Polyethersulfone flat sheet and hollow fiber membranes from solutions in ionic liquids

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ABSTRACT

We fabricated flat-sheet and hollow fiber membranes from polyethersulfone (PES) solutions in two ionic liquids: 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM]DEP) and 1,3-dimethylimidazolium dimethyl phosphate ([MMIM]DMP). The solvents are non-volatile and less toxic than organic solvents, such as dimethylformamide (DMF). The membranes morphologies were compared with those of membranes prepared from solutions in DMF, using electron microscopy. Water permeance, solute rejection and mechanical strengths were evaluated. Membranes were applied to DNA separation. While membranes based on PES were successfully prepared, polysulfone (PSf) does not dissolve in the same ionic liquids. The discrepancy between PES and PSf could not be explained using classical Flory-Huggins theory, which does not consider the coulombic contributions in ionic liquids. The differences in solubility could be understood, by applying density functional theory to estimate the interaction energy between the different polymers and solvents. The theoretical results were supported by experimental measurements of intrinsic viscosity and dynamic light scattering (DLS).

Keywords: polymer solution thermodynamics, polyethersulfone, [EMIM]DEP, [MMIM]DMP, hollow fibers, polymeric membranes, DNA separation, ionic liquids, density functional theory

1. INTRODUCTION

Polyethersulfone (PES) is an excellent material for membrane fabrication with broad application for instance in desalination, biomedical devices and water treatment [1]. PES membranes have been playing an important role in purification of biotechnology product[2], such as typical proteins, peptides, and DNA, pharmaceutical products[3] , food[4], daily[5], and water[6, 7]. However, most of the PES membranes are fabricated from solvents, which are considered toxic, such as dimethylformamide (DMF), dimethylacetamide (DMAc), and N-methyl-2 pyrrolidone (NMP), with potential environmental restrictions in the future [8]. Alternatives to replace these solvents are needed [9]. A few candidates are under consideration as greener solvents, such as supercritical fluids and ionic liquids [10, 11]. We have focused on fabrication membranes using ionic liquids. Ionic liquids practically have no measurable vapor pressure and do not produce volatile organic compounds (VOCs), which normally contribute to health risks and negative environmental impact. Not all ionic liquids are considered green, but a number of them can be tuned and designed for sustainable processes [10, 12].

Many studies of cellulose dissolution in ionic liquid have been investigated [13-16]. The use of ionic liquids for membrane manufacture is still relatively restricted. Examples are: 1-ethyl-3-methylimidazolium acetate [EMIM]OAc for polybenzimidazole [17], cellulose acetate (CA)[18], cellulose[19], and polyacrylonitrile[20]; 1-ethyl (or butyl)-3-methylimidazolium thiocyanate ([EMIM]SCN and [BMIM]SCN) for CA[21, 22]. Recently we reported the fabrication of PES flat-sheet membranes using 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP) [23]. Nano-size pore structures with high rejection of peptides were achieved.

Hollow fiber membranes are important for their large effective area, and high packing density in modules [24]. Manufacturing hollow fibers is more challenging than flat-sheet requiring a stricter viscosity control. Few studies on hollow fiber membrane fabrication based on ionic liquid polymer solutions have been reported. Xing, et al. [21] successfully spun hollow fiber membranes from the highly viscous polymer solution (approximately 100 Pa.s at 1 l/s and 23 °C) of 12 wt% CA in [EMIM]SCN. Our group has fabricated hollow fiber membranes based on CA/[EMIM]OAc with/without cosolvent [18] and polyacrylonitrile

(PAN)/[EMIM]OAc/co-solvent [20]. Here we first successfully fabricated hollow fiber membranes from highly viscous PES/[EMIM]DEP solutions and characterized them concerning the separation capacity of biotechnological product, and mechanical properties. Second, we demonstrated the feasibility of another PES /ionic liquid system for membrane preparation. Finally, we use density functional theory to explain why PES solubility allows efficient membrane preparation, while polysulfone (PSf) with very similar chemical structure cannot be dissolved in the same solvents.

2. METHODOLOGY

2.1 Materials

Polyethersulfone (PES, average Mw = 75,000 provided from BASF) was purchased from BASF (Ultrason®). Polysulfone (PSf, average Mw = 81,000) was purchased from Solvey (Udel P-3500). 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP, $\geq 98.0\%$), 1, 3-dimethyl- imidazolium dimethylphosphate ([MMIM]DMP), and dimethyl formamide (DMF, $\geq 99.8\%$) were supplied by Sigma-Aldrich. Polymers and ionic liquids used in this study are illustrated in **Figure 1**. Polyethylene glycol (PEG) and/or polyethyleneoxide (PEO) (Sigma-Aldrich), with molecular weights 0.3, 1.5, 6, 10, and 35 kg mol⁻¹, were applied for solute rejection evaluation and determination of the molecular weight cut-off (MWCO). Designed deoxyribonucleic acid (DNA, Sigma-Aldrich), with molecular weight of 3153 and 6366 g mol⁻¹, was used for DNA rejection evaluation.

