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Ind. Eng. Chem. Res., **Just Accepted Manuscript** • DOI: 10.1021/acs.iecr.7b03581 • Publication Date (Web): 20 Nov 2017

Downloaded from <http://pubs.acs.org> on December 4, 2017

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Poly (ether imide sulfone) membranes from solutions in ionic liquids

DooLi Kim and Suzana P. Nunes*

King Abdullah University of Science and Technology (KAUST), Biological and Environmental Science and Engineering Division (BESE), Thuwal, 23955-6900, Saudi Arabia

ABSTRACT: A membrane manufacture method based on non-volatile solvents and a high-performance polymer, poly (ether imide sulfone) (EXTEM™), is proposed, as greener alternative to currently industrial process. We dissolved EXTEM™ in pure ionic liquids: 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN), 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN), and 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc). The following polymer solution parameters were evaluated to optimize the manufacture: Gibbs free energy of mixing (ΔG), intrinsic viscosity ($[\eta]$) and hydrodynamic diameter. Membranes with sponge-like structure and narrow pore size distribution were obtained from solutions in [EMIM]SCN. They were tested for separation of proteins and deoxyribonucleic acids (DNA). Due to the polymer stability, we foresee that applications in more demanding chemical separations would be possible. [EMIM]SCN was 96 % purified and recovered after the membrane fabrication, contributing to the sustainability of the whole manufacturing process.

1. Introduction

Membrane technology has been used in various fields such as biomedical separations¹⁻⁴, desalination⁵, wastewater treatment⁶, and energy conversion⁷⁻⁹. It is playing a crucial role in fulfilling a sustainable process on producing water and separating, recycling, and reuse of wastes with less energy consumption and less cost, comparing with other traditional water production processes¹⁰⁻¹⁴. However, there are concerns that the sustainability can only be completely achieved if the membrane manufacture itself will be performed with less toxic and alternative chemicals to solvents, such as dimethylformamide (DMF); 1-methyl-2-pyrrolidone (NMP); and N, N-dimethylacetamide (DMAc)¹⁵⁻¹⁸.

Ionic liquids can be considered as green solvents¹⁹ from a perspective of no generation of harmful volatile organic chemicals (VOCs)²⁰. Research on ionic liquids as green solvents for polymer dissolution has increased, especially since the confirmation that they can dissolve biopolymers, such as cellulose²¹⁻²³ and chitin²⁴, which are hardly dissolved in any other organic solvent. They have been reported for production of biofuel and for membrane fabrication²⁵⁻²⁷. The use of ionic liquids to dissolve synthetic polymers with sulfone or imide groups and their use for membrane fabrication have been gradually reported^{28, 29}. Ionic liquids have been also used as additives in polymer solutions^{30, 31}.

EXTEM™ is a commercialized petroleum based polymer, which is known for excellent mechanical and chemical stability. It is structurally composed of etherimide and sulfone groups. It has been used for membrane fabrication, e.g. Xia *et al.*³² and Peng *et al.*³³ as hollow fiber membranes for gas separation. Jalal *et al.*³⁴ fabricated EXTEM™ ultrafiltration membranes for liquid separation. Recently Mazinani *et al.*³⁵ investigated the phase separation of EXTEM™, being more difficult to dissolve than other polysulfones. The membranes

however were fabricated from NMP and DMF which are good solvents, but are considered as relatively toxic.

In this study, we propose the use of ionic liquids for EXTEM™ solubilization and membrane preparation. Interestingly, we found out that high quantity of EXTEM™ can be dissolved in different ionic liquids: 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN), 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN), and 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc). This has not been reported before. For better optimization we investigated the solution thermodynamics of the EXTEM™/ionic liquids systems and kinetic aspects of phase separation. Membranes were prepared and characterized. This study will contribute to find alternative methods for greener membrane fabrication.

