Fabrication of Greener Membranes from Ionic Liquid Solutions

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ABSTRACT

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DooLi Kim

Membrane technology plays a crucial role in different separation processes such as biotechnology, pharmaceutical, and food industries, drinking water supply, and wastewater treatment. However, there is a growing concern that solvents commonly used for membrane fabrication, such as dimethylformamide (DMF), dimethylacetamide (DMAc), and 1-methyl-2-pyrrolidone (NMP), are toxic to the environment and human health. To explore the possibility of substituting these toxic solvents by less toxic or safer solvents, polymers commonly used for membrane fabrication, such as polyacrylonitrile (PAN), cellulose acetate (CA), polyethersulfone (PES), and poly(ether imide sulfone) (EXTEM™), were dissolved in ionic liquids. Flat sheet and hollow fiber membranes were then fabricated. The thermodynamics of the polymer solutions, the kinetics of phase inversion and other factors, which resulted in significant differences in the membrane structure, compared to those of membranes fabricated from more toxic solvents, were investigated. Higher water permeance with smaller pores, unique and uniform morphologies, and narrower pore size distribution, were observed in the ionic liquid-based membranes. Furthermore, comparable performance on separation of peptides and proteins with various molecular weights was achieved with the membranes fabricated from ionic liquid solutions. In summary, we propose less hazardous polymer solutions to the environment, which can be used for the membrane fabrication with better performance and more regular morphology.
Keywords: cellulose acetate, green solvents, ionic liquids, membranes, polyethersulfone, polyacrylonitrile, and poly(ether imide sulfone).
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LIST OF ABBREVIATIONS

[EMIM]OAc 1-ethyl-3-methylimidazolium acetate
[MMIM]DMP 1,3-dimethylimidazolium dimethylphosphate
[EMIM]DEP 1-ethyl-3-methylimidazolium diethylphosphate
[EMIM]SCN 1-ethyl-3-methylimidazolium thiocyanate
[BMIM]SCN 1-buty1-3-methylimidazolium thiocyanate
[OMIM]SCN 1-octyl-3-methylimidazolium thiocyanate
[BMIM]Cl 1-buty1-3-methylimidazolium chloride
[HMIM]Cl 1-hexyl-3-methylimidazolium chloride
[OMIM]Cl 1-octyl-3-methylimidazolium chloride
[BPy]Cl 1-buty1 pyridinium chloride
[BMIM]Br 1-buty1-3-methyl imidazolium bromide
[HMIM]Br 1-hexyl-3-methyl imidazolium bromide
[OMIM]Br 1-octyl-3-methyl imidazolium bromide
[BPy]Br 1-buty1 pyridinium bromide
[BMPy]Br 1-buty1-3-methyl pyridinium bromide
[HMPy]Br 1-hexyl-3-methyl pyridinium bromide
[OMPy]Br 1-octyl-3-methyl pyridinium bromide
[BMMPy]Br 1-buty1-3,5-dimethyl pyridinium bromide
[HMIM]I 1-hexyl-3-methylimidazolium iodine
[EMIM]BF4 1-ethyl-3-methylimidazolium tetrafluoroborate
[BMIM]BF4 1-buty1-3-methylimidazolium tetrafluoroborate
[HMIM]BF4 1-hexyl-3-methylimidazolium tetrafluoroborate
[OMIM]BF4 1-octyl-3-methylimidazolium tetrafluoroborate
NaBF4 Sodium tetrafluoroborate
NaPF6 Sodium hexafluorophosphate
[EMIM]PF6 1-ethyl-3-methylimidazolium hexafluorophosphate
[PMIM]PF6 1-propyl-3-methylimidazolium hexafluorophosphate
[BMIM]PF6 1-buty1-3-methylimidazolium hexafluorophosphate
[HMIM]PF6 1-hexyl-3-methylimidazolium hexafluorophosphate
[OMIM]PF6 1-octyl-3-methylimidazolium hexafluorophosphate
[EMIM]Tf2N 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[BMIM]Tf2N 1-buty1-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[MMpyr] (CF3SO2)2N 1,1-dimethylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[BPpyr] (CF3SO2)2N 1,1-buty1 methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[N1111] (CF3SO2)2N Tetramethylammonium bis(trifluoromethylsulfonyl)imide
[N1124] (CF3SO2)2N N-ethyl-N,N-dimethyl-1-butanamininium bis(trifluoromethylsulfonyl)imide
[MMIM]AlCl4 1-methyl-3-methylimidazolium tetrachloroaluminate
[EMIM]AlCl4 1-ethyl-3-methylimidazolium tetrachloroaluminate
[PMIM]AlCl4 1-propyl-3-methylimidazolium tetrachloroaluminate
[BMIM]AlCl4 1-buty1-3-methylimidazolium tetrachloroaluminate
[BBIM] AlCl$_4$ 1-butyl-3-butylimidazolium tetrachloroaluminate

[BMIM]NO$_3$ 1-butyl-3-methylimidazolium nitrate

[HMIM]NO$_3$ 1-hexyl-3-methylimidazolium nitrate

[OMIM]NO$_3$ 1-octyl-3-methylimidazolium nitrate

[BMIM] N(CN)$_2$$_2$ 1-butyl-3-methyl imidazolium dicyanamide

[BPypy]N(CN)$_2$$_2$ 1-butyl pyridinium dicyanamide

[BMPypy]N(CN)$_2$$_2$ 1-butyl-3-methyl pyridinium dicyanamide

[BMMMpy]N(CN)$_2$$_2$ 1-butyl-3,5-dimethyl pyridinium dicyanamide

REACH The registration, evaluation, authorization and restriction of chemicals

EACH The European chemicals agency

PAN Polycrylonitrile

CA Cellulose acetate

PES Polyethersulfone

PSf Polysulfone

EXTEM™ Poly (ether imide sulfone)

DMSO Dimethyl sulfoxide

DMF Dimethylformamide

DMAc Dimethylacetamide

NMP N-methyl-2-pyrrolidone

PEG and PEO Polyethylene glycol and polyethyleneoxide

VOCs Volatile organic compounds

NIPS Non-solvent induced phase separation

TFC Thin film composite

RO Reverse osmosis

NF Nanofiltration

FO Forward osmosis

UF Ultrafiltration

MF Microfiltration

MWCO Molecular weight cut-off

DLS Dynamic light scattering

XRD X-ray diffraction

SD Spinodal decomposition mechanism

NG Nucleation and growth mechanism
LIST OF SYMBOLS

\( \Delta G_m \)  Gibbs free energy of mixing
\( \Delta H_m \)  Heat of mixing
\( \Delta S_m \)  Entropy change of mixing
\( k \)  Boltzmann constant
\( \phi_i \)  Volume fraction
\( \chi_i \)  Number of segments
\( \chi \)  Flory-Huggins parameter
\( V \)  Molar volume of the solvent
\( R \)  Ideal gas constant
\( T \)  Absolute temperature
\( \delta \)  Solubility parameter
\( \delta_D \)  Dispersive contribution
\( \delta_p \)  Polar contribution produced by the dipole-dipole interaction
\( \delta_H \)  Hydrogen bonding contribution
\( \mu \)  Dynamic viscosity
\( h \)  Plank's constant in units of Js
\( N_A \)  Avogadro’s number (6.022 x 10^{23} \text{ mol}^{-1})
\( K_v \)  Proportionality constant
\( M \)  Polymer molecular weight
\( G' \)  Storage modulus
\( G'' \)  Loss modulus
\( \tan(\delta) \)  \( G''/G' \) ratio, system’s capacity to dissipate energy or mobility
\( D_h \)  Hydrodynamic diameter
\( R_h \)  Hydrodynamic radius
\( R_g \)  Radius of gyration
\( C^* \)  Critical concentration, at which the polymer coils start to entangle
\( [\eta] \)  Intrinsic viscosity
\( \eta_{rel} \)  Relative viscosity
\( \eta_{red} \)  Reduced viscosity
\( \eta/\eta_0 \)  Solution viscosity / solvent viscosity
\( T_r \)  Relative light transmittance
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Chapter 1. Introduction

1.1. Green chemistry

From industrial processing operations, an estimated 20 million ton of volatile organic compounds (VOCs) is released in the air every year [1]. VOCs are found in various organic solvent and petroleum-based products. General VOCs eventually leads to smog, serious air pollution, generation of ozone, playing an important role in the greenhouse effect, and especially aromatic VOCs, such as benzene, toluene, xylene, are carcinogens. Due to their negative impact to the environment and human health, reducing the use of products containing VOCs became an important issue with stricter regulation over the world.