Figure 1. Chemical structures of (a) PES, (b) PSf, (c) [EMIM]DEP, and (d) [MMIM]DMP.

2.2 Density functional theory (DFT) calculation

All quantum chemical calculations employ the Gaussian 09 software package [25]. Structures are optimized with the M062X hybrid meta exchange-correlation functional [26] using a 6-31G* basis set. The interaction energy between polymer and ionic liquid is calculated as:

$$E_{\text{int}} = E_{\text{polymer+IL}} - (E_{\text{polymer}} + E_{\text{IL}}), \quad (1)$$

with $E_{\text{polymer+IL}}$, E_{polymer} , and E_{IL} being the total energies of the combined system, polymer, and ionic liquid, respectively. Electrostatic, dispersion, induction, and exchange contributions to $E_{\text{int}} = E_{\text{elec}} + E_{\text{dispersion}} + E_{\text{induction}} + E_{\text{exchange}}$ are determined by symmetry adopted perturbation theory using the Psi4 program [27].

2.3 Experimental polymer solution characterization

Binary systems (polymer/solvent)

Parallel to the computational estimation, experimental measurements of the polymer coil size were provided by intrinsic viscosity ($[\eta]$), dynamic light scattering (DLS, Zetasizer, Malvern). To measure the intrinsic viscosity, different PES solutions (0.05; 0.1; and 0.2 wt%) were prepared in [EMIM]DEP, [MMIM]DMP, and DMF and the viscosity was with a Ubbelohde viscometer (Lauda iVisc) at 25 °C. From the viscosity of the series of diluted polymer solutions, the intrinsic viscosity was calculated using the following equation 3:

$$[\eta] = \lim_{c \rightarrow 0} \left(\frac{\eta_{rel}-1}{C} \right) = \lim_{c \rightarrow 0} \eta_{red} \quad (3)$$

where, η_{rel} is the relative viscosity (defined as $\eta_{rel} = \text{polymer solution dynamic viscosity} / \text{solvent dynamic viscosity}$), η_{red} is the reduced viscosity (defined as $\eta_{red} = (\eta_{rel}-1) / C$), and C is the concentration of the polymer solution. From the intrinsic viscosity, the coil size was calculated by the following equation 4 and 5 [28]:

$$C^* = \frac{1}{[\eta]} \quad (4)$$

$$C^* = \frac{M}{\frac{4}{3} \pi N_A R_g^3} \quad (5)$$

where, C^* is the concentration which the polymer coils start to entangle. $[\eta]$ is the intrinsic viscosity (cm^3/g), M is the polymer molecular weight (g mol^{-1}), N_A is the Avogadro number ($6.022 \times 10^{23} \text{ mol}^{-1}$), R_g is the radius of gyration (cm), respectively. From the intrinsic viscosity in equation 4, C^* and the radius of gyration R_g , the hydrodynamic radius R_h and the diameter D_h ($D_h = 2 * R_h$) can be calculated.

For DLS, 0.1 wt% PES solutions in [EMIM]DEP, [MMIM]DMP, and DMF were prepared and filtered through membranes with 0.2 μm pores before analysis. The experiments were done using He-Ne laser with wavelength 633 nm.

Ternary systems (polymer/solvent/non-solvent)

The phase diagram was estimated by measuring cloud points starting with binary polymer/solvent solutions and adding water. The PES solutions with various concentrations were prepared in different solvents. The detected turbid points (the cloud points) determine

the binodal curve for a specific PES/solvent/water system. The binodal denotes the boundary between the stable (one phase) region and the meta-stable region of the phase diagram.

Viscosity is an important kinetic factor to understand effects of solvent and non-solvent diffusion rate during the membrane formation and for practical reasons and limitations of membrane fabrication especially for hollow fiber membranes, appropriate viscosity is essential for the hollow fiber spinning process. The viscosity of polymer solutions was evaluated in an AR1500ex Rheometer (TA Instruments) at different temperatures at 10 s^{-1} shear rate. In this work, a polymer concentration of 12 wt% was applied for spinning hollow fibers in different temperatures.

2.4 Membrane preparation

For flat sheet membrane fabrication, four different polymer solutions, 12 wt % of PES in [EMIM]DEP; [MMIM]DMP; DMF; and 18 wt% of PES in DMF, were prepared. 12 wt% of PES was dissolved in the ionic liquids at 90 °C and stirred for a day. In the case of the PES solution in DMF, PES was dissolved at 60 °C, stirring for a day. Polymer solutions were cast on a glass plate with a doctor blade with 250 μm gap at room temperature and then immediately immersed into deionized water as non-solvent to induce the phase inversion.

