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Fabrication of Polyacrylonitrile Hollow Fiber Membranes from Ionic Liquid Solutions

DooLi Kim^a, Nicolas Moreno^{a,b}, and Suzana Pereira Nunes^{a*}

^a *Biological and Environmental Sciences and Engineering,
King Abdullah University of Science and Technology, Saudi Arabia*

^b *Center for Numerical Porous Media NUMPOR, King Abdullah University of Science and
Technology, Saudi Arabia*

**Corresponding author: suzana.nunes@kaust.edu.sa*

ABSTRACT

The interest in green processes and products has increased to reduce the negative impact of many industrial processes to the environment. Solvents, which play a crucial role in the fabrication of membranes, need to be replaced by sustainable and less toxic solvent alternatives for commonly used polymers. The purpose of this study is the fabrication of greener hollow fiber membranes based on polyacrylonitrile (PAN), substituting dimethylformamide (DMF) by less toxic mixtures of ionic liquids (IL) and dimethylsulfoxide (DMSO).

A thermodynamic analysis was conducted, estimating the Gibbs free energy of mixing to find the most convenient solution compositions. Hollow fiber membranes were manufactured and optimized. As a result, a uniform pattern and high porosity were observed in the inner surface of the membranes prepared from the ionic liquid solutions. The membranes were coated with a polyamide layer by interfacial polymerization the hollow fiber membranes were applied in forward osmosis experiments by using sucrose solutions as draw solution.

Key words: Green solvents, membranes, ionic liquid, hollow fibers, forward osmosis.

1. Introduction

Volatile organic compounds (VOC) resulting from many toxic or hazardous solvents are discharged in the air at an estimated rate of 20 million ton per year from the industry¹. These emissions cause serious environmental issues such as contamination of the atmosphere and the contamination of aqueous effluents² posing a high risk to the environment and human health. As concerns of regulatory authorities related to environmental impact grow, interest in green processes and products, by the usage of harmless chemicals, has increased through the past decade.

Green chemistry aims to reduce the usage of harmful chemicals and was summarized by Anastas et al.³ in twelve principles, which are important considerations in the design of processes and products⁴. Using safer solvents and auxiliaries is one of the main aspects of green chemistry⁵. The European Chemicals Agency (EACH), which is governed by EU public law, classified harmful or toxic solvents into a list regulated by the Registration, Evaluation, Authorization and Restriction of chemicals (REACH)⁶. In this list, chemicals which are commonly used to fabricate membranes such as DMF, NMP, and DMA, appeared as toxic compounds. This means that the commonly used solvents may soon be withdrawn from the market and will not be able to be utilized in Europe due to their high toxicity and risk for human health and the environment. This is a strong motivation to consider alternatives to conventional chemicals used as solvents, and replace them by sustainable and alternative solvents, which are less toxic to the environment and human health; such solvents are frequently referred as “green” solvents.

Membrane technologies have a crucial role as green processes in terms of energy efficiency, with their simple operation process; high performance, such as selectivity and permeability; low energetic requirement, compared to other separation processes; and high

stability under operating conditions ⁷. However, this only considers one side of “greenness” in membrane technology. It is important to think in other aspects as how can membranes be fabricated without the usage of any toxic compounds? Figoli et al. ⁸ recently summarized very well the concept of greener membranes: Firstly, the use of new and renewable materials to replace oil derived chemicals was considered; secondly, the hazard or toxicity of the other chemicals involved in the fabrication of membranes such as solvents, additives, and modification agents, needs to be minimized as possible. This study focuses on the fabrication of greener membranes by the usage of chemicals with less toxic properties.

Solvents which play a crucial role in the fabrication of membranes are derived from petroleum and generate volatile organic compounds during their production, which can cause health and environmental problems ⁹. Alternative or green solvents need to have low toxicity, be non-volatile, be easy to recycle, inert, and should not contaminate the product ¹⁰. Over the past decade, water, ionic liquids, supercritical fluids (SCFs), and fluoruous solvents have been reported as possible alternatives and green solvents ¹¹.

Ionic liquids (IL) are considered green solvents in many aspects, such as lack of measurable vapor pressure, non-flammability, reusability, high thermal stability ¹² and low corrosiveness ¹³. Due to their high solubility in water, toxicity to aquatic organisms has been a matter of some concern ¹⁴, but the substitution of hazardous volatile organic solvents frequently used for membrane fabrication by less toxic mixtures containing ionic liquids could be very beneficial. The term ionic liquid refers to liquids composed entirely of ions that are fluid at temperatures below 100 °C ^{10, 15} and do not lead to hazardous VOC generation in contrast to common organic solvents ^{15, 16}.

