equation and TMS Model, Respectively

Membrane	NaCl Solution (10^{-3} kg m^{-3})	σ_{salt}	P_{salt} (10^{-7} m s^{-1})	X (mol m^{-3})	ξ
PES	250	0.240	1.70	−5.40	−1.264
	500	0.215	0.40	−9.82	−1.149
	1000	0.206	1.39	−18.93	−1.108
				−11.39 (av.)	−1.174 (±0.081)[a]
PES/SPEEK 1	250	0.375	1.35	−8.32	−1.947
	500	0.349	1.20	−15.42	−1.804
	1000	0.247	2.35	−22.17	−1.297
				−15.30 (av.)	−1.683 (±0.342)[a]
PES/SPEEK 2	250	0.470	1.55	−10.89	−2.547
	500	0.390	1.25	−17.38	−2.033
	1000	0.355	1.29	−31.39	−1.836
				−19.88 (av.)	−2.139 (±0.367)[a]
PES/SPEEK 3	250	0.464	2.35	−10.70	−2.505
	500	0.400	2.50	−17.88	−2.092
	1000	0.355	2.95	−31.39	−1.836
				−19.99(av.)	−2.144 (±0.338)[a]
PES/SPEEK 4	250	0.470	2.45	−10.88	−2.547
	500	0.423	2.50	−21.71	−2.540
	1000	0.345	2.55	−30.47	−1.783
				−21.02(av.)	−2.290 (±0.439)[a]

[a] These data were the average value of ξ together with their standard deviation.

Table 6. Summary of the Characteristics of Self-Made Asymmetric NF Membranes

NF Membrane	[a]r_p (10^{-9} m)	X (mol m^{-3})
CA/formamide/actone[20]	0.37	9.15
PSf/DMAc/ethanol[21]	0.35	3.67
PES/NMP/H_2O/PVP K15[22]	0.59	4.05

[a]Mean values of pore radius and effective volume charge density of membranes prepared at different preparation conditions.

other membranes which were determined by SK equation are summarized in Table 5. From the table, the ξ of PES, PES/SPEEK 1, PES/SPEEK 2, PES/SPEEK 3, and PES/SPEEK 4 membranes were evaluated to be -1.17, -1.68, -2.14, -2.14, and -2.29, respectively. This indicates that the addition of SPEEK polymer into membrane has a significant effect on membrane surface charge.

Besides ξ, another electrical parameter X is also shown in Table 5. The value of X which is defined as the fixed charge density can be calculated based on the TMS model using Eq. 12. Several researchers proposed to use the effective fixed charge density (ϕ X) instead of X because the fixed charge density varies with the salt concentrations.[23,41] However, in this case, the values of X obtained from different NaCl concentrations are considered for calculating the average values of X as the main concern is to investigate the effect of SPEEK content on the X value. It is evident from Table 5 that as the SPEEK contents were increased, X values were also increased. In comparison with pure PES membrane, the blend membranes exhibited pronounced enhancement in X value when the SPEEK concentration was increased in the blends. Table 6 shows the developed blend NF have achieved higher standard of NF properties with respect to the effective volume charge density compared with the self-made asymmetric NF membrane which were prepared previously from CA, PSf, or PES individually.[20–22] The significant increases are mainly caused by the introduction of more ionic groups in the PES membrane. Figure 8 illustrates the effect of the SPEEK content on the ratio of volume charge density to the electrolyte concentration and water flux. Increasing the SPEEK content increased the negative surface charge of membrane which resulted in an increase of electrostatic repulsion between a negatively charged solute and membrane. As a consequence, salt rejection increased as more SPEEK was added to the membrane. Also, increase in the concentration of SPEEK also resulted in a higher water flux. Therefore, it is believed that the increase in both the surface charge and water flux may be due to the combination effects of hydrophilic nature and sulfonic acid groups introduced by SPEEK. It is worth mentioning that only sieving effect is considered for the single neutral solute permeation and only electrostatic effect is considered for the NaCl permeation through a NF membrane, therefore by combining both the steric and Donnan effect, the effect of SPEEK content on the morphological and electrical properties of the blends would become more understandable. Figure 9 shows the r_p and ξ of the membranes as a function of SPEEK concentration. By addition of SPEEK content up to 2 wt %, both r_p and ξ values have been increased. However, r_p decreased while ξ increased with further increasing the SPEEK content. Although r_p was decreased, it was still in the subnanometer ranges. To the best of our knowledge, decreased pore radius would not result in lower salt rejection as the rejection mechanism depends very much on the Donnan effect rather than the steric effect. These data provide valuable information of the structural and electrical properties of PES/SPEEK membranes as the combination of steric and Donnan effects between NF membrane and external solution play an important role in the separation of organic molecules and electrolytes.