2. Methodology

2.1. Materials

Poly (ether imide sulfone), EXTEM™ XH1005 was kindly provided by SABIC. The average molecular weight of 85 kg mol⁻¹ was estimated by viscosity measurements, using the Mark-Houwink equation, as shown in **Table 1S**. [EMIM]SCN (≥ 95.0 %), [BMIM]SCN (≥ 95.0 %), and DMF (≥ 99.0 %) were purchased from Sigma-Aldrich. The structures of EXTEM™ and ionic liquids are shown in **Figure 1**. Polyethylene glycol (PEG) and polyethyleneoxide (PEO) (Sigma-Aldrich), with molecular weight of 0.3, 1.5, 6, 10, and 35 kg mol⁻¹, were used for rejection evaluation and determination of the molecular weight cut-off (MWCO). Deoxyribonucleic acid (DNA, 3229 and 6441 g mol⁻¹ composed of adenine and guanine), bovine serum albumin (BSA, ~66 kg mol⁻¹), and γ -globulin (~140 kg mol⁻¹) were supplied from Sigma-Aldrich.

Figure 1. Chemical structures of (a) EXTEM™, (b) [EMIM]SCN, (c) [BMIM]SCN, and (d) [EMIM]OAc.

2.2. Polymer solution thermodynamics

For non-charged organic solvents ΔG_m can be calculated from solubility parameters (δ) and Flory-Huggins parameters (χ), which mainly take into consideration the interaction contributions of van der Waals forces, polarity and hydrogen bonds. This estimation does not count coulombic interactions, which are important in the case of ionic liquids, but can give guidance to predict the miscibility of a polymer/solvent mixture³⁶. If ΔG_m is negative, the polymer solubility is favored in the specific solvent. In contrast, if ΔG_m is significantly higher than zero, the mixture is unlikely to be homogenous. According to the Flory-Huggins theory, ΔG_m can be estimated by the following equation³⁷:

$$\frac{\Delta G_m}{N_A} = kT \left[\chi \phi_1 \phi_2 + \frac{\phi_1}{x_1} \ln \phi_1 + \frac{\phi_2}{x_2} \ln \phi_2 \right] \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature (K), and ϕ_i and x_i are the volume fraction and number of segments of the i^{th} component, respectively. χ is the Flory-Huggins parameter, which can be calculated from equation 2:

$$\chi_{ij} = \frac{V_i \delta_i - \delta_j^2}{RT} + 0.34 \quad (2)$$

where V_i is the molar volume of the solvent ($\text{cm}^3 \text{mol}^{-1}$), R is the ideal gas constant ($\text{cm}^3 \text{MPa K}^{-1} \text{mol}^{-1}$). The value of 0.34 is an empirical constant absent in the original theory and later introduced for polymer systems³⁸⁻⁴¹. δ is the solubility parameter of the solvent i and polymer j ($\text{MPa}^{1/2}$).

Few studies have attempted to calculate the δ of ionic liquids⁴²⁻⁴⁶. Here the δ values of EXTEM™, [EMIM]SCN, and [BMIM]SCN were determined using the HSPiP⁴⁰ software, based on miscibility tests with different solvents. The dispersive (δ_D), dipole-dipole (δ_P), and hydrogen bonding (δ_H) contributions to the Hansen solubility parameters⁴⁰ were computed by the software. The total solubility parameters (δ) were then calculated by the following equation 3:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (3)$$

The δ contributions for [EMIM]OAc were previously reported^{27, 28}.

2.3. Polymer solutions characterization

In the cases of homogenous polymer solutions, larger polymer coils indicate higher solubility. From the intrinsic viscosity ($[\eta]$), the size of the polymer coils was estimated. To measure $[\eta]$, different polymer solutions (0.05, 0.1, 0.2, and 0.3 wt% EXTEM™ in [EMIM]OAc, [EMIM]SCN, [BMIM]SCN, and DMF) were prepared and their viscosities were measured us-

ing an Ubbelohde viscometer (Lauda iVisc). $[\eta]$ can be calculated by equation 4:

$$[\eta] = \lim_{c \rightarrow 0} \left(\frac{\eta_{rel} - 1}{C} \right) = \lim_{c \rightarrow 0} \eta_{red} \quad (4)$$

where η_{rel} is the relative viscosity (defined as η_{rel} = dynamic viscosity / solvent 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 $[\eta]$, the radius of gyration, R_g , can be calculated. The entanglement concentration (C^*) is estimated from the inverse of $[\eta]$ (equation 5):

$$C^* = 1/[\eta] \quad (5)$$

C^* is related to R_g by equation 6:

$$C^* = \frac{M}{\frac{4}{3} \pi N_A R_g^3} \quad (6)$$

where M is the molecular weight of EXTEM™, N_A is the Avogadro number ($6.022 \times 10^{23} \text{mol}^{-1}$), respectively. From R_g , the hydrodynamic radius (R_h) and diameter (D_h) can be estimated ($R_h = 0.77 R_g$)⁴⁷. D_h calculated from $[\eta]$ was compared to those obtained by transmission electron microscopy (TEM) using a Technai 12 FEI microscope operated at 120 kV. For that a droplet of diluted EXTEM™ solutions (0.1 wt %) in different solvents was placed on a carbon-coated copper grid and the excess was removed. The samples were stained with ruthenium tetroxide (RuO_4) vapor for 3 hours.

The rheology of EXTEM™ solutions was investigated using a AR1500ex Rheometer, TA Instruments, at shear rate of 10s^{-1} in the temperature range of 25 to 90 °C.

Phase diagrams of a polymer/solvent/non-solvent system were estimated by cloud point tests. EXTEM™ solutions were prepared with different compositions. Their cloud points were determined by adding water as non-solvent at room temperature until turbidity was observed. The amount of EXTEM™, solvents, and water needed to reach each cloud point was plotted in ternary diagrams.

The phase separation kinetics was studied by light transmittance experiments. EXTEM™ solutions were cast on a glass plate with the solution gap of 250 μm and then immediately immersed in water as non-solvent. The change of light transmittance as a function of time was monitored at 600 nm (water has no absorbance peak at this wavelength)²⁶ using a Cary 5000 UV-Vis-NIR, Agilent. The relative light transmittance (T_r) was determined by equation 7^{27, 28}.

$$T_r = \frac{(T - T_{min})}{(T_{max} - T_{min})} \times 100\% \quad (7)$$

where T_{min} , T_{max} and T are the minimum, maximum, and the raw transmittance at specific time, respectively.

2.4. Membrane fabrication and characterization

All solutions were cast on non-woven with a doctor blade gap of 250 μm and with the controlled temperature of 70 °C. The cast solutions were immersed in a deionized water bath at room temperature to induce phase separation and kept in water for a day to eliminate any residual solvents.

The membrane morphologies were observed by field emission scanning electron microscopy (FESEM) (FEI Quanta 200, Quanta 600, and Nova Nano FESEM). First, membrane sam-

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ples were prepared by freeze-drying to avoid pore collapse. The membrane samples were fractured in liquid nitrogen, and then coated with iridium for cross-sectional images.

The water permeance was measured by filtering water through the membranes and then calculated by equation 8:

Water permeance = $Q \cdot A^{-1} \cdot \Delta P^{-1}$ (8)

where Q is the water flow rate (L/h), A is the effective membrane area (m^2), and ΔP is the applied pressure (bar).

Pore size, pore distribution, and MWCO were investigated by filtration tests with neutral solutes PEG and PEO, which are composed of molecular weight of 0.3, 1.5, 6, 10, and 35 kg mol^{-1} . The rejection was evaluated by equation 9:

$R(\%) = \left(1 - \frac{C_{perm}}{C_{feed}}\right) \times 100\%$ (9)

where C_{perm} and C_{feed} are the concentrations of the permeate and feed solutions, respectively, which was analyzed by gel permeation chromatography (GPC) with PL aquagel-OH 40 and 60 columns (1260 infinity GPC/SEC, Agilent technologies).

The solute Stokes radius (in cm), r , was calculated by equation 10 and 11^{48, 49}:

For PEG
 $r = 16.73 \times 10^{-10} M^{0.557}$ (10)

For PEO
 $r = 10.44 \times 10^{-10} M^{0.587}$ (11)

where M is the molecular weight (in g/mole or Da) of PEG or PEO. The relation between the solute diameter ($d = 2r$) and its rejection is shown in the equation 12 and the pore size probability of membranes is expressed by the equation 13.

$F(R) = A + B (\ln d)$ (12)

$\frac{dR(dp)}{d(dp)} = \frac{1}{dp \ln \sigma_p \sqrt{2\pi}} \exp\left[-\frac{(\ln dp - \ln \mu_p)^2}{2(\ln \sigma_p)^2}\right]$ (13)

where μ_p is the mean effective pore diameter at $R = 50\%$. 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 effects⁴⁹ and ignoring the deformation of macromolecules under pressure and shear rate in the solution⁵⁰. The molecular weight cut-off (MWCO, $R = 90\%$) was calculated by equation 12.