Many studies have focused on dissolving cellulose using hydrophilic ionic liquids such as 1-butyl-3-methylimidazolium chloride [BMIM]Cl and 1-allyl-3-methylimidazolium chloride [AMIM]Cl ¹⁷. Swatloski et al. ¹⁸ showed that ionic liquids can be used as non derivatizing

solvents for cellulose. They also reported, that ionic liquids with anions, which are strong hydrogen bond acceptors, were most effective for dissolving cellulose¹⁹. S. Livazovic et al.²⁰ recently reported a membrane manufactured based on cellulose/ionic liquid. Wang et al.²¹ reported the dissolution of polybenzimidazole (PBI) in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl). However, very few studies related to the preparation of membranes have focused on ionic liquids. Xing et al. dissolved cellulose acetate (CTA) in 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) to fabricate flat sheet membranes²². In a following study, they also fabricated hollow fiber membranes using the same polymer, but dissolved in a different ionic liquid, 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN)²³. Similarly, UF membranes were also fabricated but using only polybenzimidazole (PBI)²⁴ or blends of PBI and P84 polyimide²⁵, both studies used the same ionic liquid, 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc). Only few polymers have been used for the fabrication of membranes with ionic liquids due to their poor activity as solvents for the polymers which are commonly used for membrane fabrication, such as polysulfone (PSf), polyacrylonitrile (PAN), and polyetherimide (PEI).

DMSO, a good solvent for commercial polymers and commonly used for membrane fabrication, is considered of low toxicity according to the GSK's guide^{26,27} and is not in the REACH solvent list under concerns⁶. Low toxicity, high polarity, and water miscibility are good characteristics for a solvent in membrane manufacture, making DMSO a good candidate to replace DMF, dimethylacetamide (DMA), and 1-methyl-2-pyrrolidone (NMP).

The purpose of this study is the fabrication of PAN hollow fiber membranes using solvent mixtures of ionic liquids and DMSO, which has lower toxicity than other commonly used polar organic solvents, with good pore morphology. First, the suitable composition was estimated considering their thermodynamic interactions expressed by the Flory-Huggins parameter, χ and the Gibbs free energy of mixing. Theoretical and experimental phase

diagrams were constructed to validate the proper solvent composition. Once identified the adequate solvent and polymer compositions membranes were manufactured using such less toxic solvent mixture. The performance of hollow fiber membranes prepared from IL/DMSO, pure DMSO, and pure DMF were compared for FO systems.

2. Experiments

2.1 Materials

Polyacrylonitrile (PAN, $M_w = 324,000$) was used as the polymer in the form of fine power. The ionic liquid (IL) was 1-Ethyl-3-methylimidazolium acetate ([EMIM]OAc, $\geq 95.0\%$), supplied by Sigma-Aldrich. Dimethyl sulfoxide (DMSO, $\geq 99\%$), and dimethylformamide (DMF, 99.8%) were also purchased from Sigma-Aldrich. The used materials are summarized in Table 1. For the interfacial polymerization (IP), *m*-phenyldiamine (MPD, $>99\%$), 1,3,5-benzenetricarbonyltrichloride (TMC, 98%), triethylamine (TEA, $>99.5\%$) and (1*S*)-(+)-10-camphorsulfonic acid (CSA, 99%) were supplied by Sigma-Aldrich. Polyethylene glycol (PEG) (Sigma-Aldrich) and polyethyleneoxide (PEO) (Sigma-Aldrich), whose molecular weights were 300 g/mol, 1,500 g/mol, 6,000 g/mol, 10,000 g/mol, 35,000 g/mol, 100,000 g/mol, and 600,000 g/mol, were used for the solute rejection evaluation and determination of the molecular weight cut-off (MWCO). Sucrose (Sigma-Aldrich) was used as draw solution which was applied in the lumen side of the thin film composite (TFC) hollow fiber membranes for testing the performance in a FO system.