For hollow fiber membranes, 12 wt % PES in [EMIM]DEP and 18 wt% PES in DMF were used as dope solutions with appropriate range of viscosity. The polymer solutions were poured into the dope reservoir and degassed for two day at 70 °C under the pressure of 2 bars. The polymer solutions were spun with the spinning conditions listed in **Table 1** using a spinneret (inner: outer diameter = 0.34 mm: 0.61 mm). The spun fibers were immersed in deionized water for a day to remove residual solvents, then immersed in glycerol solution (glycerol: 2-propanol = 50: 50) for 2 hours to avoid pore collapse, and dried in atmosphere.

Table 1. Spinning conditions for hollow fiber membranes

Sample code (Solutions in ionic liquids)	18PES/ DMF-2/25	12PES/ IL-2/70	12PES/ IL-5/70	12PES/ IL-5/90	12PES/ IL-30/90
Dope solution composition (wt%)	18 wt% PES/DMF	12 wt% PES/[EMIM]DEP			
Composition of bore fluid (wt%)	Water				
Coagulant bath	Water				
Air gap (cm)	2	2	5	5	30
Flow rate of dope solution (ml/min)	5				
Flow rate of inner coagulant (ml/min)	3				
Take up speed (m/min)	Free fall				
Temperature of the dope solutions (°C)	25	70	70	90	90
Temperature of the bore fluid and the coagulant bath (°C)	25				

2.5 Membrane characterizations

The membrane morphology was observed on FEI Quanta 200, 600, and Nova Nano Field Emission Scanning Electron Microscopes (FESEM). For the cross-section images, the pretreated membranes, soaked in glycerol solution (glycerol: 2-propanol = 50: 50) and dried in atmosphere to avoid pore collapse, were fractured in liquid nitrogen and then sputter coated with iridium.

Pure water permeance was measured under 2 bar in a dead-end filtration cell with the stirring speed of 400 rpm, calculated with the following equation:

$$\text{Pure water permeance } (L\ m^{-2}\ h^{-1}\ bar^{-1}) = Q \cdot A^{-1} \cdot \Delta P^{-1} \quad (6)$$

where Q is the permeated pure water rate ($L\ h^{-1}$), A is the effective membrane area (m^2), and ΔP is the pressure (bar).

For measuring the PEGs rejection, mixed and single PEG solutions were prepared. In the case of the mixed feed solution, the 0.1 wt% PEGs with the molecular weight of 6; 10; 35; and 100 $kg\ mol^{-1}$, were mixed together in water. For the single PEG feed solutions, the 0.1 wt% PEGs of 1.5; 3; and 6 $kg\ mol^{-1}$ were prepared in water separately. Using the PEG feed solutions, all membranes were tested in a dead-end cell with stirring speed of 400 rpm under 2 bar. The PEG concentration of the feed and permeated solution was analyzed by Gel Permeation Chromatography (GPC) with PL aquagel-OH 40 and 60 columns, (1260 infinity GPC/SEC, Agilent technologies). The PEG rejection were calculated by the equation 7:

$$\text{PEG rejection, } R (\%) = (1 - \frac{C_{perm}}{C_{feed}}) \times 100 \% \quad (7)$$

where C_{perm} and C_{feed} are the concentrations of the permeate and feed solutions, respectively.

Based on the results of the PEG rejection, pore size, pore distribution, and MWCO of all membranes were calculated. The solute (PEG and PEO) diameter was calculated using the Stokes radius equation [29, 30]:

For PEG

$$r = 16.73 \times 10^{-10} M^{0.557} \quad (8)$$

For PEO

$$r = 10.44 \times 10^{-10} M^{0.587} \quad (9)$$

where r is the Stokes radius (in cm) and M is the molecular weight of PEG and PEO (g mol^{-1}). The rejections were plotted as a function of the Stokes diameters ($d = 2r$) corresponding to each molecular weight and their relations are shown the equation 10 and the pore size probability of membranes is expressed by the equation 11.

$$F(R) = A + B (\ln d) \quad (10)$$

$$\frac{\partial R(d_p)}{\partial d_p} = \frac{1}{d_p \ln S_p \sqrt{2\rho}} \exp \left[-\frac{(\ln d_p - \ln m_p)^2}{2(\ln S_p)^2} \right] \quad (11)$$

where μ_p is the mean effective pore size diameter at $R = 50 \%$ and σ_p is the geometric standard deviation, defined as the ratio of d values at $R = 84.13$ and 50% by neglecting the steric and hydrodynamic hindrance effects [31] and ignoring the deformation of macromolecules under pressure and shear rate in the solution [32]. From the plot of the equation 10, the mean pore size (d_s) and the molecular weight cut-off (MWCO, the molecular weight corresponding to 90% rejection) were determined at $R = 90 \%$.

2.6 DNA separation

The capacity of DNA separation of all flat sheet membranes was examined. The DNA samples were designed with molecular weight 3153 and 6366 g mol^{-1} , and dissolved in deionized water. The solutions were filtered in a dead-end ultrafiltration set-up (Amicon cell). The permeate and feed solutions were collected to calculate the rejection. The concentration of the collected solutions was analyzed by a UV spectrometer at 260 nm (Thermo scientific, Nanodrop 2000c). The rejection was calculated by equation 5.