2.5. Proteins and DNA separation

The water permeance and rejection of all membranes were examined by filtration of DNA, BSA, and γ -globulin solutions ($1g\ mL^{-1}$) through the membranes, using a dead-end ultrafiltration set-up (Amicon cell). The feed solutions for BSA, and γ -globulin were prepared in the phosphate buffered saline solution (20 mM). Primary DNA with designed molecular weights 3220 and 6440 $g\ mol^{-1}$ were dissolved in water and used as feed solutions. Their rejections were calculated by equation 6

based on their permeate and feed concentrations, which were analyzed by a UV spectrometer at 260 nm (Thermo scientific, Nanodrop 2000c).

3. Results

3.1. Binary polymer solutions in ionic liquids

The difference between EXTEM™ and ionic liquid solubility parameters was taken as a first indication of potential solubility. Table 1 shows the solubility parameters of all components used in this study and the polymer-solvent parameter difference. The solubility of EXTEM™ in different solvents would then decrease in the following order: DMF > [BMIM]SCN > [EMIM]OAc > [EMIM]SCN.

Table 1. Solubility parameters of the polymer and solvents

	δ_D	δ_P	δ_H	δ [MPa ^{1/2}]	$ \delta_{EXTEM^\text{TM}} - \delta_{\text{solvent}} $
EXTEM™	21	10.9	10.6	26	-
[EMIM]SCN ^a	22.7	19.1	15.6	33.5	7.5
[BMIM]SCN ^a	19.5	17.1	12.6	28.9	2.9
[EMIM]OAc ^a	22.2	15.9	16.9	32.1	6.1
DMF ^b	17.4	13.7	11.3	24.9	1.1
Water ^b	15.5	16	42.3	47.8	

used in this study.

^aCalculated using HSPiP and ^bfrom Ref.⁴⁰

Figure 2. ΔG estimation for EXTEM™ in different ionic liquids at 25 (dash lines) and 90 °C (solid lines).

Values of Gibbs free energy of mixing (ΔG), which are calculated using Flory-Huggins parameters estimated from solubility parameters, are illustrated in Figure 2. Although the strong coulombic interactions involved in solutions containing ionic liquids are not completely taken into account by Flory-Huggins, the values of ΔG were taken as a guidance for solubility. Values close to zero or below are an indication of homogeneous systems. The ΔG for EXTEM™/[BMIM]SCN and

DMF was below zero. It denotes that the EXTEMTM solutions in [BMIM]SCN and DMF are thermodynamically stable and homogenous. In case of EXTEMTM/[EMIM]OAc and EXTEMTM/[EMIM]SCN, the values of ΔG were positive, but not far from zero, still enough for solubilization. EXTEMTM therefore seems to have weaker interactions with [EMIM]OAc and [EMIM]SCN than with DMF and [BMIM]SCN. Furthermore, it is important to note that high temperature is critical to dissolve polymers in the investigated ionic liquids. By increasing the temperature from 25 to 90 °C, all ΔG values slightly decreased, following equation 2 for χ . As the temperature increases, χ decreases and the interaction between polymers and solvents increases (lower ΔG).

The intrinsic viscosity ($[\eta]$) leads to the calculation of molecular weight and coil size of polymers in solution. The $[\eta]$ values for EXTEMTM in different solvents are shown in **Table 1S** and **Table 2**. The values of $[\eta]$ for EXTEMTM decreases in the following order: [BMIM]SCN > [EMIM]OAc > DMF > [EMIM]SCN and the hydrodynamic diameter (D_h) calculated from $[\eta]$ was consistent with the D_h calculated from TEM images shown in **Figure 3** and **Table 2**. The EXTEMTM polymer coils in ionic liquid solutions were imaged by TEM, after deposition on TEM grids coated with carbon films. They are shown in **Figure 3**.

Table 2. Critical concentration (C^*) and the radius of gyration (R_g) calculated from $[\eta]$ of all diluted polymer solutions and TEM.