The 12 principles of green chemistry (Table 1.1) give us a guideline on how to design a chemical process. One of the most focused principles is to use safer solvents and additives. Although compared to other separation process, a membrane process is energy efficient and accordant with principle 7, the membrane manufacture and most of solvents used for that are unfortunately toxic and detrimental. Thus, less harmful alternatives should be taken into account to fulfill greener process in membrane technology.
Table 1.1. The 12 principles of green chemistry.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Prevention: it is better to prevent waste production than to treat or clean up waste after it has been created.</td>
</tr>
<tr>
<td>2</td>
<td>Atom economy: synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.</td>
</tr>
<tr>
<td>3</td>
<td>Less hazardous chemical syntheses: wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.</td>
</tr>
<tr>
<td>4</td>
<td>Design safer chemicals: chemical products should be designed to fulfill their desired function while minimizing their toxicity.</td>
</tr>
<tr>
<td>5</td>
<td>Safer solvents and auxiliaries: the use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.</td>
</tr>
<tr>
<td>6</td>
<td>Design for energy efficiency: the energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.</td>
</tr>
<tr>
<td>7</td>
<td>Use of renewable feedstocks: a raw material or feedstock should be renewable, rather than depleting whenever technically and economically practicable.</td>
</tr>
<tr>
<td>8</td>
<td>Reduce derivatives: unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.</td>
</tr>
<tr>
<td>9</td>
<td>Catalysis: catalytic reagents (as selective as possible) are superior to stoichiometric reagents.</td>
</tr>
<tr>
<td>10</td>
<td>Design for degradation: chemical products should be designed so that at the end of their function, they break down into innocuous degradation products and do not persist in the environment.</td>
</tr>
<tr>
<td>11</td>
<td>Real-time analysis for pollution prevention: analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.</td>
</tr>
<tr>
<td>12</td>
<td>Inherently safer chemistry for accident prevention: substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.</td>
</tr>
</tbody>
</table>

Sources: [2, 3]
1.2. Toxicity of common organic solvents and alternatives

Table 1.2 shows the solvent selection guidance, classified as preferred, usable, and undesirable, depending on their toxicities [4, 5]. Similarly, A. Figoli et al. [6] classified the commonly used solvents, according to their regulation and toxicity. In these classifications, the most common solvents for membrane fabrication, such as dimethyl formamide (DMF), N-methyl pyrrolidone (NMP), and dimethyl acetamide (DMAc), are categorized in the undesirable group, due to their toxicity. Furthermore, they are classified as toxic solvents in the list of the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) [7], which is governed by the EU public law. To compare how toxic they are, their acute toxicity is listed in Table 1.4.

Table 1.2. Solvent selection guide.

<table>
<thead>
<tr>
<th>Preferred</th>
<th>Usable</th>
<th>Undesirable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Dimethylsulfoxide (DMSO)</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>t-Butanol</td>
<td>Chloroform</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>1-Propanol</td>
<td>1,2-Dichloroethane</td>
</tr>
<tr>
<td>Dimethyl carbonate</td>
<td>2-Propanol</td>
<td>Dimethyl formamide (DMF)</td>
</tr>
<tr>
<td>(DMC)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic liquids</td>
<td>Acetone</td>
<td>N-Methyl pyrrolidone (NMP)</td>
</tr>
<tr>
<td>Supercritical CO₂</td>
<td>Toluene</td>
<td>Pyridine</td>
</tr>
<tr>
<td>Fluorous media</td>
<td>Heptane</td>
<td>Dimethyl acetamide (DMAc)</td>
</tr>
<tr>
<td>Bio-sourced solvents</td>
<td>Tetrahydrofuran (THF)</td>
<td>Hexane</td>
</tr>
</tbody>
</table>

Sources (modified) from GSK and Pfizer’s solvent selection guide [4, 5]

LD₅₀ is the dose of a chemical, which kills 50% of test animals, usually rats or mice, and LC₅₀ is the concentration in air or water of the chemical, at which 50% of test animals are killed. The values are different, significantly depending on the dose methods: oral,
dermal, and inhalation and animals: rats, mice, rabbits, etc. The lower values of LD$_{50}$ and LC$_{50}$ denote more toxic chemicals [8]. Among several scales for understanding how toxic the chemical is to human, the Hodge and Sterner toxicity scale (Table 1.3), developed based on LD$_{50}$ values (oral and rats), is commonly used. According to this toxic scale, undesirable aprotic organic solvents, such as DMF (2000-7600 mg kg$^{-1}$); NMP (3100-5560 mg kg$^{-1}$); and DMAc (3000-6000 mg kg$^{-1}$) are slightly toxic. DMSO ($> 20,000$ mg kg$^{-1}$), which is categorized as a usable solvent, is relatively harmless. A preferred solvent, such as DMC (13,000 mg kg$^{-1}$), is rated as a practically non-toxic solvent.

<table>
<thead>
<tr>
<th>Toxicity rating</th>
<th>Toxicity term</th>
<th>LD$_{50}$ (Oral, rats) mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Extremely Toxic</td>
<td>1 or less</td>
</tr>
<tr>
<td>2</td>
<td>Highly Toxic</td>
<td>1-50</td>
</tr>
<tr>
<td>3</td>
<td>Moderately Toxic</td>
<td>50-500</td>
</tr>
<tr>
<td>4</td>
<td>Slightly Toxic</td>
<td>500-5000</td>
</tr>
<tr>
<td>5</td>
<td>Practically Non-toxic</td>
<td>5000-15,000</td>
</tr>
<tr>
<td>6</td>
<td>Relatively Harmless</td>
<td>15,000 or more</td>
</tr>
</tbody>
</table>

As the most common solvents for membrane fabrication are toxic, alternatives have been explored. The most common alternative solvents, which are explored for their usability in polymer science and engineering, are supercritical carbon dioxide (scCO$_2$), fluorous media, water, bio-sourced solvents, and ionic liquids. Advantages and disadvantages on the usage of the green solvents are summarized in Table 1.5. As a class of benign solvents, ionic liquids have no measurable volatile pressure and thus do not produce VOCs. This is one of the big advantages in using them. More features and benefits will be discussed in the next section.
## Table 1.4. Acute toxicity of common organic solvents.

<table>
<thead>
<tr>
<th>Solvents (category in Table 1.2.)</th>
<th>1272/2008 EC Relevant toxicological information</th>
<th>Reason for inclusion (REACH)</th>
<th>LD(_{50}) (Oral-Rats)</th>
<th>LC(_{50}) (Inhalation-Rats)</th>
<th>Vapor pressure</th>
</tr>
</thead>
</table>
| DMF (undesirable)                 | • Germ cell mutagenicity: mouse, lymphocyte  
• Mutations in mammalian somatic cells | Toxic for reproduction | • 2800 mg kg\(^{-1}\) [9]  
• 2000-7600 mg kg\(^{-1}\)  
• 3040 mg kg\(^{-1}\) bw | 9400 mg/m\(^3\)/2h (4.7 ppm/h) in MSDS  
• > 5900 mg/m\(^3\)/4h (1.475 ppm/h) in MSDS | 2.7 mmHg (20 °C) |
| NMP (undesirable)                | • Damage to fetus possible                    | Toxic for reproduction | • ∼4000 mg kg\(^{-1}\) [10]  
• 4150 (3100-5560) mg kg\(^{-1}\) bw [11]  
• 3906 (3100-4400) mg kg\(^{-1}\) bw [12] | > 5.1 ppm/4h (1.275 ppm/h) [12, 13] | 0.29 mmHg (20 °C) |
| DMAc (undesirable)               | • May cause congenital malformation to the fetus  
• Presumed human reproductive toxicant  
• Overexposure may cause reproductive disorders based on test with laboratory animals | Toxic for reproduction | • 3000 mg kg\(^{-1}\) bw to 6000 mg kg\(^{-1}\) bw in MSDS  
• 5,809 (male) and 4,930 (female) mg kg\(^{-1}\) [14]  
• 4300 mg kg\(^{-1}\) in MSDS | 2.2 ppm/1h in MSDS (~8.81 ppm/ 4h) | 2 mmHg (25 °C)  
|                                |                                             |                           |                          | 1.5 mmHg (20°C) |               |
| DMSO (usable)                    | -                                             | Negative results [15]    | 14,500 mg kg\(^{-1}\) in MSDS  
> 20,000 mg kg\(^{-1}\) bw in MSDS | > 5,000 mg/m\(^3\)/4 h (1.25 ppm/h) in OECD TG 403  
1600 mg/m\(^3\)/4 h in MSDS (0.4 ppm/h) | 0.42 mmHg (20 °C) |
| DMC (preferred)                  | -                                             | Negative results          | 13,000 mg kg\(^{-1}\) in MSDS | 140 ppm/4 h (35 ppm/h) | 42 mmHg (20°C) |

Sources (modified): 1272/2008[6], the Registration, Evaluation, Authorization and Restriction of chemicals (REACH)[7], and references, MSDS and the vapor pressure data from Sigma Aldrich.
Table 1.5. Advantages and disadvantages for alternative solvents.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Key solvent properties</th>
<th>Ease of separation and reuse</th>
<th>Health and safety</th>
<th>Cost of use</th>
<th>Cradle to grave environmental impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>scCo$_2$</td>
<td>Poor solvent for many compounds; may be improved with co-solvents or surfactants</td>
<td>Excellent, facile, efficient, and selective</td>
<td>Non-toxic; high pressure reactors required</td>
<td>Energy cost is high, needs special reactors, but CO$_2$ is cheap and abundant</td>
<td>Sustainable and globally available, no significant end of life concerns</td>
</tr>
<tr>
<td>Ionic Liquids</td>
<td>Designer/tailor made properties; always polar</td>
<td>Easy to remove volatile products with distillation. Others: extraction and adsorption etc.</td>
<td>Limited data available; some are flammable and/or toxic</td>
<td>Expensive, but low cost versions may become available</td>
<td>Mainly sourced from petroleum but some sustainable variants exist, synthesis may be energy intensive</td>
</tr>
<tr>
<td>Fluorous media</td>
<td>Non-polar solutes only; best used in biphasic systems</td>
<td>Readily forms biphases; may be distilled</td>
<td>Bioaccumulative greenhouse gases; perfluoropolyethers thought to be less problematic</td>
<td>Very expensive</td>
<td>Very resource demanding; may persist in environment</td>
</tr>
<tr>
<td>Water</td>
<td>Possible to dissolve at least very small quantities of many compounds; generally poor for non-polar</td>
<td>May be separated from most organics; purification may be energy demanding</td>
<td>Non-toxic, non-flammable and safe to handle</td>
<td>Very low cost; energy costs high</td>
<td>Sustainable and safe to the environment; may need purification</td>
</tr>
<tr>
<td>Bio-sourced solvents</td>
<td>Wide range: ethers, esters, alcohols and acids are available</td>
<td>May be distilled</td>
<td>Generally low toxicity, can be flammable</td>
<td>Mixed cost will decrease with greater market volume and through biotech advances</td>
<td>Sustainable resources biodegradable, VOCs will cause problems</td>
</tr>
</tbody>
</table>

Source (modified): adapted from ref. [16]
1.3. Ionic liquids

1.3.1. Designable solvents, ionic liquids

Ionic liquids are solvents, which are entirely composed of two ions: a cation and an anion. In general, one or both ions are large and the cation has a low degree of symmetry. These factors lead to lower lattice energy of crystal formation. Thus, the ionic liquids have low melting point, below 100 °C [17], and exist as liquids in room temperature [18]. These large and structured ions lead to three main interactions: hydrogen bonding, \( \pi-\pi \) stacking, and electrostatic interactions, which are unlikely to occur in commonly used organic solvents [19]. Some of the commonly combined cations and anions for the production of ionic liquids [20] are illustrated in Figure 1.1.