Table 7. Geometric Mean Pore Size, μ_p and Geometric Standard Deviation, σ_p of Membranes

Membrane Type	[a]μ_p (10^{-9} m)	σ_p
PES	0.47	1.45
PES/SPEEK 1	0.55	1.42
PES/SPEEK 2	0.61	1.36
PES/SPEEK 3	0.56	1.44
PES/SPEEK 4	0.47	1.63

[a]Mean pore radius is determined at 50% rejection of solute.

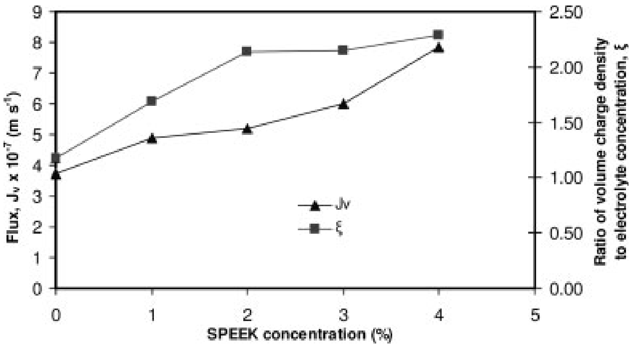

Figure 8. Fluxes and ratio of volume charge density to electrolyte concentration of membranes at different SPEEK concentrations.

Effect of SPEEK content on membrane pore size distribution

The values of the mean pore size and the geometric standard deviation of all the membranes were calculated from the

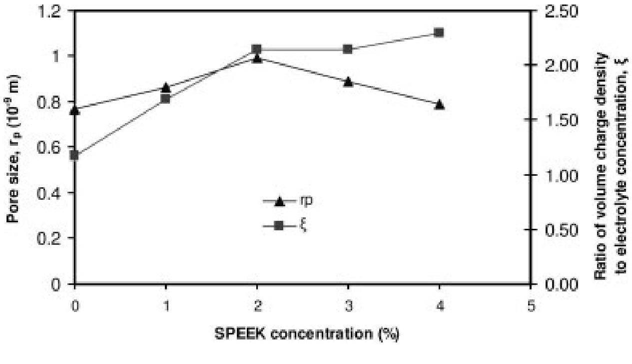

Figure 9. Pore size and ratio of volume charge density to electrolyte concentration of membranes at different SPEEK concentrations.

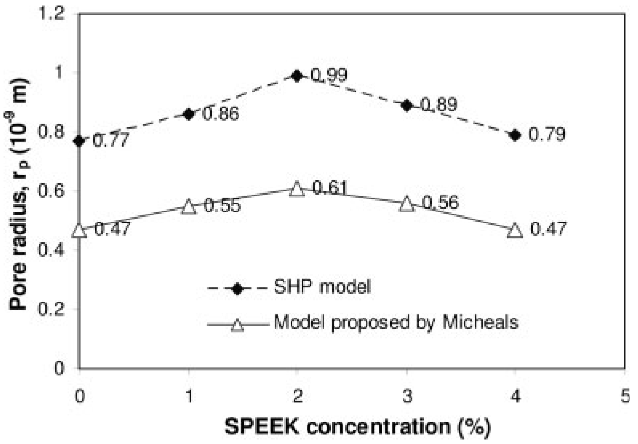

Figure 10. Comparison of membranes pore radius predicted by SHP model and model proposed by Micheals.[25]