Table 1. Polymer and solvents used in this study

Materials	Structures
Polyacrylonitrile (PAN)
1-Ethyl-3-Methylimidazolium acetate ([EMIM]OAc)
Dimethyl sulfoxide (DMSO)
Dimethylformamide (DMF)

2.2 Thermodynamic analysis

Prediction of the Gibbs free energy of mixing (ΔG_m) and the Flory- Huggins parameter

Understanding the polymer-solution system from the thermodynamic standpoint is an important tool to optimize the ionic liquid composition in the dope solution for the fabrication of membranes. The free energy of mixing for polymer dissolution can be written as

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (1)$$

where, T is the absolute temperature, whereas ΔH_m and ΔS_m are the enthalpic and entropic change of mixing, respectively. According to Flory-Huggins theory²⁸, the Gibbs free energy of mixing can be approximated by the expression:

$$\Delta G_m / N_0 = kT [\chi \phi_1 \phi_2 + \phi_1 / x_1 \ln \phi_1 + \phi_2 / x_2 \ln \phi_2] \quad (2)$$

where k is the Boltzmann constant, ϕ_i and x_i are the volume fraction and number of segments of the i th component, respectively. Spontaneous dissolution processes take place only if ΔG_m is negative. The enthalpy change of mixing can be calculated from the Flory-Huggins parameter, χ , which can be estimated from the solubility parameters of the species according to equation (3)²⁹⁻³²:

$$\chi_{ij} = V_i(\delta_i - \delta_j)^2 / RT + 0.34 \quad (3)$$

where, χ_{ij} is the Flory-Huggins parameter; V_i is the molar volume of the solvent, (cm^3 / mol); δ is the Hildebrand solubility parameter for the solvent (i) and the polymer (j), ($\text{Mpa}^{1/2}$); R is the ideal gas constant ($8.314 \text{ cm}^3 \text{ Mpa K}^{-1} \text{ mol}^{-1}$); T is the absolute temperature, (K); and 0.34 is an empirical constant absent in the original theory that has been found important for polymer systems²⁹⁻³². According to the Flory-Huggins approximation, if χ is smaller than 0.5, homogeneous polymer solutions are expected³⁰. Taking into account the inherent simplifications in the Flory-Huggins model²⁸, the value of $\chi = 0.5$ is used as an initial guess to decrease the experimental solvent-composition space to study. The solubility parameters can be computed using the Hansen solubility parameters³¹, given by the contribution of dispersive, dipole-dipole, and hydrogen bonding interactions as

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (4)$$

In particular, for ionic liquids the electrostatic³³ and Coulombic interactions may have an important contribution that is not included in the traditional Hansen approach. Therefore, experimental or computational based estimations are suitable for improving the free energy calculation. Xing et al.^{22, 23, 25} calculated the solubility parameter of the ionic liquids, [EMIM]OAc and [EMIM]SCN, using molecular dynamic simulations³⁴, leading finally to ΔG_m values.

Phase diagram

Polyacrylonitrile solutions with the following solvents or solvent mixture were investigated for membrane preparation: (20/80, 30/70, and 40/60) (wt%/wt%) IL/DMSO; pure DMSO; and pure DMF. Each point in the phase diagrams for each polymer solution was plotted after detecting cloud points, i.e. the abrupt increase of turbidity while titrating the originally homogeneous solution with addition of water as a non-solvent at $25^{\circ}\text{C} \pm 1$.

2.3. Fabrication of membranes

PAN was dissolved in a 3-neck flask in each solvent at 60°C for 12 hours. The polymer solutions were prepared with the ionic liquid (IL), 1-Ethyl-3-methylimidazolium acetate, (HF-20IL 1, 2, and 3); with pure DMSO (HF-DMSO); or pure DMF (HF-DMF). In the case of HF-20IL 1, 2, and 3, the ionic liquid was added after complete polymer dissolution in DMSO and all polymer solutions were stirred for 12 hours at room temperature. The prepared dope solutions were degassed inside the reservoir of the dope solution during 24 hours. Then, hollow fiber membranes were prepared by using a double spinneret with $0.34\text{ }\mu\text{m}$ inner diameter (ID) and $0.64\text{ }\mu\text{m}$ outer diameter (OD) at room temperature. After spinning, the hollow fiber membranes were immersed in a mixture of 50% glycerol and 50% 2-propanol for 2 hours and were dried again. The spinning conditions are summarized in Table 2. These spinning conditions were designed to fabricate hollow fiber membranes with thin walls with thicknesses of approximately $100\text{ }\mu\text{m}$, which is convenient in forward osmosis to improve water flux. In case of the composition of the bore fluids, the concentration of water was always 10 wt%; 90 wt % DMSO or DMF was used, depending on solvent used in the dope solutions.