2.7 Mechanical properties

The mechanical properties of flat sheet and hollow fiber membranes, such as tensile strength and elongation at break, were measured by dynamic mechanical analysis (Q800, TA instrument) at room temperature with the force rate of 0.05 N/min.

3. RESULTS

The solubility of PES and PSf in [EMIM]DEP, [MMIM]DMP, and DMF was tested, by adding 1 wt% polymer to each solvent. PES completely dissolved in all solvents. PSf was not soluble in the ionic liquids, but dissolved in DMF. As shown in **Figure 1**, the main difference in chemical structure between PES and PSf is that the repeating unit of PSf contains diphenyl dimethyl groups. Two methyl and two phenyl groups in PSf monomer may affect on the total energy (or electron) distribution and result in not being miscible with ionic liquids, which have strong hydrogen bonds and Coulombic forces.

3.1 Density functional theory (DFT) calculation

To explain why PES but not PSf dissolves in [EMIM]DEP and [MMIM]DMP, the interaction energy of PES and PSf with the ionic liquids is calculated by density functional theory for monomers (PES1 and PSf1) and dimers (PES2 and PSf2). The ionic liquids are placed at different sites of PES and PSf to identify, by means of relaxation, the lowest energy structures (illustrated for monomers in **Figure 2**), which then are used for further analysis. For the monomers, the interaction energy turns out to be $-13.1 \text{ kcal mol}^{-1}$ for PES1/[EMIM]DEP and $-5.4 \text{ kcal mol}^{-1}$ for PSf1/[EMIM]DEP, while for the dimers it is $-13.1 \text{ kcal mol}^{-1}$ for PES2/[EMIM]DEP and $-7.9 \text{ kcal mol}^{-1}$ for PSf2/[EMIM]DEP. More negative values for PES than for PSf can explain why PES is soluble in the ionic liquids in contrast to PSf. Equivalent results are found for [MMIM]DMP, with the interaction energy for the PES monomer and dimer amounting to -15.5 and $-20.8 \text{ kcal mol}^{-1}$, respectively, and that for the PSf monomer and dimer to -8.3 and $-6.9 \text{ kcal mol}^{-1}$. To understand the nature of the interaction, the energy contributions are decomposed in each case, see the results given in **Table 2**. The electrostatic energy always exceeds the dispersion and induction energies. Only for PES1/[EMIM]DEP and PES1/[MMIM]DMP the induction energy is larger than the dispersion energy.

(a)

(b)

Figure 2. Lowest energy structures of monomers (PES1 and PSf1) and dimers (PES2 and PSf2) surrounded by ionic liquid cations and anions: (a) $[\text{EMIM}]^+$ and DEP^- and (b) $[\text{MMIM}]^+$ and DMP^- .

Table 2. Energy decomposition analysis.

Polymer/ Ionic liquid	Energy (kcal mol ⁻¹)				
	E _{int}	E _{elec}	E _{dispersion}	E _{induction}	E _{exchange}
PES1/[EMIM]DEP	-13.1	-33.6	-11.9	-16.4	46.9
PES2/[EMIM]DEP	-13.1	-24.3	-16.1	-7.9	34.2
PSf1/[EMIM]DEP	-5.4	-11.5	-8.2	-4.3	17.9
PSf2/[EMIM]DEP	-7.3	-14.9	-14.4	-5.4	26.4
PES1/[MMIM]DMP	-15.5	-36.8	-9.6	-18.0	46.1
PES2/[MMIM]DMP	-20.8	-37.7	-20.0	-10.8	46.5
PSf1/[MMIM]DMP	-8.3	-17.0	-12.6	-6.5	26.8
PSf2/[MMIM]DMP	-6.9	-16.9	-12.2	-4.8	26.1

3.2 Polymer solutions characterization

Diluted polymer solution (polymer/solvent binary systems)

In the cases of homogenous polymer solutions, large polymer coils indicate a strong polymer solvent interaction, leading to high thermodynamic stability. The size (hydrodynamic diameter) of PES coils in diluted solutions with different solvents was estimated by DLS and intrinsic viscosity (**Table 3**). The hydrodynamic diameter of diluted PES in [MMIM]DMP was the largest among all systems, independently of the measurement method. The order of the hydrodynamic diameter was PES/[MMIM]DMP $\geq$ PES/[EMIM]DEP $\geq$ PES/DMF. PES/[MMIM]DMP seems to have a stronger interaction than PES/[EMIM]DEP, which is consistent with the results of DFT calculation. It can be interpreted that the ionic liquids, [MMIM]DMP and [EMIM]DEP, are good solvents for PES, better than DMF.

Table 3. Intrinsic viscosity ($[\eta]$), entanglement concentration (C^*), radius of gyration (R_g), hydrodynamic diameter obtained from the intrinsic viscosity (D_h ($[\eta]^{-1}$)) and DLS (D_h (DLS)), and solvent density.