data plotted using Eq. 16 and the results are presented in Table 7. Mean pore sizes ranged from 0.47 nm to 0.61 nm and geometric standard deviation ranged from 1.36 to 1.63 as determined from solute transport data. Mean pore size was the largest for the PES/SPEEK 2 membrane whereas it was the smallest for the PES and PES/SPEEK 4 membranes. It is found that there was not much difference for the values between the membranes. Overall, these values were close to each other. Compared with the pore radius predicted by SHP model, the mean pore sizes measured by the solute transport model (model proposed by Micheals) were about 0.3 nm to 0.38 nm smaller than that of calculated by SHP model, as shown in Figure 10. Similar to SHP model, the mean pore radius determined by solute transport model also referred to the percentage of neutral solute separation at different MWs, the only difference is that the solute separation efficiency at different volume fluxes is negligible. According to SK equation, at highly permeate volume flux the solute rejection will increase because the filtration flow overtakes solute diffusion. An increase in the water flux reduces the concentration of solute in permeate, thereby increasing solute rejection. Therefore, it is noteworthy that the pore radius obtained can vary as a consequence of fitting experimental rejection data with different transport models. Because of this reason, the pore radius predicted by the SHP model would be considered more accurate and reliable than the ones determined by solute transport model because it takes into account the interaction between the solvent (permeate) and the solute. However, to generate probability density function curves of membrane, the mean pore size, and the geometric standard deviation determined by solute transport model are the key parameters to be used for the evaluation. The probability density function curves as obtained by using Eq. 18 for the studied membranes are shown in Figure 11 as a function of pore sizes. In this figure, it is clear that the PES/SPEEK 3 and PES/SPEEK 4 membranes (Figure 11b) presented broader tailed pore size distribution than the membranes with lower SPEEK content or without presence of SPEEK (Figure 11a). This therefore resulted in lower peak values of the pore size distributions for the membranes. Furthermore, it is evident that there is a change in pore size distributions of the blends. Rightward shift of the pore size distribution curves was observed with an increase of SPEEK content from zero to 2 wt % in dope solution. However, leftward shift was experienced with further increasing SPEEK content, indicating a decrease in the pore size. The trend of changes in pore radius was in a good accordance with the results predicted by SHP model, though there was difference between the values of pore radius.

Conclusion

The separation performance as well as the structural parameters and electrical properties of the blend membranes at different SPEEK contents could be obtained using theoretical models. The theoretical results offer a better understanding on the effect of SPEEK concentration on the properties of the blends. Based on this study, the following conclusions have been drawn:

(a) The addition of small amount of SPEEK into PES membranes significantly enhanced the water flux due to the increase in hydrophilic nature of blend membranes.

(b) The blend membrane possessed the largest pore radius when 2 wt % SPEEK was added. With further increasing SPEEK content, decreased pore radius was observed in the membrane. The slight decrease in pore radius may be attributed to higher viscosity of the polymer solutions.

(c) The SPEEK shows a significant effect on membranes surface charge. Both X and ξ were increased with increasing SPEEK content. It is because of the introduction of $-SO_3^-$