Table 2. Spinning conditions

Sample code	HF-20IL 1	HF-20IL 2	HF-20IL 3	HF-DMSO	HF-DMF
Dope solution composition (wt%)	12% PAN 88% (20/80) IL/DMSO	12% PAN 88% (20/80) IL/DMSO	12% PAN 88% (20/80) IL/DMSO	12% PAN 88% DMSO	12% PAN 88% DMF
Composition of bore fluid (wt%)	90/10 DMSO/H ₂ O	90/10 DMSO/H ₂ O	90/10 DMSO/H ₂ O	90/10 DMSO/H ₂ O	90/10 DMF/H ₂ O
Coagulant	DI water	DI water	DI water	DI water	DI water
Air gap (cm)	10	10	10	10	10
Pressure (bar)	2	2	2	2	2
Flow rate of dope solution (mL/min)	2.8	3.7	7.4	6.7	5.0
Flow rate of inner coagulant (mL/min)	3	3	5	3	3
Take up speed (m/min)	17.8	17.8	17.8	17.6	17.7
Temperature of dope solution, bore fluid and coagulant (°C)	25	25	25	25	25

To apply the hollow fiber membranes in FO, the membranes need to have selective layers with fine pores (less than 10 Å) to reject monovalent ions such as NaCl. Interfacial polymerized polyamide is commonly used as selective layer. Thin film composite (TFC) hollow fiber membranes were prepared by interfacial polymerizing on the outer surface of the hollow fiber supports. Each hollow fiber support, which was blocked by epoxy in both sides to prevent the MPD aqueous solution from invading the lumen of the hollow fibers, was immersed for 3 minutes in an aqueous solution containing 2wt% of MPD, 1% of CSA, and 1% of TEA. After removing the MPD solution excess on the surface of the hollow fiber, the fiber was immersed for 20 seconds in an organic solvent which was composed of 0.1% TMC in

hexane to obtain the thin film polyamide selective layer on the surface of the hollow fiber by interfacial polymerization. The TFC hollow fiber membrane was rinsed in pure hexane to remove unreacted functional groups for 1 minute. After removing excess hexane, the TFC hollow fiber membranes were immersed in a mixture of 25% glycerol and 75% water for 2 hours and were dried in room temperature.

2.4 Characterization of the polymer solutions and the membranes

Characterization of the polymer solutions

Rheological measurements (AR1500ex Rheometer, TA Instruments) were performed to measure the storage (G') and loss (G'') modulus, which indicate the elastic and viscous character, respectively.

The viscosity (AR1500ex Rheometer, TA Instruments) of the polymer solution affects the thickness and diameter of the fibers and also has an effect on the spinning conditions. In addition, it is also important data to investigate and gain insight into the effects of the ionic liquids during membrane fabrication. To prepare the UF membrane using NIPS method, the polymer solution needs to have a proper range of viscosity, which depends on the polymer and solvents kind and concentrations. It is also different for different polymer molecular weights.

Membrane morphology

The morphologies of the hollow fiber support membranes and thin film composite (TFC) layers were examined by Field Emission Scanning Electron Microscopy (FESEM), FEI Quanta 600 and Nova Nano FESEM. The water in the membrane pores was exchanged with methanol and hexane. After freeze drying in liquid nitrogen, the hollow fiber samples were fractured and the membrane cross-sections coated by iridium.

Characterization of the membranes

FT-IR (Spectrum 100, PerkinElmer) was used to identify remaining ionic liquid. Hydrophilicity or hydrophobicity of the hollow fiber membranes was evaluated by contact angle measurement (CAM 200, KSV Instruments). The mechanical properties of the hollow fiber membranes were measured at the room temperature by dynamic mechanical analysis (Q800, TA Instruments).

Water permeance test and solute rejection tests were conducted to evaluate the performance of the membranes. The water permeance and rejection were calculated by the following equations:

$$\text{Water permeance test, PWP (LM}^{-2}\text{H}^{-1}\text{Bar}^{-1}\text{)} = Q \cdot A^{-1} \cdot \Delta P^{-1} \quad (5)$$

$$\text{Solute rejection, R (\%)} = (1 - C_{\text{perm}}/C_{\text{feed}}) \times 100 \quad (6)$$

where Q is the pure water permeation rate (L/ h), A is the effective membrane area (m^2), ΔP is the pressure which is applied in this test, and C_{perm} and C_{feed} are the concentrations of permeate solution and the feed solution respectively, analyzed by Gel Permeation Chromatography with PL aquagel-OH 40 and 60 columns (GPC) (1260 infinity GPC/SEC, Agilent technologies). The molecular weight cut-off (MWCO), the molecular weight 90% rejected by the membrane, was calculated from rejection results for PEG of different sizes.

2.5 Performance in forward osmosis experiments

The hollow fiber membranes were tested in cross-flow forward osmosis experiments under the following conditions: 2M and 1 M sucrose solution as draw solution, deionized water as feed solution, 1L/min flow rate, 25°C test temperature, pH 7, and TFC active layer facing the feed solution. The reversible solute flux (gMH), which indicates the amount of solutes, which permeates from the draw solution to the feed side, was measured by refractometry (AR2008 Digital Abbe Refractometer, KRÜSS) and by vapor pressure osmometer (Model 5600 Vapro vapor pressure osmometer, Wescor).