PES/solvents	Intrinsic viscosity (η) (cm^3/g)		C^* ($[\eta]^{-1}$) (g/cm^3)	R_g ($[\eta]^{-1}$) (nm)	R_h ($[\eta]^{-1}$) (nm)	D_h ($[\eta]^{-1}$) (nm)	D_h^c (DLS) (nm)	Solvent ^d density (g/cm^3)
	Exp. ^a	Ref.						
[EMIM]DEP	58.5	-	0.017	12.0	15.6	31.2	15.1	1.1458
[MMIM]DMP	96.4	-	0.010	14.2	18.5	36.9	18.2	1.2532
DMF	52.0	41.6 ^b [33]	0.019	11.6	15.0	30.0	13.1	0.9474

^a Measured for PES ($M_w = 75 \text{ kg mol}^{-1}$) at 25 °C

^b Measured for PES ($M_w = 70 \text{ kg mol}^{-1}$) at 23 °C; $[\eta] = 63.3 \text{ cm}^3/\text{g}$ for $M_w = 113 \text{ kg mol}^{-1}$.

^c Measured by DLS (D_h (DLS)) at 25 °C

^d Measured with a pycnometer at 22 ± 1 °C.

Phase diagram (ternary system, polymer/solvents/water)

Figure 3 shows the phase diagrams for different PES/solvent/water systems, obtained by cloud point measurements. The phase diagrams are similar. Minor differences were observed, with the two-phases regions increasing in the following order: PES/[MMIM]DMP $\approx$ PES/[EMIM]DEP $\leq$ PES/DMF.

Figure 3. Ternary phase diagram for PES/solvents/water systems

Viscosity

The aspects discussed above are mainly connected to the thermodynamics of the polymer solutions. Viscosity adds information on kinetics. Viscosity is very important for the fabrication of hollow fibers, to evaluate the feasibility and choose spinning conditions. Viscosity values as a function of temperature are shown in **Figure 4**. The viscosity of 12 wt% PES in [EMIM]DEP and [MMIM]DMP is 97 and 60 Pa.s at 25 °C, which is enormous for spinning. By increasing the temperature from 25 to 90 °C, the viscosity dropped down to 4 Pa.s for all polymer solutions, which is up to 25-fold smaller. According to the Hagen–Poiseuille equation ($R_{\text{hyd}} = 8\eta LQ / \pi r^4$) [34] in non-ideal fluid dynamics, the hydraulic resistance (R_{hyd} , the pressure drop) in a tube is proportional to viscosity (η). Thus, the hydraulic resistance can be reduced up to 200 times ($8 \cdot 25$) in tubes connected with spinning machine and the less viscous polymer solution can be spun without the troubles that the high hydraulic resistance could cause.

The viscosity ratio between solution (η) and solvent (η_0) is shown in **Figure 4b** and **Table 4**. The normalization discounts the pure solvent contribution. At 25 °C the ratio for 12 wt% PES decreased in the following order: [MMIM]DMP > [EMIM]DEP > DMF. This is the order of increasing C^* in **Table 3**. PES in [MMIM]DMP starts to entangle from C^* equal to

0.01 g/cm³ (1 wt%), the lowest value compared to others. 12 wt% PES solutions in [MMIM]DMP are highly entangled and the viscosity ratio is higher than in other solvents. By increasing temperature, the ratio for all polymer solutions became similarly low.

Figure 4. (a) Viscosity of polymer solutions at different temperatures and (b) ratios between solution and the solvent viscosities.

Table 4. Viscosity of concentrated PES solutions (η) and solvents (η_0) and their ratios at 25 °C.

PES concentration (wt %)	Solvents	η (Pa.s)	η_0 (Pa.s)	η/η_0 Ratio
12	[EMIM]DEP	97.1	0.384	250
12	[MMIM]DMP	59.7	0.189	320
12	DMF	0.1	0.00077	130
16	DMF	0.3	0.00077	390
18	DMF	0.6	0.00077	780

3.3 Flat sheet membranes characterization

Figure 5 shows the morphologies of membranes cast with different solvents. The membranes prepared from 12 wt % PES in [EMIM]DEP and [MMIM]DMP have homogeneously distributed sponge-like structures with very small pores, which were hardly seen by high magnification of SEM images. On the other hand, the membrane cast from 12 wt % PES in DMF has finger-like void structure. By increasing the PES concentration in

DMF from 12 to 18 wt%, the size of finger voids decreased and the membrane thickness increased. The clear difference in structure might be a consequence of different mechanisms of membrane formation.