The structure of ionic liquids and the physical properties of ionic liquids, such as the melting points, viscosity, and hydrophilicity, can be tunable, by simply changing the length and number of the alkyl side chain (R group) in cations or the composition of cation and anion [21]. Huddleston et al. [22] compared the physical properties of ionic liquids with different chain length of 1- alkyl-3-alkylimidazolium group in cations and anions, as shown in Table 1.6. Based on the data of water miscibility and surface tension, the choice of anion and substituents (R\(_{1,2}\) group) in cations influences the hydrophobicity. Hydrophilicity increases with shorter chain length of 1- alkyl (R\(_1\)) and 3-alkyl (R\(_2\)) imidazolium and with the selection of anions such as halide (Cl\(^-\), Br, and I\(^-\)), nitrate (NO\(_3\)), acetate (CH\(_3\)CO\(_2\)^-), trifluoroacetate (CF\(_3\)CO\(_2\)^-), tetrafluoroborate (BF\(_4\)^-), triflate (CF\(_3\)SO\(_3\)^-), hezafluorophosphate (PF\(_6\)^-), and bis(trifluoromethylsulfonyl)imide [(CF\(_3\)SO\(_2\))\(_2\)N^-] [1, 23]. Furthermore, depending on the chain length of 1- alkyl group in cations and the degree of the cation’s symmetry, the melting point is different. For example, if the alkyl chain length
is longer, the melting points of 1-alkyl-3-alkylimidazolium hexafluorophosphates (PF₆) [24], tetrafluoroborates (BF₄) [25], and tetrachloroaluminate (AlCl₄) decrease. The symmetric structure of cations significantly influences their melting temperature [20, 26]. For instance, the melting points of symmetrical ([N₁₁₁₁] (CF₃SO₂)₂N) and asymmetrical ([N₁₁₂₄] (CF₃SO₂)₂N) quaternary ammoniums are 133 and -8 °C, respectively. Similarly, symmetrical ([MMpyr] (CF₃SO₂)₂N) and asymmetrical ([BMpyr] (CF₃SO₂)₂N) pyrrolidinium are 132 and -18 °C, respectively. Other physical properties also are different, based on composition and structures of the cation and anion. For the desired solvent properties, ionic liquids can be designed and it is one of the huge advantages on employing them for catalytic synthesis [27, 28], analytical chemistry [29], polymer materials [30, 31], and nanotechnology [32].

Figure 1. Most commonly used combinations of cations and anions in ionic liquids (adapted from ref. [20]).
Table 1.6. Physical properties of ionic liquids.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Carbon atoms in $R_1, R_2$ (n)</th>
<th>Water miscibility (water equilibrated in ppm)</th>
<th>Melting point ($^\circ$C)</th>
<th>$T_g$ ($^\circ$C)</th>
<th>Viscosity (cP)</th>
<th>Surface tension (dyn cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[BMIM]Cl</td>
<td>4</td>
<td>Miscible</td>
<td>41</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[HMIM]Cl</td>
<td>6</td>
<td>Miscible</td>
<td>-</td>
<td>-75</td>
<td>716</td>
<td>43</td>
</tr>
<tr>
<td>[OMIM]Cl</td>
<td>8</td>
<td>Miscible</td>
<td>-</td>
<td>-87</td>
<td>337</td>
<td>34</td>
</tr>
<tr>
<td>[BMIM]I</td>
<td>4</td>
<td>Miscible</td>
<td>-72</td>
<td>-</td>
<td>1110</td>
<td>54.7</td>
</tr>
<tr>
<td>[EMIM]BF$_4$</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>154 (20 $^\circ$C)</td>
<td>-</td>
</tr>
<tr>
<td>[BMIM]BF$_4$</td>
<td>4</td>
<td>Miscible</td>
<td>-81</td>
<td>-97</td>
<td>233 (20 $^\circ$C)</td>
<td>47</td>
</tr>
<tr>
<td>[HMIM] BF$_4$</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>314 (20 $^\circ$C)</td>
<td>-</td>
</tr>
<tr>
<td>[EMIM] PF$_6$</td>
<td>2</td>
<td>-</td>
<td>58-60</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[PMIM] PF$_6$</td>
<td>3</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[BMIM]PF$_6$</td>
<td>4 (11700)</td>
<td>Miscible</td>
<td>10</td>
<td>-80</td>
<td>371 (20 $^\circ$C)</td>
<td>49</td>
</tr>
<tr>
<td>[HMIM]PF$_6$</td>
<td>6 (8837)</td>
<td>-</td>
<td>-61</td>
<td>-78</td>
<td>680 (20 $^\circ$C)</td>
<td>43</td>
</tr>
<tr>
<td>[OMIM]PF$_6$</td>
<td>8 (6666)</td>
<td>-</td>
<td>-</td>
<td>-82</td>
<td>866 (20 $^\circ$C)</td>
<td>37</td>
</tr>
<tr>
<td>[EMIM] Te$_2$N</td>
<td>2</td>
<td>-</td>
<td>4</td>
<td>-98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[BMIM]Te$_2$N</td>
<td>4 (3280)</td>
<td>-</td>
<td>-104</td>
<td>69</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>[MMIM]AlCl$_4$</td>
<td>1</td>
<td>-</td>
<td>125</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[EMIM]AlCl$_4$</td>
<td>2</td>
<td>-</td>
<td>84</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[PMIM]AlCl$_4$</td>
<td>3</td>
<td>-</td>
<td>60</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[BMIM]AlCl$_4$</td>
<td>4</td>
<td>-</td>
<td>65</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[BBIM]AlCl$_4$ R$_1$ (n=4), R$_2$ (n=4)</td>
<td>4</td>
<td>-</td>
<td>55</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Sources: [20, 22]
1.3.2. Toxicity of ionic liquids

Ionic liquids are considered green solvents with the perspective of no measurable VOCs generation and therefore no contribution to air pollution. However, the impact to the aqueous environment might be negative in some cases, once ionic liquids are discarded as effluent. It is reported that some ionic liquids may be significant toxic [33], but they can be tunable to become environmentally benign [21]. To do that, the tendency of ionic liquid toxicity might be understood. As shown in Table 1.7, the effect of the cationic and anionic compounds, the length of the alkyl chain in the cations, and the number of the alkyl chains, on their acute toxicity to plants, enzyme, flash water snails, microorganisms and fishes have been investigated by adding ionic liquids to water with small aqueous plants and animals [34-41].