3. Results

3.1 Thermodynamic analysis

Prediction of the Gibbs free energy of mixing (ΔG) and the Flory-Huggins parameter (χ)

The Flory-Huggins parameter was calculated by equation (3) using the total solubility parameter as shown in Table 3. Figure 1(a-c) shows the variation of χ for PAN in different binary solvent mixtures with the solvent composition. For PAN solutions in DMSO/IL and DMSO/water, χ increases as the concentration of ionic liquid or water increases, reflecting a weaker interaction between polymer and solvent. According to this estimation for DMSO/IL solvent mixtures, PAN is soluble in 100 % DMSO, whereas the maximum concentration of the ionic liquid which could be added to maintain the polymer solution homogeneous with $\chi \lesssim 0.5$, would be 13%. In the case of the water and DMSO binary solvent, water can be added until around 5 %, maintaining the polymer solution homogeneous. Furthermore, the PAN interactions with DMSO/Water/IL ternary solvents are shown in Figure 1d. The dark

blue zone with $\chi < 0.5$ represents the solvent concentrations in which PAN is soluble. This prediction indicates that PAN is soluble in pure DMSO and solvent mixtures with up to 13% of the ionic liquid. This was the starting consideration for choosing the solvent mixture that could be used in the membrane preparation.

Table 3. Solubility parameters

	δ_d	δ_p	δ_h	δ (Mpa ^{1/2})
PAN ^a	17.9	16.7	6.3	25.2
[EMIM]OAc ^b	-	-	-	32.8
DMSO ^a	18.4	16.4	10.2	26.6
DMF ^a	17.4	13.7	11.3	24.8
Water ^a	15.5	16	42.3	47.8

δ_d , dispersive contribution; δ_p , polar contribution; δ_h , hydrogen bonding contribution³¹; ^a Hansen solubility parameter; ^b Calculated by Materials Studio (molecular dynamics simulation)^{24,25}; 1-Ethyl-3-Methylimidazolium acetate ([EMIM]OAc)

Figure 1. Flory-Huggins parameters estimated for PAN in (a) binary or (b) ternary solvent mixtures.

Effects of the polymer composition are not included in the calculation of χ , therefore the proper range of the solvent mixture composition can be derived from the free energy. Figure 2 shows the Gibbs free energy of mixing for each solvent mixture, calculated from the Flory-Huggins parameters, applying equation (2). The Gibbs free energy of mixing considers the interaction parameter, as well as polymer and solvent volume fractions, ϕ_2 and ϕ_1 respectively. In Figure 3 the Gibbs free energy of mixtures containing 12% PAN in solvent mixtures is presented. As shown in Figure 3(a), binary DMSO/IL solvent mixtures lead to negative values of ΔG (dark blue zone) with ionic liquid concentrations up to 42%. With this amount of ionic liquid the solution should remain homogeneous. In the case of DMSO/Water, 19% water can be added, without leading to positive ΔG values. Figure 2b shows ΔG for PAN in ternary solvents. Based on the free energy analysis the theoretical solvent mixture composition was chosen to fabricate the membranes was identified.

Once the range of solvent composition was narrowed by the theoretical predictions, the proper solvent composition for membrane preparation was validated experimentally. PAN was dissolved in different mixtures containing ionic liquid, as depicted in Figure 2b. 12 wt% PAN was not soluble in pure ionic liquid. Systems with 12% PAN in (20/80, 30/70 or 40/60) IL/DMSO solvent mixtures were homogeneous. Solutions with 12% PAN in (50/50) IL/DMSO solvent mixture was also homogeneous, but had a very high viscosity, behaving practically like a gel. These compositions match the theoretically predicted range.

(a)

(b)

Figure 2. The Gibbs free energy of mixing for 12 % PAN in (a) binary and (b) ternary solvent mixtures

Cloud Points and Phase Diagram

The phase diagram in Figure 3 is relative to the polymer, solvent mixtures, and water as non-solvent, giving an important thermodynamic information related to the phase inversion process, which takes place when the polymer solution is immersed in water (non-solvent for PAN). The phase diagram was constructed from cloud point measurements, that is, the limit between the stable and unstable regions, where the polymer solution changes from homogeneous to turbid³⁵. Ternary phase diagrams can give an indication of the final structure of membranes^{36, 37}. However kinetic aspects such as the solvent-non solvent exchange speed also play an important role in the pore formation.