As we reported in our previous study, the mechanism of nucleation and growth (NG) might predominate during the membrane formation of 12 wt% PES/[EMIM]DEP and [MMIM]DMP. The higher viscosity favors a slow path into the 2 phases region of the phase diagram, with long time under metastable conditions. Furthermore, once the phase separation starts, the high viscosity contributes for a slow evolution of domain size, before the whole system solidifies to form the final sponge-like pore structure. In opposite the DMF system is characterized by low viscosity. This promotes fast solvent-water exchange and a fast path into the demixing region of the phase diagram delimited by the spinodal curve. Spinodal decomposition (SD) then predominates. These NG and SD mechanisms explain the formation of the membranes nanopores. Apart from that, the presence or absence of finger-like cavities is defined by other set of considerations: (i) viscosity, (ii) solvent-water mixing Gibbs energy and (iii) homogeneity of the water-polymer solution interface. Abrupt water-solvent exchange favors the formation of finger-like cavities. Solutions in DMF are more prone to that, due to the low viscosity.

Figure 5. Morphology of PES flat sheet membranes, fabricated from PES solutions in different solvents.

The performance of flat-sheet membranes prepared from 12 wt% PES solutions in different solvents is summarized in **Table 5** and **Figure 6**. When [EMIM]DEP and [MMIM]DMP were the used solvents, the membranes water permeances were 55 and 43 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, respectively. In **Figure 6** and **Table 5**, the pore sizes and their distributions, estimated from PEG rejection tests, are illustrated and summarized. Normally there is a permeance-rejection trade-off. While the water permeance is higher when the membranes are prepared from solutions in DMF, the MWCO is clearly smaller when using [EMIM]DEP and [MMIM]DMP. **Figure 6b** shows that when using [EMM]DEP, membranes with particularly narrow pore size distribution are obtained, with a mean pore size around 2 nm.

Figure 6. (a) PEG rejection and (b) pore size distribution of flat sheet membranes. The mixed PEG feed solution was composed of 0.1 wt% of each of the following molecular weights: 6, 10, 35, and 100 kg mol^{-1} .

Table 5. Performance of flat-sheet membranes prepared from 12 wt% PES solutions in different solvents; measurements at 2 bar, 25°C.

Casting solvent	Water permeance ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$)	PEG rejection (%)					MWCO (kg mol^{-1})
		0.3	1.5	6	10	35	
[EMIM]DEP	55 ± 5	16.7	40.9	100			5.1
[MMIM]DMP	43 ± 3	7.5	17.9	86.8	98.3	100	7.9
DMF	135 ± 5	17.2	32.8	77.6	88.9	99.6	10.3

After analyzing the PEG rejection results of **Table 5**, the membranes capability for DNA separation were evaluated. DNA samples with molecular weights of 3153 and 6366 g mol⁻¹ were used. The results are summarized in **Table 6**. Flat sheet membranes prepared from 12 wt% PES/[EMIM]DEP and 12 wt% PES/[MMIM]DMP solutions rejected respectively 99 and 92 % of DNA with 3153 g mol⁻¹ molecular weight, indicating that the rejection curves are even sharper than characterized by PEG measurements (Figure 8a). The membranes prepared from solutions in DMF with the same polymer concentration rejected only 7 %, a values lower than obtained with PEG measurements, using PEG mixtures. 100 % DNA with 6366 g mol⁻¹ molecular weight was removed by membranes prepared from solutions in ionic liquids. The membrane separation of charged solutes, like DNA, could be affected by size exclusion and Donnan exclusion. This is clearly seen for PES/[EMIM]DEP membranes, which have pores in the range of tight ultrafiltration and loose nanofiltration, separating DNA with molecular weights 5.7 and 7.9 kg mol⁻¹. PEG is neutral and Donnan exclusion is not relevant for the separation.

Table 6. DNA separation by flat sheet membranes.

	Rejection (%)	
	DNA (M _w = 3153 g mol ⁻¹)	DNA (M _w = 6366 g mol ⁻¹)
12 wt% PES/[EMIM]DEP	98.8	100
12 wt% PES/[MMIM]DMP	92.2	100
12 wt% PES/DMF	7.0	27.2

When comparing only membranes prepared by the two ionic liquids, [EMIM]DEP and [MMIM]DMP, thermodynamic and kinetic aspects have to be considered. From the thermodynamic point of view the two systems are similar, with small differences in the DFT calculations. The membrane morphologies are also highly influenced by the phase separation kinetics, and for that viscosity is an important factor. As shown in Figure 4, the viscosity of PES/[EMIM]DEP is 100 Pa.s, which is about 970 times higher than that of PES/DMF. The viscosity of PES/[MMIM]DMP is approximately 600 times higher than that of PES/DMF, still much lower than that of PES/[EMIM]DEP. Both membranes have sponge-like structure with fine and well-connected pores. However, because of the high viscosity, PES/[EMIM]DEP has less mobility, the evolution of the phase separation is slower, the pores are smaller (lower MWCO) and the pore distribution narrower, as shown in Figure 6b. The difference of water permeance between the two membranes was less pronounced.