EXTEM TM / solvents	$[\eta]$	C^{*a}	R_g^a	D_h^a	D_h^b	ρ^c
[EMIM]SCN	18.5	0.054	9	22	18	1.1181
[EMIM]OAc	39.9	0.025	11	29	31	1.0992
[BMIM]SCN	52.5	0.019	12	32	47	1.0707
DMF	33.7	0.030	11	27	-	0.9474

^aEstimated from viscosity measurements; ^bEstimated from TEM images; ^cMeasured at room temperature (22 ± 1 °C); $[\eta]$ (cm³ g⁻¹), C^* (g cm⁻³), R (nm), D (nm), and solvent density (ρ , g cm⁻³)

Figure 3. TEM of diluted EXTEMTM polymer coils (0.1 wt%) in different ionic liquids: (a) [EMIM]SCN, (b) [EMIM]OAc, and (c) [BMIM]SCN.

3.2. Rheology of semi-diluted polymer solutions

The viscoelastic properties of all EXTEMTM solutions were studied and illustrated in **Figure 4**. To fabricate membranes and understand the membrane structure, the viscoelastic properties are important, especially for semi-crystalline polymers,

such as EXTEMTM. X-ray diffraction (XRD) in **Figure 1S** shows a strong crystalline peak at 21.5 degrees. **Figure 4a** shows that 20 wt% EXTEMTM solutions in [EMIM]SCN and [EMIM]OAc have the highest viscosities. When the total viscosity is normalized by the solvent one (η / η_0) as shown in **Figure 4b**, we see that the main contribution to the high viscosity of the EXTEMTM solution in [EMIM]OAc is the solvent viscosity itself. For the 20 wt% EXTEMTM solution in [EMIM]SCN the reason for the high viscosity is different, since after the normalization it remains high. The main contribution comes from the poor interaction between EXTEMTM segments and [EMIM]SCN. From the investigated systems, [EMIM]SCN is the worse solvent, confirmed by the lowest intrinsic viscosity and lowest R_g . While the solvent polymer interaction is poor, the friction between polymer-polymer segments is high. In an entangled system ($c > C^*$) this leads to high viscosity with the system behaving like a gel with high storage modulus, as shown in **Figure 4c**. Solutions in DMF have low viscosity and low storage modulus. **Figure 4d** plots $\tan(\delta)$ as a function of temperature. $\tan(\delta)$ corresponds to the ratio between the loss and storage moduli. Low $\tan(\delta)$ indicates high elasticity, confirming once again the gel-like behavior of solutions in [EMIM]SCN. Solutions in [BMIM]SCN have the lowest elasticity. This is the best solvent, among those investigated for EXTEMTM, according to $[\eta]$ values. 20 wt% solutions in [BMIM]SCN are far above C^* , being highly entangled systems. But in opposite to the case of [EMIM]SCN, the solvent acts as a lubricant between polymer-polymer segments, substantially reducing the friction, increasing the mobility and leading to a liquid-like behavior.

3.3. Ternary Phase diagram

The phase diagrams of different EXTEMTM/solvent/water systems in **Figure 5** were obtained by measuring their cloud points. The two-phases region of the diagram increases in the following order: EXTEMTM/[EMIM]OAc < EXTEMTM/[BMIM]SCN $\approx$ EXTEMTM/DMF < EXTEMTM/[EMIM]SCN. The marked points were obtained by adding water until the turbidity starts. The cloud points for the EXTEMTM/[EMIM]OAc system were hardly detected, due to low turbidity.

The values of $[\eta]$ and D_h for binary EXTEMTM/solvent systems decrease in the following order: EXTEMTM/[BMIM]SCN > EXTEMTM/[EMIM]OAc > EXTEMTM/DMF > EXTEMTM/[EMIM]SCN. This order reflects the decreasing solvent quality. The addition of the non-solvent water destabilizes the solution. It is expected that in an initially better solvent, the solution would sustain larger water addition before reaching the cloud point.