The toxicity increases as their hydrophobicity increase. Imidazolium-based cations are less toxic than those of pyridinium, which are longer, and have higher number of alkyl side chains. The selection of anionic compounds also affects the toxicity as well. Higher hydrophobicity leads to higher acute toxicity. For example, with 1-butyl pyridinium or 1-butyl-3,5-dimethyl pyridinium cationic compounds, N(CN$_2$)$_2$ anions are more toxic than bromide. It is because of structural similarity of ionic liquids to detergents, pesticides, and antibiotics, which are attacking lipid cell in microorganism [35, 42]. It may lead to membrane protein disruption [38]. Thus, decreasing the hydrophobicity of ionic liquids, designing shorter R groups in cations or selecting hydrophilic cations and anions would help to have less environment impact and to be more eco-friendly.
Table 1.7. Acute toxicity of different ionic liquids and common organic solvents.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Carbon atoms in R&lt;sub&gt;1&lt;/sub&gt; (n)</th>
<th>EC&lt;sub&gt;50&lt;/sub&gt; (mg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>LC&lt;sub&gt;50&lt;/sub&gt;-48h (mg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>IC&lt;sub&gt;50&lt;/sub&gt;-48h (mg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Tested microorganisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Octyl-3-methyl imidazolium bromide [OMIM]Br</td>
<td>8</td>
<td>1.2</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>1-Octyl-3-methyl pyridinium bromide [OMPy]Br</td>
<td>8</td>
<td>1.8</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>1-Hexyl-3-methyl imidazolium bromide [HMIM]Br</td>
<td>6</td>
<td>6.4</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td><strong>o-Xylene</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Hexyl-3-methyl pyridinium bromide [HMPy]Br</td>
<td>6</td>
<td>10</td>
<td></td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>6</td>
<td>31</td>
<td>10–17</td>
<td></td>
<td>(2)(4)</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Butyl-3,5-dimethyl pyridinium N(CN&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4</td>
<td>56</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td><strong>Methyl isobutyl ketone</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Butyl-3-methyl pyridinium N(CN&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;[BMPy] N(CN&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4</td>
<td>98</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methyl pyridine (starting compound)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Butyl-3,5-dimethyl pyridinium bromide</td>
<td>4</td>
<td>119</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>1-Butyl-3-methyl pyridinium bromide [BMPy]Br</td>
<td>4</td>
<td>131</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>1-Butyl pyridinium N(CN&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4</td>
<td>410</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>1-Butyl pyridinium chloride</td>
<td>4</td>
<td>440</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>1-Butyl pyridinium bromide</td>
<td>4</td>
<td>538</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td><strong>Ethylene glycol</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Butyl-3-methyl imidazolium chloride [BMIM]Cl</td>
<td>4</td>
<td>897</td>
<td>15 (13–17)</td>
<td>(1)(4)</td>
<td></td>
</tr>
<tr>
<td>1-Butyl-3-methyl imidazolium N(CN&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;[BMIM] N(CN&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4</td>
<td>966</td>
<td></td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methyl imidazole (starting compound)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Butyl-3-methyl imidazolium bromide [BMIM]Br</td>
<td>4</td>
<td>2248</td>
<td>8 (6.6–9.4)</td>
<td>(1)(4)</td>
<td></td>
</tr>
<tr>
<td>Dichloromethane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical name (continued)</td>
<td>Carbon atoms in R₁ (n)</td>
<td>EC₅₀ (mg L⁻¹)</td>
<td>LC₅₀-48h (mg L⁻¹)</td>
<td>IC₅₀-48h</td>
<td>Tested microorganisms</td>
</tr>
<tr>
<td>---------------------------</td>
<td>------------------------</td>
<td>---------------</td>
<td>-------------------</td>
<td>---------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>Methanol</td>
<td>101068</td>
<td>3289</td>
<td></td>
<td></td>
<td>(2)(4)</td>
</tr>
<tr>
<td>Chlorine</td>
<td></td>
<td>0.1–0.2</td>
<td></td>
<td></td>
<td>(2)(4)</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td></td>
<td>2.9–6.9</td>
<td></td>
<td></td>
<td>(4)</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td></td>
<td>29</td>
<td></td>
<td></td>
<td>(4)</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM]PF₆</td>
<td>4</td>
<td>20</td>
<td></td>
<td></td>
<td>(4)</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF₄</td>
<td>4</td>
<td>11</td>
<td>0.5–1</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td>1-Hexyl-3-methylimidazolium tetrafluoroborate [HMIM]BF₄</td>
<td>6</td>
<td>0.05</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium thiocyanate [BMIM]SCN</td>
<td>4</td>
<td>0.5–1</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>1-Octyl-3-methylimidazolium thiocyanate [OMIM]SCN</td>
<td>8</td>
<td>0.1–0.5</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>1-Butyl-3-methylimidazolium nitrate [BMIM]NO₃</td>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>1-Hexyl-3-methylimidazolium nitrate [HMIM]NO₃</td>
<td>6</td>
<td>0.5</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>1-Octyl-3-methylimidazolium nitrate [OMIM]NO₃</td>
<td>8</td>
<td>0.005</td>
<td></td>
<td></td>
<td>(3)</td>
</tr>
<tr>
<td>NaPF₆</td>
<td></td>
<td>9345</td>
<td></td>
<td></td>
<td>(4)</td>
</tr>
<tr>
<td>NaBF₄</td>
<td></td>
<td>4766</td>
<td></td>
<td></td>
<td>(4)</td>
</tr>
</tbody>
</table>

Sources: [34-36]

*Test organism: Vibrio fischeri (1), Photobacterium phosphoreum (2), P. freudenreichii (3), and Daphnia magna (4)
1.3.3. Ionic liquid recovery

Recycling or recovering is important. First of all, although using ionic liquids contribute to prevent the air pollution from VOCs emission, ionic liquids effluence into water may cause negative impact to aqueous environment [43]. The recovery of ionic liquids has to be considered to be an environmentally greener process. Another reason that ionic liquids are currently expensive. There is a limited number of industrial processes using ionic liquids, because of their high cost. An efficient recovery will be a solution to resolve this price issue. Mai et al. [44] explored various methods for ionic liquid recovery (Table 1.8) with their advantages and disadvantages. Distillation is the simplest method to separate chemicals, which can be vaporized in low temperature from thermally stable ionic liquids. Although this method may cause high energy-consumption, it is used for ionic liquid recovery in most of the studies, due to nonvolatile property of ionic liquids and it can efficiently purify ionic liquids. Huang et al. [45] recycled 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) with distillation and the ionic liquid was reused 5 times in the homogeneous cellulose acetylation system under optimal conditions. Xing et al. [46] recycled 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) and re-applied the recovered ionic liquid for membrane fabrication. Similary, 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP) [47] and 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN) [48] were recovered in our study by distillation with vacuum and heat (Figure 1.2) up to 96 and 95 %, respectively. The recovery then reached 99 and 96 % with further steps: absorption with MgSO₄ as absorbent for removing moisture remained in ionic liquids and centrifugation.

Membranes separation technology as one of methods for ionic liquid recovery has
been studied by Haerens et al. [49], using commercial reverse osmosis (RO), nanofiltration (NF), and pervaporation (PV) membranes for recycling Ethaline 200 ([HOC₂H₄N(CH₃)₃Cl] (ChCl)). The retention of Ethaline 200 was 20 and 88 % through two different NF membranes and 90.5 and 91 % for two different RO membranes. In the case of PV, small amount of water was removed and it was suggested that larger area of membranes need to be applied to improve water flux. NF membrane was applied for the separation of ionic liquids from the mixture of bromophenol blue/[BMIM]BF₄, lactose/[MMIM]MeSO₄[50], and saccharide/[MMIM]DMP[51] and ionic liquids were recovered up to 93 % of [BMIM]BF₄ and 80 % of [MMIM]DMP. Electrodialysis (ED) also can be an effective method for recovering ionic liquids with high recovery ratio [52].

![Figure 1.2. Recovery of [EMIM]DEP and [EMIM]SCN.](image)
Table 1.8. Summary of methods used for recovery and recycling of ionic liquids (ILs) (adapted from ref. [44]).

<table>
<thead>
<tr>
<th>Methods</th>
<th>Comments</th>
<th>Advantages</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Distillation of ionic liquids</td>
<td>Distilled as neutral compounds (carbon molecules) or as intact ions</td>
<td>Simple, rapid, and robust method</td>
<td>Energy consuming method</td>
</tr>
<tr>
<td>Distillation of volatile solutes / impurities in ionic liquids</td>
<td>Volatile compounds/impurities are distilled while ILs are remained as residual</td>
<td></td>
<td>Partial decomposition</td>
</tr>
<tr>
<td>Extraction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>Organic solvent/water are used to extract various compounds from ILs, thus allowing the recovery and reuse of ILs</td>
<td>Simple, no complex equipment, controlled recovery, selectivity, and flexibility</td>
<td>Emulsion formation, not efficient, loss of compounds, complicated, laborious, pre-concentration step required</td>
</tr>
<tr>
<td>CO2 extraction</td>
<td>Various non-volatile, thermal sensitive compounds in ILs are extracted by supercritical CO2</td>
<td>Green process with good extraction quality, efficient, selective, minimized product degradation, eliminates solvent residues</td>
<td>High cost, technical skill required</td>
</tr>
<tr>
<td>Adsorption</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption/desorption process</td>
<td>Various adsorbents are used to adsorb ILs from dilute stream. A desorption step with solvent are carried out to recover ILs</td>
<td>Robust, relatively easy to operate</td>
<td>Require equilibrium adsorption and desorption data; desorption solvent</td>
</tr>
<tr>
<td>Chromatography</td>
<td>Batch or continuous chromatography are used to separate ILs and other solutes based on different of their adsorption isotherm</td>
<td>Robust, easy to operate; efficient, non-disruptive, selective method</td>
<td>Equipment complexity; concentration step is required</td>
</tr>
<tr>
<td>Induced Phase Separation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salting-out process</td>
<td>Electrolytes or salts are introduced into ILs aqueous solution to form aqueous bi-phases system (ABS) including ILs rich phase and water-rich phase</td>
<td>Simple, effective; using less expensive inorganic salts</td>
<td>Environmental problems of high inorganic salt in salt-rich phase</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO2 are introduced to induce a phase separation including ILs, solute and CO2-rich phase</td>
<td>Green process; CO2 can be recycled; minimized degradation</td>
<td>High cost, technical skill required</td>
</tr>
<tr>
<td>Temperature</td>
<td>Some aqueous solution of ILs possess LCST phase behavior that can be separated into different phases by changing the temperature</td>
<td>Simple, ease of operation, less energy consumption</td>
<td>Restrict to some special ILs system</td>
</tr>
<tr>
<td>Membrane based process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Two operation modes where ILs is permeated or retained</td>
<td>Simple, less energy and solvents demand</td>
<td>Relatively low flux and recovery yield</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>Ionic selective migration through ion-exchange membranes with the aid of an electrical driving force</td>
<td>Low energy consumption, osmotic pressure is not a limited factor</td>
<td>Elaborate control is required, material for membranes and stack is important</td>
</tr>
<tr>
<td>Reverse osmosis</td>
<td>Pressure driven process</td>
<td>Low energy requirement; compact and less space requirement; modular design</td>
<td>Require pretreatment of mixture; limited by osmotic pressure</td>
</tr>
<tr>
<td>Pervaporation</td>
<td>Separation by partial vaporization through selective membrane</td>
<td>Effective for concentrating ILs</td>
<td>Require large membrane area</td>
</tr>
<tr>
<td>Other techniques</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnetic separation</td>
<td>Magnetic ILs is recovered by applying magnetic fields</td>
<td>Simple, low energy consumption</td>
<td>Only applied for ILs that response to magnetic field</td>
</tr>
<tr>
<td>Centrifugation</td>
<td>Separation of emulsion containing ILs</td>
<td>Simple, low energy consumption</td>
<td>Less effective, low processing rate</td>
</tr>
</tbody>
</table>
1.3.4. Polymer dissolution in ionic liquids and their membrane fabrication