The cloud points were obtained for 5 different solvents or solvent mixtures: DMSO, DMF, and (20/80, 30/70, 40/60) IL/DMSO. All polymer solutions tend to phase separate by titrating water as a non-solvent. Starting with solutions prepared with IL/DMSO solvent mixtures, phase separation is induced with slightly smaller amount of water than with solutions in pure DMF or DMSO. Polymer solution tendency to phase separate with addition of water was DMSO < DMF < (20/80) IL/DMSO < (30/70) IL/DMSO < (40/60) IL/DMSO. Taking into account the processability requirements for fabrication of hollow fiber membranes (i.e., viscosity of the solution and polymer concentration), a solution with 12% PAN in (20/80) IL/DMSO was chosen to construct posterior hollow fiber membrane fabrication and was compared to hollow membranes with pure DMSO and DMF in terms of various properties.

Figure 3. Phase diagram and cloud point for PAN in different solvents or solvent mixtures and water as non solvent, obtained at $25^{\circ}\text{C} \pm 1$.

3.2 Membrane morphologies

Hollow fiber support membranes

Hollow fiber membranes prepared from polymer solutions with the ionic liquid, showed morphologies with a fully developed finger like structure (Figure 4) and regular unique patterns on the inner surface (Figures 4 and 5). On the other hand, membranes prepared with pure DMSO, exhibited finger like morphology, but different porosity and patterns in the inner surface. As the hollow fibers were fabricated for application in forward osmosis (FO), the wall of the hollow fiber membranes was designed to obtain the highest flux as support in a FO system. The wall thickness of all hollow fiber membranes was less than $100\mu\text{m}$ approximately.

Figure 4. FESEM images of hollow fiber membrane cross-sections and surfaces: HF-20IL1, HF-20IL 2, HF-20IL 3 (IL/DMSO), HF-DMSO (DMSO), and HF-DMF (DMF).

Figure 5. FESEM images of inner surface of (a) HF-20IL 1 (IL/DMSO) and (b) HF-DMSO (DMSO) hollow fiber membranes.

Thin film composite hollow fiber membranes

Thin film composite (TFC) hollow fiber membranes, which were prepared by interfacial polymerization on hollow fiber support membranes with 20 % ionic liquid, pure DMSO, and pure DMF, showed morphologies with a typical ridge-and-valley structure (Figure 6).

Figure 6. FESEM images of outer surfaces and cross-sections of TFC hollow fiber membranes.

3.3 Characteristic of the polymer solution and the membranes

Rheological measurement and viscosity of the polymer solutions

The viscosity of dope solutions with DMSO, DMF and IL/DMSO is shown in Figure 7.

Figure 7. Viscosity of dope solutions.

(a)

(b)

(c)

Figure 8. Storage (G') and loss (G'') modulus as a function of oscillation strain (%) at 1 Hz:

12 % PAN (a) in DMSO, (b) in (20/80) IL/DMSO, and (c) in DMF.

The viscosity of the solution in DMF was lower than that in DMSO. However, it is important to note that the viscosity of the DMSO alone was twice that of DMF. In order to better understand the viscoelastic properties of the polymer solutions, the storage and loss modulus were measured on a rheometer under oscillation. Figure 8 shows the rheological behavior of the dope solutions used for the membrane manufacture, comparing those with pure DMSO, IL/DMSO, and DMF as solvents. In the case of the polymer solution in DMSO without the ionic liquid (Figure 8a), the storage modulus (G'), which denotes elasticity, was much lower than the loss (G'') modulus, which reflects viscous behavior. The G''/G' ratio, which can be seen as an indication of the system capacity to dissipate energy or mobility is 2.6 for solutions with DMSO. This means that the solution behaves more like a liquid and less like a gel. For the polymer solution with the (20/80) IL/DMSO solvent mixture there was just a small difference between two modulus and they were around 50 Pa (Figure 8b).

The G''/G' ratio is around 1.4. The elasticity increases by adding ionic liquid in relation to dissipative viscous flow. In the case of the polymer solution with DMF (Figure 8c), the G''/G' ratio is around 3.8, being the largest one.