3.4. Kinetics of phase separation

The non-solvent induced phase separation of EXTEMTM casting solutions, which have different viscosity and thermodynamic interactions, was monitored by measuring the relative light transmittance (T_r) as a function of time, as illustrated in **Figure 6**. The phase separation for membranes prepared from solutions in ionic liquids is slow. The turbidity reaches its maximum only after 40 s (EXTEMTM/[EMIM]SCN), 75 s (EXTEMTM/[BMIM]SCN), and 55 s

(EXTEM™/[EMIM]OAc). These systems might stay long in a metastable condition, before separating in two phases. A metastable condition separates the binodal and spinodal curves in a phase diagram estimated from values of Gibbs free energy. On the other hand, the 20 wt% EXTEM™/DMF system becomes turbid only 3 s after immersion in water. A fast phase separation, with a fast pathway into the 2 phases region of the phase diagram, normally follows the mechanism of spinodal decomposition (SD). The solutions in ionic liquids probably follow a mechanism of phase separation characterized by nucleation and growth (NG). The conditions for phase separation are a combination of many factors, such as thermodynamic interaction between solvent and non-solvent, polymer and solvent, and between polymer and non-solvent. The mechanism of phase separation is also highly influenced by its kinetics. An important factor in determining the kinetics of phase separation, leading to SD or NG, might be the solution viscosity. As shown in **Figure 4**, solutions in ionic liquid have significantly higher viscosity than in DMF. Furthermore, although the viscosity of the system [BMIM]SCN is lower than other ionic liquid based polymer solutions, the phase separation of the system [BMIM]SCN is slightly more delayed than the others. This might be because of the miscibility with water, the non-solvent. The difference in solubility parameters between ionic liquids and water increases in the following order: [EMIM]SCN < [EMIM]OAc < [BMIM]SCN. The lower miscibility and the slightly more hydrophobic properties of [BMIM]SCN delays the solvent-non-solvent exchange and therefore also the phase separation, more than other ionic liquids.

Figure 4. Rheology of 20 wt% EXTEM™ solutions in different solvents as a function of temperature: (a) viscosity at shear rate of 10 s^{-1} , (b) viscosity ratio between solutions and solvents, (c) storage moduli, and (d) $\tan(\delta)$ at shear rate of 20 s^{-1} .

Figure 5. Phase diagram of EXTEM™ solutions using water as a non-solvent at room temperature.

Figure 6. Kinetics of phase separation of EXTEM™ solutions cast on a glass plate and immersed in water.

3.5. Membrane characterization

The membranes fabricated from EXTEM™/[EMIM]SCN solutions have sponge-like structure with fine pores, promoted by the NG mechanism. In contrast, the finger-like cavities can be seen in membranes prepared from solutions in DMF. The cavities resulted from an abrupt water intrusion in the low viscosity polymer solutions. The mean pore size of the membranes prepared from 20 % EXTEM™/[EMIM]SCN was smaller (approximately 1.5 nm) than that of 20 % EXTEM™/DMF. Membranes prepared from EXTEM™/[EMIM]SCN solutions had narrower pore size distribution (Figure 7). The mean pore size was in the nanometer range in all [EMIM]SCN based membranes.

Although EXTEM™ was also soluble in [EMIM]OAc and [BMIM]SCN and had better thermodynamic interactions than that in [EMIM]SCN, the membranes prepared from these ionic liquids were very brittle with low elasticity (Figure 4). They

Figure 7. Cross-sectional and surface morphologies cast from the following solutions: (a) 18 wt% in [BMIM]SCN, (b) 18 wt% and (c) 20 wt% EXTEM™ in [EMIM]SCN with pore distributions, and (d) 20 wt% EXTEM™ in DMF with its pore distribution.

were not further characterized in terms of pore size, separation performance and permeance.

All membranes prepared from solutions in [EMIM]SCN have very high water permeance, when compared to those with similar range of pore size, cast from solutions in DMF, as shown in Figure 8. In particular, membranes from 20 wt% EXTEM™ solutions in [EMIM]SCN had a permeance of 230 L m⁻² h⁻¹ bar⁻¹, which is 50 % larger than that of membranes prepared from 20 % EXTEM™ in DMF.

Figure 8. (a) Water permeance and (b) PEG rejection of different membranes.

3.6. DNA and protein separation

All membranes rejected more than 97 and 99 % of BSA and γ -globulin, respectively (**Table 3**). In case of membranes fabricated from 22 and 24 wt% EXTEM™ in [EMIM]SCN, they reject DNA up to 84 and 93 % with the molecular weight of 3.4 kg mol⁻¹ and 94 and 93 % with the molecular weight of 6.4 kg mol⁻¹, respectively.