3.4 Hollow fiber membranes

After demonstrating the feasibility and the performance of flat-sheet membranes prepared from solutions in ionic liquids, hollow fibers were manufactured. PES/[EMIM]DEP was chosen because of the combination of low MWCO and high flux, demonstrated as flat-sheet. Hollow fiber manufacture is more sensitive to viscosity than flat-sheet. 12 wt% PES/[EMIM]DEP solutions led to well-formed hollow fibers, after optimization of spinning conditions, as shown in **Table 7**. For hollow fibers only one ionic liquid was used: [EMIM]DEP. They are referred as PES/IL, followed by values of air gap difference and dope temperature. The viscosity of 12 wt% PES/DMF solutions is too low for hollow fiber manufacture. Attempts led to deformed fibers. 18 wt% PES/DMF could be spun to fabricate hollow fiber membranes, which were compared to those prepared from solutions in [EMIM]DEP.

The morphologies of all fabricated hollow fiber membranes are depicted in **Figure 7**. Similarly to results for flat sheet membranes, [EMIM]DEP and DMF lead to membrane structures and pore sizes, which are clearly different. 18PES/DMF-2/25 in **Figure 7** had double layered finger-like voids in outer and inner surfaces. The double layers are formed because the polymer solutions contact water as a strong non-solvent from both sides; the inner surface from the bore fluid and the outer surface from the coagulant water. Similar to flat-sheet membranes finger-like structures are formed with DMF. In contrast all hollow fibers prepared from solutions in [EMIM]DEP had the spongy-like structures with fine pores and a small number of voids.

By increasing the air-gap and the temperature of the dope solution, the thickness of hollow fiber membranes was decreased as depicted in **Figure 7** and **Figure 8**. By changing the air-gap, which are the distance from the extrusion point to the air to the surface of non-solvent, from 2 (12PES/IL-2/70) to 5 cm (12PES/IL-5/70), the thickness of the hollow fibers was reduced from 276 to 245 μm and when the gap increased from 5 (12PES/IL-5/90) to 30 cm (12PES/IL-30/90), the thickness decreased from 232 to 165 μm due to spun stretching by gravity. Furthermore, the effect of the dope solution temperature on membrane thickness could be seen, by comparing 12PES/IL-5/70 and 12PES/IL-5/90. As a consequence of decreasing the viscosity of the dope solutions, by increasing the temperature, the spun dope solution becomes thinner and flexible, with stretching by gravity being more accentuated. Similar results were obtained for membranes prepared from 18PES/DMF (**Figure 8**).

Figure 7. Morphology of manufactured hollow fiber membranes.

Table 7. Summary of hollow fiber preparation conditions and resulting dimensions.

Hollow fibers	18PES/DMF- 2/25	12PES/IL- 2/70	12PES/IL- 5/70	12PES/IL- 5/90	12PES/IL- 30/90
Dope solutions	18 wt% PES/DMF	12 wt% PES/[EMIM]DEP			
Air gap (cm)	2	2	5	5	30
Temperature of dope solutions (°C)	25	70	70	90	90
Outer diameter (μm)	770	1300	1117	1060	985
Wall thickness (μm)	119	276	245	232	165

The pure water permeance of all hollow fiber membranes is summarized in Table 8. The permeance of hollow fiber membranes prepared from 18PES/DMF-2/25 solutions was higher than that of those prepared from 12PES in [EMIM]DEP. By decreasing the wall thickness from 276 μm (12PES/IL-2/70) to 165 μm (12PES/IL-30/90) in **Table 7**, the pure water permeance was increased from 22.4 to 45.8 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$. The higher porosity, resulted from the bigger pore size and the finger-like voids, and the thinner wall thickness of 18PES/DMF-2/25 may have an effect on the high water permeance. However, the PEG rejection of all hollow fibers prepared in [EMIM]DEP was higher than that prepared from 18PES/DMF-2/25, as shown in **Figure 9** and **Table 8**. MWCOS of fibers prepared from 12PES in [EMIM]DEP and 18PES/DMF were 1.4 and 10.5 kg mol^{-1} , respectively, using a mixture of PEG molecular weights. As far as pore distribution is concerned, as shown in **Figure 9**, a broad distribution was measured for 18PES/DMF-2/25, while those for all fibers prepared from 12PES/[EMIM]DEP solutions was very narrow. Overall, the PEG rejection and the pore distribution were respectively higher and narrow once higher polymer concentration was used for membrane preparation.

We had two different procedures for PEG rejection tests: (i) using a mixture of molecular weights at once or (ii) measuring separately the rejection of single molecular weights one by one. The results were slightly different, as shown in **Table 8**. The rejection values were higher, when measured with the PEG mixture. The difference was even more significant for 18PES/DMF than for those membranes prepared from solutions in [EMIM]DEP. This can be probably explained by considering the formation of a cake layer of larger PEG molecules, deposited on the membrane surface when tested in dead-end cells. The membrane fabricated from the PES/DMF polymer solution has very broad pore size distribution. When the PEG mixture is used for rejection measurements, the high molecular weight PEG fraction might form a gel layer or cake, partially filling the larger pores and masquerading the results. The rejection is therefore apparently higher than when single samples of defined molecular weight are used. Membranes prepared from solutions in [EMIM]DEP have narrow pore size distribution, with smaller average size. The rejections are higher for all solutes. The variations in results with single and mixture of PEGs are less pronounced and only detectable for low molecular weight.