The pore formation in membranes by phase inversion depends on the interplay between thermodynamics and kinetics of the polymer solution. By immersing in water, the solvent-non solvent exchange will drive the system to phase separation, reaching the unstable region of the phase diagram (Figure 3). The phase separation proceeds by spinodal decomposition or nucleation and growth, depending on the solvent exchange path guiding to the 2 phases region. The pore morphology and size will depend on how fast the phase separation evolves before the system gels. Fast gelation should lead to a fast interruption of the phase separation process and also might help to keep any pre-established order in the solution. If phase separation is allowed to progress to late stages, coalescence and disorder can be favored, leading also to a more disordered pore structure. By adding ionic liquid the gel character of the solution seems to be enhanced. The ionic liquid might also contribute to a better-organized system, with highly elastic character, which gels faster when water initiates the phase separation. At the same time, the presence of ionic liquid increases the interaction with water (solubility parameter closer to water's) and facilitates the water-solvent exchange. These factors might have contributed to the regular and open pore structure shown in Figure 5.

Additionally to the surface morphology, the cross-sections of membranes prepared with ionic liquids differ from those prepared from solutions in pure DMSO. A fine finger-like cavity structure is observed when ionic liquid is used, while a rather heterogeneous structure with sponge like morphology and scattered pear-like cavities can be seen when using pure DMSO.

The formation of the finger- or pear-like structures depends less on the mechanism of phase separation (spinodal decomposition or nucleation and growth) and more on how homogeneous the interface between the polymer solution and water is, how fast and abrupt the water-solvent exchange takes place, as well as how viscous the polymer solution is.

Characteristic of the membranes

To analyze the existence of remaining ionic liquid in the membranes, Fourier transformed infrared spectroscopy (FTIR), was performed. Figure 9 shows the peaks of PAN, membranes with 20% ionic liquid and without the ionic liquid, and pure ionic liquid. Typical peaks for PAN appeared at 2939 cm^{-1} for C-H stretching vibration, at 2243 cm^{-1} for $\text{C}\equiv\text{N}$ stretching vibration, at 1453 cm^{-1} for C-H bending in CH_2 , and at 1358 cm^{-1} for C-H bending in CH. In addition, the peaks of [EMIM]OAc are at 3135 cm^{-1} for =C-H stretching, at 2973 cm^{-1} for -C-H stretching, at 1559 cm^{-1} for C=O stretching of acetate anions, and below 1500 cm^{-1} resulted from the imidazolium cations. Particularly at 1559 cm^{-1} , the peak for the ionic liquid is strong and could not be seen in the membranes. We can affirm that no rest of ionic liquid was observed at least in the range of detection allowed by FT-IR. The ionic liquid was therefore removed by dissolution in water while the phase inversion occurred and by rinsing fabricated hollow fiber membranes in water for a day.

Figure 9. FT-IR spectra of: hollow fiber with 20% IL (red), hollow fiber without IL (blue), pure ionic liquid (grey), and PAN (green).

The results of the water permeance for each membrane, molecular weight cut-off (MWCO), mechanical strength (stress and strain values at the breaking point), Young's modulus, and contact angle are summarized in Table 4. The water permeance was measured in a dead-end set-up and it was calculated by using equation (5). Membranes prepared with ionic liquid, HF-20IL 2, had 2.5 times higher water permeance than those prepared from solution in DMSO alone, HF- DMSO. Higher porosity is a reason for that (see the inner surface morphology in Figures 4 and 5). Also, the molecular weight cut-off of the HF-DMSO membrane is smaller, indicating smaller pores in the selective outer layer. Therefore, the hollow fiber membranes prepared from solutions with ionic liquid have better performance in terms of the water permeance. HF-20IL1, 3, and HF-DMF were deformed while testing their water permeance due to their mechanical properties. As their Young's modulus showed low values in table 4 which denotes that their elasticity are higher, these properties were affected on deforming the circle shape of the hollow fiber membranes and

elongating the hollow fiber membranes under the pressure. The rejection of solutes in a feed solution with 300 g/mol PEG to 35,000 g/mol PEO is summarized in Table 5. The membrane prepared with the ionic liquid is only slightly more hydrophilic than the one without the ionic liquid (Table 4). The mechanical strength of the hollow fiber with the ionic liquid, in terms of the fiber breaking stress and strain, is stronger than the one with DMF alone, but lower than the one with DMSO alone, which had also a higher Young's modulus than other membranes, indicating more rigidity.

Table 4. Results of water permeance, molecular weight cut-off (MWCO), mechanical strength, Young's modulus, and contact angle.