In comparison with membranes cast from solutions of similar polymer concentration, the PEG rejection of the ionic liquid based membranes was generally higher than that of membranes fabricated from DMF.

3.7. Ionic liquid recovery

The use of ionic liquids as solvents for membrane separation would only be sustainable if recovery and recycling would be possible. Mai *et al.*⁵¹ explored various methods such as membrane separation⁵²⁻⁵⁴ and distillation⁵⁵⁻⁵⁷ for ionic liquid recovery with their advantages and disadvantages. In this study, the distillation which is the simplest method, but efficient purification method, was applied with vacuum, heat, and absorption with an absorbent. Waste water of 500 ml after the phase separation was taken from the coagulant bath to recover [EMIM]SCN. We recovered the ionic liquid from the waste after the membrane preparation by 3 steps. First, the initial waste was applied in a rotavapor with the rotation speed of 200 rpm, temperature of 80 °C under the vacuum of 180 mbar. Then, further vacuum was applied at 130 °C for 20 hours. As a last step, magnesium sulfate (MgSO₄) was added to absorb residual moisture and the recovered ionic liquid was separated from sediments included MgSO₄ by centrifugation. The initial concentration of [EMIM]SCN in the bath was 1.6 %. After 3 steps of recovery, the final ionic liquid concentration could be increased to 96 % as plotted in **Figure 9**. The purity of the ionic liquid for casting solution preparation was ≥ 95 %. Therefore, it can be fully recovered for reuse.

Table 3. Results of DNA and protein separation

EXTEM™ in solvents	MWCO [kg mol ⁻¹]	Rejection (%)			
		DNA	DNA	BSA	γ -Globulin
		(M _w =3.4 kg mol ⁻¹)	(6.4 kg mol ⁻¹)	(69 kg mol ⁻¹)	(140 kg mol ⁻¹)
20 wt% in [EMIM]SCN	7.3	-	-	97.7	99.4
22 wt% in [EMIM]SCN	5.2	84.4	94.1	98.3	99.7
24 wt% in [EMIM]SCN	5.3	92.7	93.1	98.1	99.2
20 wt% in DMF	9.7	-	-	99.7	99.4
24 wt% in DMF	5.3	-	-	99.7	99.4

Figure 9. Ionic liquid recovery.

4. Conclusion

EXTEM™ solutions dissolved in pure ionic liquids: [BMIM]SCN, [EMIM]OAc, and [EMIM]SCN. The solutions were examined theoretically and experimentally. Membranes cast from EXTEM™ solutions in [EMIM]SCN were characterized with the following conclusions:

- (1) The order of EXTEM™ solubility in different solvents is DMF > [BMIM]SCN > [EMIM]OAc > [EMIM]SCN, all forming thermodynamically stable solutions.
- (2) Membranes cast from EXTEM™ in [EMIM]SCN were mechanically more stable than those cast from [EMIM]OAc and [BMIM]SCN.
- (3) $[\eta]$ for EXTEM™ solutions in different solvents decreased in the following order: [BMIM]SCN > [EMIM]OAc > DMF > [EMIM]SCN.
- (4) Membranes cast from EXTEM™ in [EMIM]SCN have sponge-like structure with narrow pore size distribution and nano-sized pores. In contrast, finger-like cavities were found in the membranes cast from solutions in DMF.
- (5) The membranes cast from 20, 22, and 24 wt% EXTEM™ solutions in [EMIM]SCN have very high water permeance and higher PEG rejection than those prepared from solutions in DMF. The MWCO values were the following: 7.3; 5.2; and 5.3 kg mol⁻¹, respectively. Membranes cast from solutions in [EMIM]SCN rejected BSA and γ -globulin more than 97 and 99 % and DNA with molecular weight of 6.4 kg mol⁻¹ up to 94 and 93 %.
- (6) Through 3 steps of recovery, the waste [EMIM]SCN after membrane formation was concentrated from 1.6 to 96 wt% ionic liquid.

Author information

Corresponding Author

Suzana P. Nunes*, email: suzana.nunes@kaust.edu.sa

Author Contributions

The manuscript was written through contributions of all authors.

Acknowledgment

This work was sponsored by King Abdullah University of Science and Technology (KAUST).

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