Ionic liquids can dissolve polymers, which does not dissolve in common organic solvents such as cellulose. Cellulose is a natural sourced polymer, having difficulty on dissolution with common organic solvents but can be dissolved in ionic liquids. Since the discovery of ionic liquid potential as good solvents for cellulose, many studies of cellulose dissolution in ionic liquids have been investigated. Especially, this discovery contributes to find a big potential of using many different nature cellulosic polymers, which can dissolve in ionic liquids [53-57] and also to increase the efficiency of biofuel production with deconstruction of lignocellulosic biomass using ionic liquids [58-60]. The use of ionic liquids for other polymer dissolution and membrane manufacture is still relatively restricted. Examples are: 1-ethyl-3-methylimidazolium acetate [EMIM]OAc for polybenzimidazole (PBI)[61] along with 1-butyl-3-methylimidazolium chloride [BMIM]Cl[62], cellulose acetate (CA) [63], cellulose[64], and polyacrylonitrile [65]; 1-ethyl (or butyl)-3-methylimidazolium thiocyanate ([EMIM]SCN and [BMIM]SCN) for CA [46, 66]. Recently we reported that PES could be dissolved in 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP) and fabricate flat-sheet and hollow fiber membranes [47, 67]. Nano-size pore structures with the high rejection of peptides were achieved compared to other PES membranes fabricated form literature as shown in Chapter 5. Furthermore, poly (ether imide sulfone) (EXTEM™) was dissolved in [EMIM]OAc, [EMIM]SCN, and [BMIM]SCN [48] and their membranes were detailed in Chapter 7. **Table 1.9** shows the summary of the polymer dissolution from many literature and these studies.
Table 1.9. Summary of the polymer dissolution in ionic liquids and their membrane performance.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Solubility</th>
<th>Membrane structure, water permeance (L m⁻² h⁻¹ bar⁻¹) /MWCO (kg mol⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylonitrile (PAN)</td>
<td>[EMIM]OAc/ DMSO</td>
<td>&gt; 12 wt% at 25 ℃</td>
<td>* Fully developed finger-like, 540 ± 30 (HF) / 54</td>
<td>This study[68]</td>
</tr>
<tr>
<td></td>
<td>[EMIM]OAc</td>
<td>No at 25 ℃</td>
<td>* N/A</td>
<td>This study</td>
</tr>
<tr>
<td>Polyethersulfone (PES)</td>
<td>[EMIM]DEP</td>
<td>&gt; 18 wt% at 90 ℃</td>
<td>* Sponge-like, 55 ± 5(FS) / 5.1, 45.8 (HF) / 1.4</td>
<td>This study[47, 67]</td>
</tr>
<tr>
<td></td>
<td>[MMIM]DMP</td>
<td>&gt; 18 wt%</td>
<td>* Sponge-like, 43 ± 3(FS) / 7.9</td>
<td>This study[47]</td>
</tr>
<tr>
<td>Polysulfone (PSf)</td>
<td>[EMIM]DEP</td>
<td>No, at 90 ℃</td>
<td>N/A</td>
<td>This study[67]</td>
</tr>
<tr>
<td></td>
<td>[MMIM]DMP</td>
<td>No, at 90 ℃</td>
<td>N/A</td>
<td>This study[67]</td>
</tr>
<tr>
<td>Poly (ether imide sulfone (EXTEM™, XH 1005)</td>
<td>[EMIM]OAc</td>
<td>&gt; 12 wt% at 60 ℃</td>
<td>* Sponge-like, 130 (FS) / 77</td>
<td>This study[63]</td>
</tr>
<tr>
<td></td>
<td>[EMIM]OAc/ [EMIM]OAc</td>
<td>&gt; 28 wt% at 60 ℃</td>
<td>* Sponge-like, 330 (FS) / 74</td>
<td>This study[63]</td>
</tr>
<tr>
<td></td>
<td>[EMIM]SCN</td>
<td>&gt; 12 wt% at 50 ℃</td>
<td>* Sponge-like, 90 (HF) / mean pore size (R=50%) 17.5 nm</td>
<td>This study[66]</td>
</tr>
<tr>
<td></td>
<td>[BMIM]SCN</td>
<td>&gt; 12 wt% at 50 ℃</td>
<td>* Sponge-like, 114.14 (FS) / mean pore size (R=50%) 39.16 nm</td>
<td>This study[46]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>[EMIM]OAc</td>
<td>≥ 13.5 wt%</td>
<td>Cellulose composite membranes, 13.8 (FS) / 3</td>
<td>[70, 71]</td>
</tr>
<tr>
<td></td>
<td>80 ionic liquids</td>
<td>Various solubility</td>
<td>-</td>
<td>[53, 54, 57, 72-75]</td>
</tr>
<tr>
<td>Chitin</td>
<td>6 ionic liquids</td>
<td>Various solubility</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

* Natural polymers 8 ionic liquids Various solubility - [76, 77]

** Polystyrene-b-poly (4-vinyl pyridine) (PS-b-PV4P) **

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Solubility</th>
<th>Membrane structure, water permeance (L m⁻² h⁻¹ bar⁻¹) /MWCO (kg mol⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[EMIM]Cl</td>
<td>≥ 10 wt% at 140 ℃</td>
<td>-</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>[BMIM]BF₄</td>
<td>No, at 140 ℃</td>
<td>-</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>[BMIM]OH</td>
<td>≥ 8 wt% at 140 ℃</td>
<td>-</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>[EMIM]OAc</td>
<td>≥ 20 wt% at 120 ℃</td>
<td>* Sponge-like with finger voids, 141.3(FS) / 109</td>
<td>[61]</td>
</tr>
<tr>
<td>Polymideimide (PBI)</td>
<td>[EMIM]OAc</td>
<td>≥ 20 wt% at 120 ℃</td>
<td>* Sponge-like with finger voids, 216 (FS) / 104</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>84+ PBI</td>
<td>[EMIM]OAc</td>
<td>≥ 20 wt% at 120 ℃</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>84 co-polyimide</td>
<td>[EMIM]OAc</td>
<td>≥ 20 wt% at 120 ℃</td>
<td>[69]</td>
</tr>
<tr>
<td></td>
<td>polyamideimide (Torlon, 4000T)</td>
<td>[EMIM]OAc</td>
<td>≥ 10 wt% at 120 ℃</td>
<td>[69]</td>
</tr>
<tr>
<td>Polymide (Matrimid, 5218)</td>
<td>[EMIM]OAc</td>
<td>No, at 120 ℃</td>
<td>-</td>
<td>[69]</td>
</tr>
</tbody>
</table>

*The concentration of polymers: * 12 wt%, * 16 wt%, * 24 wt%, * 7 wt%, * 10 wt%, * 20 wt%, hollow fiber (HF), and flat sheet (FS), * Natural polymers: Wool keratin fibers, fibroin, sericin, etc.
1.4. Objectives and overview

The main goal of this research is the fabrication of greener membranes. In order to achieve this, homogeneous polymer solutions need to first be prepared, then they should be well processed to become membranes. The biggest challenge in this study is finding a suitable composition for the polymer solution. In order to achieve this, the identification of the best suitable solvents, polymers to be dissolved, and their right combination for membrane fabrication need to be considered. Also, it is necessary to understand the interaction or compatibility between the polymers and solvents, especially of ionic liquids, to prepare homogeneous polymer solutions. Several polymer solution systems will be determined as a consequence of considering their thermodynamic and kinetic aspects. Once the homogeneous ionic liquid based polymer solutions are obtained, greener membranes will be fabricated from the solutions and they should have comparable performance to conventional membranes.

This work is divided by 3 sections (Figure 1.3). In section 1, partially greener membranes will be discussed which were fabricated from ionic liquid-mild solvent mixtures. In this section, two different polymer solutions, polyacrylonitrile (PAN) with 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) - dimethylsulfoxide (DMSO) mixtures and cellulose acetate (CA) with [EMIM]OAc - acetone mixture, were prepared. The results of each system were described in Chapters 3 and 4, respectively.

In section 2, fully greener membranes which were formed from pure ionic liquid solutions without any organic solvents will be discussed. Two polymer systems, polyethersulfone (PES) with 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP) and poly (ether imide sulfone) (EXTEM™) with 1-ethyl-3-
methylimidazolium thiocyanate ([EMIM]SCN), and their resultant membranes will be examined in Chapters 5, 6, and 7. In all chapters, relevant thermodynamic and kinetic aspects of polymer solutions which were prepared from ionic liquids, as well as ideas for greener membrane fabrication from a membrane engineering point of view will be discussed.

**Figure 1.3.** Overview of this work
Chapter 2: Methodology

2.1 Polymer solution thermodynamics

2.1.1. Gibbs free energy of mixing

To fabricate membranes, homogeneous polymer solutions need to be prepared and for that understanding the interaction between polymer and solvent is essential.

Dissolving an amorphous polymer can be explained by the Gibbs free energy of mixing:

\[ \Delta G_m = \Delta H_m - T \Delta S_m \]  

where \( \Delta G_m \) is the Gibbs free energy of mixing, \( \Delta H_m \) is the heat of mixing, \( T \) is the absolute temperature, and \( \Delta S_m \) is the entropy change of mixing. This factor gives us the idea of estimating if a certain polymer is going to dissolve in the solvent or not. A negative value of \( \Delta G_m \) promotes dissolution, but if positive, dissolution is hindered. The molecules turn into a more chaotic arrangement, when it becomes a liquid state from a solid state, thus \( \Delta S_m \) is positive. The absolute temperature (T) is always positive. However, the value of \( \Delta H_m \) is positive or negative.