Sample No.	1	2	3	4	5	6	7	8
Outer diameter (μm)	1010	930	950	870	780	900	850	770
Wall thickness (μm)	190	210	155	165	130	140	140	119

Figure 8. Morphologies of the hollow fiber membranes spun from 18 wt% PES/DMF solutions.

Figure 9. PEG rejection and the pore distribution of tested hollow fiber membranes.

Table 8. Summary of pure water permeance and PEG rejection for hollow fiber membranes; experiments with feeds containing a mixture of PEG molecular weights or single PEG molecular weights.

Hollow fibers	Water permeance (Lm ⁻² h ⁻¹ bar ⁻¹)	PEG rejection (%) (PEG mixture / single PEG)						MWCO (kg mol ⁻¹)
		0.3	1.5	3	6	10	35	
18PES/DMF-2/25	87.6	18 / -	33 / -	- / 7	79 / 14	88 / -	100 / -	11 / 37
12PES/IL-2/70	22.4	51 / -	94 / 72	- / 89	100 / 96			1.4 / 3.5
12PES/IL-5/70	17.8	45 / -	98 / 82	- / 94	100 / 96			1.3 / 2.5
12PES/IL-5/90	25.9	48 / -	94 / 77	- / 87	100 / 96			1.4 / 3.9
12PES/IL-30/90	45.8	37 / -	95 / 11	- / 34	100 / 97			1.4 / 5.7

Table 9 shows the mechanical properties for flat-sheet and hollow fiber membranes. Overall, the membranes have values of tensile strength at break in the same order of magnitude. Slight differences can be observed. The values of elongation at break for membranes fabricated from PES/DMF were higher than for those fabricated from PES/ionic liquids, but in all cases the membranes were strong enough for testing and for further application.

Table 9. Membrane mechanical properties.

	PES solutions	Mechanical strength		Young's modulus (MPa)
		Tensile strength at break (MPa)	Elongation at break (%)	
Flat sheet	12 wt% PES/[EMIM]DEP	2.2 ± 0.2	18 ± 1	0.4
	12 wt% PES/[MMIM]DMP	1.8 ± 0.3	13 ± 2	0.2
	12 wt% PES/DMF	3.5 ± 0.3	65 ± 18	0.8
	18 wt% PES/DMF	7.0 ± 0.5	131 ± 60	1.5
Hollow fiber	18PES/DMF-2/25	6.0 ± 1.3	84 ± 56	1.4
	12PES/IL-2/70	2.3 ± 0.3	40 ± 29	0.3
	12PES/IL-5/70	3.0 ± 0.1	46 ± 6	0.3
	12PES/IL-5/90	4.0 ± 0.3	51 ± 12	0.5
	12PES/IL-30/90	2.8 ± 0.1	25 ± 5	0.4

4. CONCLUSION

We have theoretically and experimentally studied the interaction and solubility of PES and PSf in ionic liquids. We fabricated flat sheet and hollow fiber membranes from PES solutions in [MMIM]DMP and [EMIM]DEP. The following conclusions can be taken:

- (1) Evaluation of the interaction energy of PES and PSf with ionic liquids, using DFT, shows that the electrostatic contribution is higher for PES than for PSf, which can explain that only PES is soluble.
- (2) The polymer coil size of the diluted PES solution in different solvents was calculated by the intrinsic viscosity and was measured by DLS. The order of the PES coil size was $\text{PES/[MMIM]DMP} \geq \text{PES/[EMIM]DEP} \geq \text{PES/DMF}$. It is consistent with the results of DFT calculation. From the thermodynamic point of view, the ionic liquids, [MMIM]DMP and [EMIM]DEP, are better solvents for PES than DMF.

- (3) The polymer solutions in [MMIM]DMP and [EMIM]DEP were highly viscous. Much lower viscosity was measured in DMF.
- (4) Flat-sheet and hollow fiber membranes were fabricated. The membrane prepared from 12 wt % PES in [EMIM]DEP and [MMIM]DMP had sponge-like structures with small pores. On the other hand, the membrane cast from 12 wt % PES in DMF had finger-like structures.
- (5) The membranes fabricated from 12 wt % PES in [EMIM]DEP and [MMIM]DMP had lower pure water permeance but higher PEG rejection and narrower pore size distribution than those prepared from 12 wt % PES solution in DMF.
- (6) 99 and 92 % of DNA with 3153 g mol^{-1} were rejected by the membranes prepared from 12 wt% PES/[EMIM]DEP and 12 wt% PES/[MMIM]DMP, respectively. DNA with 6366 g mol^{-1} was completely removed by membranes prepared from solutions in ionic liquids.

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