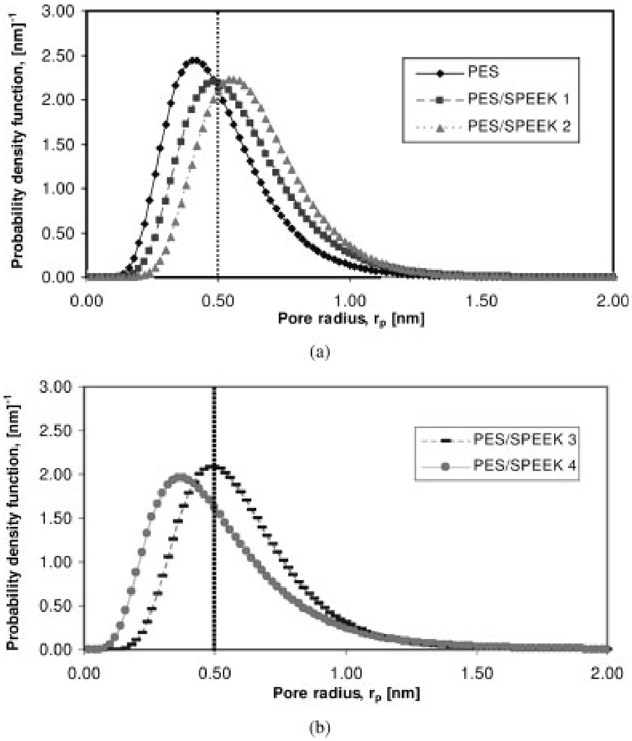

Figure 11. Probability density function curves as function of pore size for (a) PES, PES/SPEEK 1, and PES/SPEEK 2, and (b) PES/SPEEK 3 and PES/SPEEK 4 membranes.

ionic groups into membranes. This phenomenon resulted in a higher salt rejection without affecting the water flux.

(d) The results shown in probability density function curves were in good agreement with the results predicted by SHP model where pore radius increased with the addition of SPEEK content up to 2 wt % and started to decrease with further increasing the SPEEK content.

(e) The addition of SPEEK content has been proven to be one of the paramount parameters in developing the charged NF membrane with enhanced water flux while retaining the pore radius in the nanometer range.

Future Work

In the following study, we will investigate the effect of sulfonation degree of SPEEK at various contents on the morphological and electrical properties of PES membranes because higher degree of sulfonation is expected to increase the membrane surface charge thus resulting in higher salt rejection.

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Notation

$A_k/\Delta x$ = ratio of porosity to thickness of a membrane (m^{-1})
C = mean concentration over the thickness of membrane (mol m^{-3})
C_b = concentration of solute in the bulk solution (mol m^{-3})
C_m = concentration of solute in the fluid at the feed/membrane interface (mol m^{-3})
C_p = concentration of solute in the permeate solution (mol m^{-3})
d_p = the pore diameter (10^{-9} m)
d_s = the solute diameter (10^{-9} m)
D_s = the diffusivity of solute molecule in a dilute solution (m^2 s^{-1})
H_D = the steric parameter related to wall correction factors in diffusion coefficient
H_F = the steric parameter related to wall correction factors in convection coefficient
J_s = flux of solute (mol m^{-2} s^{-1})
J_v = volume flux (m s^{-1})
k = Boltzmann's constant (1.38×10^{-23} kg m^2 s^{-2} K^{-1})
P = solute permeability (m s^{-1})
P_s = solute permeability of salt (m s^{-1})
r_p = pore radius (10^{-9} m)
r_s = Stokes radius (10^{-9} m)
R = rejection (%)
S_D = the distribution coefficient of solute in diffusion condition
S_F = the distribution coefficient of solute in convection condition
T = absolute temperature (K)
Δx = membrane thickness (m)
X = effective volume charge density (mol m^{-3})

Greek letters

α = the transport number of cation in free solution
σ = reflection coefficient
σ_g = the geometric standard deviation about the mean diameter
σ_s = reflection coefficient of salt
λ = ratio of solute radius to pore radius
ξ = the ratio of effective volume charge density of membrane to the electrolyte concentration of feed solution
μ = solvent viscosity (water viscosity at 25°C, 0.8937×10^{-3} kg m^{-1} s^{-1})
μ_s = the geometric mean diameter of solute molecule at $R = 50\%$ (10^{-9} m)

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