According to the Flory-Huggins theory[79], the Gibbs free energy of mixing can be approximated by the expression:

\[ \frac{\Delta G_m}{N_0} = kT \left[ \chi \phi_1 \phi_2 + \phi_1 / x_1 \ln \phi_1 + \phi_2 / x_2 \ln \phi_2 \right] \]  

(2)

where \( k \) is the Boltzmann constant, \( \phi_i \) and \( x_i \) are the volume fraction and number of segments of the \( i^{th} \) component, respectively. The enthalpy change of mixing can be
calculated from the Flory-Huggins parameter, $\chi$, which can be estimated from the solubility parameters of the species according to equation (3) [80-83]:

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

(3)

where, $\chi_{ij}$ is the Flory-Huggins parameter, $V_i$ is the molar volume of the solvent (cm$^3$ mol$^{-1}$), $\delta$ is the Hildebrand solubility parameter for the solvent ($i$) and the polymer ($j$) (Mpa$^{1/2}$), $R$ is the ideal gas constant (8.314 cm$^3$ Mpa K$^{-1}$ 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 systems [80-83]. According to the Flory-Huggins approximation, if $\chi$ is smaller than 0.5, homogeneous polymer solutions are expected [81]. Taking into account the inherent simplifications in the Flory-Huggins model [79], the value of $\chi = 0.5$ is used as an initial guess to decrease the experimental solvent-composition space to study.

The solubility of the polymer in the solvents is determined by their chemical structure. If the polymer has a polar functional group in their structure, it will dissolve in a polar solvent because of the better solubility, caused by the similarity of the structure between solutes and solvents [84].

The solubility parameter of species $i$ ($\delta_i$) is defined as the equation (4)[85] proposed by Hildebrand and Scott [82, 84-86].

$$\delta = (E/V)^{1/2}$$

(4)

where $E$ is the energy of vaporization and $V$ is the molar volume. In the case of the common organic solvents, their Hildebrand solubility can be divided in three components corresponding to three interactions, as proposed by Hansen [82]: dispersive interactions,
polar cohesive forces, which is produced by the dipole-dipole interaction, and hydrogen bonding interactions, described in equation 5:

\[ \delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \]  \hspace{1cm} (5)

Polymers will dissolve in solvents, which have similar value of solubility parameter. For example, polyacrylonitrile (PAN) can dissolve in solvents of similar solubility value, such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone (NMP). Table 2.1 shows the Hansen solubility parameters of materials commonly used for the fabrication of membranes.

In the case of the ionic liquids, very limited information exists, regarding their solubility properties. One method that has been used to calculate their solubility parameter is based on intrinsic viscosity. Since the energy of vaporization \((E_{\text{vap}})\) is difficult to measure, especially in ionic liquids, \(E_{\text{vap}}\) can be substituted by the molar energy of activation related to viscosity and a proportionality constant (Eq. 6) [87]. Part of this equation \((\Delta G^0_{\text{vis}})\) can be substituted by equation (7) [87], leading to the final equation (8) [88], which gives the Hildebrand parameter, based on the measureable intrinsic viscosity.

\[ \delta = (E_{\text{vap}}^2/V)^{1/2} \]  \hspace{1cm} (4)

\[ E_{\text{vap}} = K_v \Delta G^0_{\text{vis}} \]  \hspace{1cm} (6)

\[ \Delta G^0_{\text{vis}} = RT \ln (\mu V_1 / hN_A) \]  \hspace{1cm} (7)

\[ \delta = [K_v RT / V_1 \ln [(1 \times 10^{-9}) \mu V_1 / hN_A]]^{1/2} \]  \hspace{1cm} (8)

where \(\mu\) is the dynamic viscosity of the ionic liquid in units of cP, \(V_1\) is the molar volume in units of cm3/mol, \(h\) is Plank’s constant in units of Js, \(NA\) is Avogadro’s number, \(Kv\) is
a proportionality constant, R is the ideal gas constant, and T is the absolute temperature (K). Kilaru and Scovazzo [88] also calculated the solubility parameter of ionic liquids by using the Hildebrand parameter derived through their intrinsic viscosities. Similarly, Weerachanchai et al. [89] calculated the solubility parameter of different ionic liquids with or without DMAc, using their intrinsic viscosities.

Another method for the calculation of the ionic liquid solubility parameter can be that used for common organic solvents (Eqn. 5). In particular, for ionic liquids the electrostatic [90] and Coulombic interactions may have an important contribution that is not included in the traditional Hansen approach. Therefore, experimentally- or computationally-based estimations are suitable for improving the free energy calculation.

Lastly, the solubility parameters of ionic liquids have been also obtained through simulations. Xing et al. [46, 66, 69] calculated the solubility parameter of the ionic liquids, [EMIM]OAc and [EMIM]SCN, using molecular dynamic simulations with the Materials Studio 5.5 software as described in Derecskei-Kovacs’s study [91].
Table 2.1. Hansen solubility parameters of commonly used materials for the fabrication of membranes.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$\delta_{exp.}$</th>
<th>$\delta_{ref.}$ (Hildebrand)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylonitrile (PAN)</td>
<td>17.9</td>
<td>16.7</td>
<td>6.3</td>
<td></td>
<td>25.2[82]</td>
</tr>
<tr>
<td>Polyethersulfone (PES)</td>
<td>19.6</td>
<td>10.8</td>
<td>9.2</td>
<td></td>
<td>24.2[82]</td>
</tr>
<tr>
<td>Polysulfone (PSf)</td>
<td>20.0</td>
<td>8.0</td>
<td>8.0</td>
<td></td>
<td>23[82]</td>
</tr>
<tr>
<td>Cellulose</td>
<td>18.7</td>
<td>12.5</td>
<td>23.4</td>
<td></td>
<td>32.5[82]</td>
</tr>
<tr>
<td>Cellulose acetate (CA)</td>
<td>18.6</td>
<td>12.7</td>
<td>11.0</td>
<td></td>
<td>25.1[82]</td>
</tr>
<tr>
<td>Cellulose triacetate (CTA)</td>
<td>17.2</td>
<td>5.7</td>
<td>6.0</td>
<td></td>
<td>19.1[82]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride) (PVDF)</td>
<td>17.0</td>
<td>12.1</td>
<td>10.2</td>
<td></td>
<td>23.2[82]</td>
</tr>
<tr>
<td>EXT</td>
<td>21.0</td>
<td>10.9</td>
<td>10.6</td>
<td>26[48]</td>
<td></td>
</tr>
<tr>
<td>Polyetherimide (PEI)</td>
<td>19.6</td>
<td>7.6</td>
<td>9.0</td>
<td></td>
<td>22.9[82]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvents</th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$\delta_{exp.}$</th>
<th>$\delta_{ref.}$ (Hildebrand)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl acetaamide (DMAc)</td>
<td>16.8</td>
<td>11.5</td>
<td>10.2</td>
<td></td>
<td>22.7[82]</td>
</tr>
<tr>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>18.4</td>
<td>16.4</td>
<td>10.2</td>
<td></td>
<td>26.5[82]</td>
</tr>
<tr>
<td>N-methyl-2-pyrrolidone (NMP)</td>
<td>18.0</td>
<td>12.3</td>
<td>7.2</td>
<td></td>
<td>22.9[82]</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
<td></td>
<td>24.8[82]</td>
</tr>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7.0</td>
<td></td>
<td>19.9[82]</td>
</tr>
<tr>
<td>Water</td>
<td>15.5</td>
<td>16.0</td>
<td>42.3</td>
<td></td>
<td>47.8[82]</td>
</tr>
<tr>
<td>[EMIM]OAc</td>
<td>22.2</td>
<td>15.9</td>
<td>16.9</td>
<td>32.1[63]</td>
<td>25.2[89], 32.8[61]</td>
</tr>
<tr>
<td>[EMIM]DEP</td>
<td>20.0</td>
<td>13.5</td>
<td>14.8</td>
<td>28.3[67]</td>
<td>25.4[89]</td>
</tr>
<tr>
<td>[MMIM]DMP</td>
<td>22.3</td>
<td>16.2</td>
<td>17.2</td>
<td>32.5[47]</td>
<td></td>
</tr>
<tr>
<td>[EMIM]SCN</td>
<td>22.7</td>
<td>19.1</td>
<td>15.6</td>
<td>33.5[48]</td>
<td>25.2[92]</td>
</tr>
<tr>
<td>[BMIM]SCN</td>
<td>19.5</td>
<td>17.1</td>
<td>12.6</td>
<td>28.9[48]</td>
<td>24.6[92]</td>
</tr>
</tbody>
</table>

*1-ethyl-3-methylimidazolium Acetate ([EMIM]OAc), 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP), 1,3-dimethylimidazolium dimethylphosphate ([MMIM]DMP), 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN), 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN)
2.1.2. Computational interaction energy estimation

The big advantage of the computational estimation, such as molecular dynamics (MD) and density functional theory (DFT), for the interaction energy calculation between polymers and ionic liquids is that the electrostatic force can be taken into account. Therefore, it would accurately calculate the interaction energy in ionic liquid-based polymer solutions, including hydrogen bond and Coulombic force. The interaction energy between polymers and ionic liquids has been calculated by MD, using Material studio [91, 93] with the protocol shown in Figure 2.1. The structure was optimized using Forcite module and the interaction energy was calculated for the system equilibrium.

![Diagram](image)

**Figure 2.1.** MD simulation protocol using Material studio.

DFT using Gaussian package also has been applied to estimate the interaction energy of ionic liquid/polymer systems [47, 94, 95]. The interaction energy between polymers and ionic liquids (IL) was calculated using equation (9):

\[
\text{Interaction energy} = E_{\text{Polymer-IL}} - (E_{\text{polymer}} + E_{\text{IL}})
\]

with \(E_{\text{polymer+IL}}, E_{\text{polymer}}, \) and \(E_{\text{IL}}\) being the total energies of the polymer/ionic liquid combined system. Several polymer chains and ionic liquids are a heavy system for DFT calculation. Thus, one or two monomers and a couple pairs of ionic liquids can be applied depending on the number of atoms in the components. After the geometry optimization of
the polymer, ionic liquids, and the mixture, the interaction energy can be calculated. In Chapter 6, the interaction energy of the PES/[EMIM]DEP and [MMIM]DMP systems was estimated by the DFT calculation.