	HF support membrane		Mechanical strength		Young's modulus	Contact angle (°)
	Water permeance (Lm ⁻² h ⁻¹ bar ⁻¹)	Molecular weight cut-off (g/mol)	Stress (Mpa)	Strain (%)		
HF-20IL 1	428* ± 10	60,000	4.8 ± 0.2	37 ± 1	1.17	52 ± 2
HF-20IL 2	540 ± 30	54,000	5.8 ± 0.1	31 ± 1	1.69	
HF-20IL 3	175*± 10	67,000	3.9 ± 0.2	24 ± 5	1.12	
HF - DMSO	209 ± 10	32,000	6.3 ± 0.3	43 ± 3	2.02	56 ± 2
HF-DMF	22*± 10	80,000	4.1 ± 0.2	14 ± 2	0.81	

*: deformation of the hollow fiber was observed during the test
Feed solution: 300 g/mol, 1,500 g/mol, 6,000 g/mol, 10,000 g/mol, 35,000 g/mol, 100,000 g/mol, 600,000 g/mol PEG solutions

Table 5. PEG rejection by hollow fiber membranes.

Solute molecular weight (g/mol)	HF-20IL 1 (%)	HF-20IL 2 (%)	HF-20IL 3 (%)	HF-DMSO (%)	HF-DMF (%)
300	48	39	18	23	43
1,500	49	42	22	52	48
6,000	59	56	42	62	53
10,000	62	62	50	68	56
35,000	85	87	82	94	70
100,000	100	100	100	100	100

Test conditions: 2 bar (pressure), 0.1 wt% 6000 g/mol PEG, 0.1 wt% 10,000 g/mol PEG, 0.1 wt% 35,000 g/mol PEG, 0.1 wt% 100,000 g/mol PEO, 0.1 wt% 600,000 g/mol PEO (feed solution)

3.4 Performance in forward osmosis tests

An interfacial polymerized polyamide layer was prepared on the outer surface of the hollow fiber membranes (Figure 6). Table 6 shows the performance results for hollow fiber membranes in FO system using sucrose solutions as a draw solution. The water flux of the hollow fiber membrane with the ionic liquid was slightly higher than the others. For example HF-20IL 1, which is a hollow fiber prepared with ionic liquid, was about 2 LMH higher than the other membranes with DMSO alone (HF-DMSO) and DMF alone (HF-DMS) in the condition of 1M sucrose draw solution. The reversible solute fluxes, which is amount of permeated solutes from the draw solution to the feed solution through membranes per membrane area and time, were measured by refractometry and vapor pressure osmometer both as showed it in table 4. No reversible sucrose was detected in the feed solution for any of the TFC hollow fiber membranes.

Table 6. Performance of hollow fiber membranes in forward osmosis tests.

Membranes	1M Sucrose		2M Sucrose		Thickness (μm)
	Water flux (LMH)	Reversible solute flux (gMH)	Water flux (LMH)	Reversible solute flux (gMH)	
HF-20IL 1	6.7 ± 0.5	0	5.6 ± 0.5	0	77
HF-20IL 2	6.5 ± 0.5	0	6.8 ± 0.5	0	90
HF-20IL 3	5.6 ± 0.5	0	7.0 ± 0.5	0	108
HF-DMSO	4.3 ± 0.5	0	5.3 ± 0.5	0	71
HF-DMF	4.4 ± 0.5	0	6.3 ± 0.5	0	80

Test conditions: 2M and 1 M sucrose solution as a draw solution, deionized water as a feed solution, 1L/min as flow rate, at 25°C as a test temperature, cross-flow, pH 7, and active layer of HF membranes facing the feed solution

4. Conclusion

The estimation of the Gibbs free energy of mixing, indicated that the maximum concentration of the ionic liquid which can be added while keeping the polymer solution homogeneous, was of 42%. This was experimentally confirmed.

The cloud point curve denoted that the polymer solution tendency to phase separate with addition of water is DMSO < DMF < (20/80) IL/DMSO < (30/70) IL/DMSO < (40/60) IL/DMSO.

The hollow fiber membranes were successfully fabricated using less toxic solvents and ionic liquid. The hollow fiber membranes with the ionic liquid had a fully developed finger like structure and regular patterns of inner surface. In contrast, membranes prepared without

ionic liquid had a porous structure with macrovoids or pear-like cavities, but without regular patterns in the inner surface.

The properties of the polymer solution systems and prepared membranes were characterized. No traces of ionic liquid were found by FTIR. Molecular weight cut-offs of 54 to 67 kg/mol were measured for membranes prepared with ionic liquid. The water permeance was as high as $540 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$.

The hollow fiber membranes were tested in FO measurements, after adding a selective layer by interfacial polymerization. Sucrose solutions were used as draw solution. The water flux of the hollow fiber membrane with the ionic liquid was higher than the others and no reversible solute flux was measured.

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Phase diagram for preparation of hollow fibers from solutions with ionic liquids
254x142mm (72 x 72 DPI)