2.2. Membrane fabrication

2.2.1. Classification

The membrane can be defined as a barrier to separate two phases that can reject the transport of various components from one side to the other [96]. The rejected compounds depend on the classification of the membrane. Membranes can be classified based on different criteria such as: the driving force, the pore size, the membrane materials, and the structure of the membrane. In the case of pressure driven membranes, they are mainly divided into 4 types, according to their pore size. Nanofiltration (NF) and Reverse osmosis (RO) membranes have smaller pore sizes compared with Microfiltration (MF) and Ultrafiltration (UF) membranes. This allows them to be good for the removal of ions, water softening, and desalination purposes. MF and UF membranes present better water fluxes and work under lower pressures than NF and RO membranes. Table 2.2 shows the ranges of flux, operating pressure, effective pore size, and membrane efficiency of the rejected species for membranes used in hydraulic pressure driven separations (MF, UF, NF, RO) and for forward osmosis (FO) membranes, used for osmotic pressure gradient driven separations. The pore size of a FO membrane is similar to those of NF and RO. The difference between them is their driving forces [97, 98]. Figure 2.2 shows the concepts of FO and RO membranes and water flows of these systems. In the case of FO, the feed solution, which has lower osmotic pressure e.g. water containing lower amounts of salts or
deionized water, diffuses into a higher osmotic pressure solution (draw solution) e.g. a highly salinity solution, thus, purifying the feed solution. In contrast to the FO system, RO systems consist of the diffusion of water from a highly concentrated solution, such as brine or sea water, into a less concentrated permeate by hydraulic pressure [97].

Table 2.2. Classification of membranes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Flux (L m⁻² h⁻¹)</th>
<th>Operating pressure (bar)</th>
<th>Effective pore size</th>
<th>Membrane efficiency Species rejected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration (MF)</td>
<td>150 - 1500</td>
<td>0.5 - 5</td>
<td>0.05 - 2 μm</td>
<td>Bacteria, cysts, large colloids</td>
</tr>
<tr>
<td>Ultrafiltration (UF)</td>
<td>40 - 500</td>
<td>0.5 - 5</td>
<td>1 - 100 nm</td>
<td>Organic matter, viruses, bacteria, large pathogens</td>
</tr>
<tr>
<td>Nanofiltration (NF)</td>
<td>20 - 50</td>
<td>4 - 20</td>
<td>0.8 - 8 nm</td>
<td>Organic matter, multivalent ions</td>
</tr>
<tr>
<td>Reverse osmosis (RO)</td>
<td>10 - 50</td>
<td>20 - 100</td>
<td>0.1 - 1.5 nm</td>
<td>Organic matter, monovalent ions</td>
</tr>
<tr>
<td>Forward osmosis (FO)</td>
<td>10 - 30</td>
<td>25 - 100*</td>
<td>0.1 - 1.5 nm</td>
<td>Dilution of the draw solution or concentration of the feed solution</td>
</tr>
</tbody>
</table>

Source (modified): [96, 99, 100]  
* The conditions of the pressure are different depending on the differences between the concentrations of feed and draw solutions: 25 bar (0.5M NaCl), 100 bar (2M NaCl)

Figure 2.2. Water flows in FO and RO systems.
2.2.2. Membrane formation mechanism

The membranes fabricated in this study can be applied for ultrafiltration (UF), nanofiltration (NF), and forward osmosis (FO). The fabrication methods of these membranes are different. First, commonly used UF membranes have an asymmetric structure, which are composed of support and selective layers, formed by non-solvent induced phase separation (NIPS). The NIPS method is more commonly used to control the pore size and structures, particularly for UF, NF, as supports for thin film composite (TFC) NF, reverse osmosis (RO), and FO, and gas separation membranes. In this method, the polymer solution is immersed into the non-solvent bath and the phase separation is induced by exchanging the solvent in the polymer solution and non-solvent in the bath. A key point of forming the structure and pore size using this method is controlling the rate of solvent exchange. Depending on the polymer-solvent, the solvent-non solvent, and the polymer-non solvent thermodynamic interactions, the consequences of the pore size, the shape, and the structure of the membrane are different. The structure of the membranes that are formed by this method is usually asymmetric and porous with a skinned selective layer [101].

Thin film composite NF and FO membranes are formed by an interfacial polymerization of polyamide (PA) onto the asymmetric porous support layer (Figure 2.3).
Figure 2.3. Asymmetric porous support and TFC membranes.

Figure 2.4 explains the formation of the asymmetric porous structure with ternary phase diagram, which is composed of polymer/solvent/non-solvent systems. A non-equilibrium state is immobilized once the casting solution is immersed into water, as non-solvent, and the solvent-water exchange proceeds. By mixing with water, the initial solution composition changes and moves to the meta stable condition, between binodal and spinodal boundaries, and then enters eventually the unstable region (2-phase) of the phase diagram shown in Figure 2.4 [102]. Depending on how fast or long the system stay in the metastable zone, different membrane morphology is obtained [86].
**Figure 2.4.** Ternary phase diagram adapted from ref. [102].

Once the solvent/non/solvent exchange and the liquid-liquid demixing start, the initial solution composition can change its phase with the path A and B as shown in Figure 2.5. Depending on the polymer solution thermodynamics, the liquid-liquid (solvent/non-solvent) and solid-liquid (polymer/solvent and polymer/non-solvent) interaction and kinetic parameters, such as viscosity, the phase separation follows different paths. This is well explained in ref. [101].

In case of polymer solutions, which possess high viscosity such as polymer/ionic liquid systems, the phase separation might be mainly dominated by delayed liquid-liquid demixing. It might result in nucleation and growth (NG) demixing, which is favoured to follow the path A. It may stay longer in the metastable region and take a relatively long time to have the continuous 2-phase. If NG finishes in the early stage of the phase
separation, the pore structure may be closed and not interconnected. However, if the nuclei grow until the last phase separation stage, the pores are well interconnected.

In the case of polymer solutions, which have the instant liquid-liquid demixing with low viscosity such as the PES/common organic solvent system, the phase separation mechanism might be predominantly spinodal decomposition (SD). SD is favoured in path B, crossing the critical point and entering the unstable region in a short time. The resultant morphology of this path B has interconnected pore structure from the early stage of the phase separation until it finishes and forms the asymmetric structure due to the time gradients of the phase separation from the top to the bottom.

**Figure 2.5.** NG and SD demixing adapted from ref. [101].
2.2.3. Flat sheet and hollow fiber membrane fabrication

For flat sheet membrane fabrication, the prepared polymer solutions are cast using a casting knife, whose thickness can be controlled on a glass plate and the cast polymer solutions are immersed into the non-solvent, mainly deionized water.

Hollow fiber membranes prepared by NIPS also have the same formation mechanism as the flat sheet membranes. However, using a spinneret instead of the casting knife, two surfaces (inner and outer layers) might contact two coagulants to induce the phase separation. A polymer solution (dope solution) is poured into a reservoir and needs to be degassed for 24 hours. The prepared polymer solution is spun together with a bore fluid by a spinneret, which has the certain inner (ID) and outer diameters (OD). The spun hollow fiber starts to be coagulated by the non-solvents in the coagulant bath and bore fluid. The hollow fibers have different morphologies and membrane performance in accordance with the selection of the composition of polymer solutions, bore fluids, and coagulants, spinning conditions, and the spinneret size and configurations. Figure 2.6 shows an example of the spinning machine and spinneret. The fabricated membranes are characterized and tested their performance depending on their applications. To test the performance of hollow fiber membranes, the spun hollow fiber membranes were placed in modules and potted the ends with epoxy glue. Figure 2.7 shows the water permeance and rejection set up for hollow fiber UF membranes and depicts the FO performance test set up such as the water flux and reversible solute flux for hollow fiber membranes applied in FO system.
**Figure 2.6.** Scheme of the spinning machine and spinneret.

**Figure 2.7.** Dead-end UF and FO test set up.
Chapter 3. Fabrication of Polyacrylonitrile Hollow Fiber Membranes

from Ionic Liquid Solutions

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3.1 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 industry [1]. These emissions cause serious environmental issues such as contamination of the atmosphere and the contamination of aqueous effluents [103] 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. [2] in twelve principles, which are important considerations in the design of processes and products [104]. Using safer solvents and auxiliaries is one of the main aspects of green chemistry [105]. 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) [106]. 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 (e.g. selectivity and permeability), low energetic requirement compared to other separation processes, and their high stability under operating conditions [107]. 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. [6] 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 far as possible. This study focuses on the fabrication of greener membranes by the usage of chemicals with lower toxicity.

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 [108]. Alternative or green solvents need to have low toxicity, be non-volatile, easy to recycle, inert, and should not contaminate the product [16]. Over the past decade, water, ionic liquids, supercritical fluids (SCFs), and fluorous solvents have been reported as possible alternatives and green solvents [109].
Ionic liquids are considered green solvents in many aspects, such as lack of measurable vapor pressure, non-flammability, reusability, high thermal stability [110] and low corrosiveness [55]. Due to their high solubility in water, toxicity to aquatic organisms has been a matter of some concern [111], 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 [16, 33] and do not lead to hazardous VOC generation, in contrast to common organic solvents [33, 112].

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 [56]. Swatloski et al. [54] 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 cellulose [53]. S. Livazovic et al. [64] recently reported a membrane manufactured based on cellulose manufactured using an ionic liquid. Wang et al. [62] 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 (CA) in 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) to fabricate flat sheet membranes [46]. 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) [66]. Similarly, ultrafiltration (UF) membranes were also fabricated but using only polybenzimidazole (PBI) [61] or blends of PBI and P84 polyimide [69], with both studies used the same ionic
liquid, 1-ethyl-3-metylimidazolium acetate ([EMIM]OAc). Only a 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 [4, 5] and is not in the REACH solvent list under concerns [105]. 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 (DMAc), and 1-methyl-2-pyrrolidone (NMP).

The purpose of this study is the fabrication of PAN hollow fiber membranes with good pore morphology, using solvent mixtures of ionic liquids and DMSO, which has lower toxicity than other commonly used polar organic solvents. First, the suitable composition was estimated considering their thermodynamic interactions expressed by the Flory-Huggins parameter, \( \chi \) and the Gibbs free energy of mixing. Theoretical and experimental phase diagrams were constructed to validate the proper solvent composition. Once the appropriate solvent and polymer compositions had been identified, membranes were manufactured using these less toxic solvent mixtures. The performances of hollow fiber membranes prepared from IL/DMSO, pure DMSO, and pure DMF were compared for FO systems.
3.2. Experiments

3.2.1. Materials

Polyacrylonitrile (PAN, Mw = 324,000) was used as the polymer in the form of fine power. The ionic liquid was 1-Ethyl-3-methylimidazolium acetate ([EMIM]OAc, ≥95.0 %), supplied by Sigma-Aldrich. Dimethyl sulfoxide (DMSO, ≥99 %), and dimethylformamide (DMF, 99.8 %) were also purchased from Sigma-Aldrich. The used materials are summarized in Table 3.1. For the interfacial polymerization (IP), M-phenyldiamine (MPD, >99 %), 1, 3, 5-benzenetricarbonyltrichloride (TMC, 98 %), triethylamine (TEA, >99.5%) and (1S)-(+)10-camphorsulfonic acid (CSA, 99%) were supplied by Sigma-Aldrich. Polyethylene glycol (PEG) (Sigma-Aldrich) and polyethyleneoxide (PEO) (Sigma-Aldrich), with molecular weights of 300 g mol⁻¹, 1500 g mol⁻¹, 6000 g mol⁻¹, 10,000 g mol⁻¹, 35,000 g mol⁻¹, 100 g mol⁻¹, and 600,000 g mol⁻¹, 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 forward osmosis (FO) system.
Table 3.1. Polymer and solvents used in this study.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylonitrile (PAN)</td>
<td>![Structure of PAN]</td>
</tr>
<tr>
<td>1-Ethyl-3-Methylimidazolium acetate ([EMIM]OAc)</td>
<td>![Structure of [EMIM]OAc]</td>
</tr>
<tr>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>![Structure of DMSO]</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>![Structure of DMF]</td>
</tr>
</tbody>
</table>

3.2.2. Thermodynamic analysis

3.2.2.1. Prediction of the Gibbs free energy of mixing ($\Delta G_m$) 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:

$$\Delta G_m = \Delta H_m - T \Delta S_m$$  \hspace{1cm} (1)

where, $T$ is the absolute temperature, whereas $\Delta H_m$ and $\Delta S_m$ are the enthalpic and entropic change of mixing, respectively. According to Flory-Huggins theory [79], the Gibbs free energy of mixing can be approximated by the expression:
\[ \Delta G_m / N_0 = kT \left[ \chi \phi_1 \phi_2 + \phi_2 / \chi_1 \ln \phi_1 + \phi_1 / \chi_2 \ln \phi_2 \right] \]  

(2)

where \( k \) is the Boltzmann constant, \( \phi_i \) and \( x_i \) are the volume fraction and number of segments of the \( i^{th} \) component, respectively. Spontaneous dissolution processes take place only if \( \Delta G_m \) is negative. The enthalpy change of mixing can be calculated from the Flory-Huggins parameter, \( \chi \), which can be estimated from the solubility parameters of the species according to equation (3) [80-83]:

\[ \chi_{ij} = V_i (\delta_i - \delta_j)^2 / RT + 0.34 \]  

(3)

where, \( \chi_{ij} \) is the Flory-Huggins parameter, \( V_i \) is the molar volume of the solvent (cm\(^3\) mol\(^{-1}\)), \( \delta \) is the Hildebrand solubility parameter for the solvent (\( i \)) and the polymer (\( j \)) (Mpa\(^{1/2}\)), \( R \) is the ideal gas constant (8.314 cm\(^3\) Mpa K\(^{-1}\) 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 systems [80-83]. According to the Flory-Huggins approximation, if \( \chi \) is smaller than 0.5, homogeneous polymer solutions are expected [81]. Taking into account the inherent simplifications in the Flory-Huggins model [79], 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 parameters [82], given by the contribution of dispersive, dipole-dipole, and hydrogen bonding interactions as:

\[ \delta^2 = \delta_{D}^2 + \delta_{P}^2 + \delta_{H}^2 \]  

(4)

In particular, for ionic liquids the electrostatic [90] and Coulombic interactions may have an important contribution that is not included in the traditional Hansen approach.
Therefore, experimentally- or computationally-based estimations are suitable for improving the free energy calculation. Xing et al. [46, 66, 69] calculated the solubility parameter of the ionic liquids [EMIM]OAc and [EMIM]SCN using molecular dynamic simulations [91], leading finally to $\Delta G_m$ values.

3.2.2.2. Phase diagram

Polyacrylonitrile solutions with the following solvents or solvent mixtures 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 ±1 °C.

3.2.3. 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 mixture of the ionic liquid (IL), 1-ethyl-3-methylimidazolium acetate and DMSO; with pure DMSO; and with pure DMF. Hollow fiber membranes were fabricated from the mentioned polymer solutions resulting in HF-20IL 1, 2, and 3; HF-DMSO; and HF-DMF, respectively. In the case of the polymer solutions with the ionic liquid, the ionic liquid was added after complete polymer dissolution in DMSO, then they were stirred for 12 hours more at room temperature. The prepared dope solutions were degassed inside the reservoir of the dope solution for 24 hours. Hollow fiber membranes were then prepared by using a double spinneret with 0.34 μm inner diameter (ID) and 0.64 μm outer diameter (OD) at room temperature. After
spinning, the hollow fiber membranes were immersed in water for a day, then immersed in a mixture of 50% glycerol and 2-propanol for 2 hours, and dried in a room temperature. The spinning conditions are summarized in Table 3.2. These spinning conditions were designed to fabricate hollow fiber membranes with thin walls with thicknesses of approximately 100 μm, which is convenient in forward osmosis to improve water flux. In the 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 the solvent used in the dope solutions. 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. Interfacially polymerized polyamide is commonly used as a selective layer.

TFC hollow fiber membranes were prepared by interfacially 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 2 wt% 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 at room temperature.
Table 3.2. Spinning conditions.

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

3.2.4. Characterization of the polymer solutions and the membranes

3.2.4.1. Characterization of the polymer solutions

Rheological measurements (AR 1500ex rheometer, TA Instruments) were performed to measure the storage \(G'\) and loss \(G''\) moduli, 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 for investigating and gaining insight into the effects of the ionic liquids during membrane fabrication. To prepare the UF membrane using the non-solvent induced phase separation (NIPS) method, the polymer solution needs to have a proper range of viscosity, which depends on the types of polymer and solvents and their concentrations. It is also different for different polymer molecular weights.

3.2.4.2. Characterization of the membranes

The morphologies of the hollow fiber support membranes and TFC layers were examined by field emission scanning electron microscopy (FESEM), using a FEI Quanta 600 and a 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.

FT-IR spectroscopy (Spectrum 100, Perkin Elmer) 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 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:
Water permeance \( (L \ m^{-2} \ h^{-1} \ bar^{-1}) = Q \ A^{-1} \ \Delta P^{-1} \) \hspace{1cm} (5)

Solute rejection, \( R(\%) = (1 - \frac{C_{\text{perm.}}}{C_{\text{feed}}}) \times 100 \) \hspace{1cm} (6)

where \( Q \) is the pure water permeation rate \( (L \ h^{-1}) \), \( A \) is the effective membrane area \( (m^2) \), \( \Delta P \) is the pressure which is applied in this test and \( C_{\text{perm.}} \) and \( C_{\text{feed}} \) are the concentrations of permeate solution and the feed solution, respectively, analyzed by gel permeation chromatography (GPC) with PL aquagel-OH 40 and 60 columns (1260 infinity GPC/SEC, Agilent technologies). The molecular weight cut-off (MWCO), \( i.e. \) the molecular weight at which 90\% of the solute was rejected by the membrane, calculated from rejection results for PEG of different sizes.

3.2.5. Performance in forward osmosis experiments

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

3.3.1. Thermodynamic analysis

3.3.1.1. Prediction of the Gibbs free energy of mixing ($\Delta G$) and the Flory-Huggins parameter ($\chi$)

The Flory-Huggins parameter was calculated by equation (3), using the total solubility parameter as shown in Table 3.3. Figure 3.1a shows the variation of $\chi$ for PAN in different binary solvent mixtures with the solvent composition. For PAN solutions in DMSO/IL and DMSO/water, $\chi$ increases as the concentration of the ionic liquid or water increases, reflecting a weaker interaction between the polymer and solvents. 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 $\chi \leq 0.5$, 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 3.1b. 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 in 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 3.3. Solubility parameters.

<table>
<thead>
<tr>
<th></th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$\delta$ (Mpa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>17.9</td>
<td>16.7</td>
<td>6.3</td>
<td>25.2</td>
</tr>
<tr>
<td>[EMIM]OAc $^b$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>32.8</td>
</tr>
<tr>
<td>DMSO</td>
<td>18.4</td>
<td>16.4</td>
<td>10.2</td>
<td>26.6</td>
</tr>
<tr>
<td>DMF</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
<td>24.8</td>
</tr>
<tr>
<td>Water</td>
<td>15.5</td>
<td>16</td>
<td>42.3</td>
<td>47.8</td>
</tr>
</tbody>
</table>

$\delta_D$, dispersive contribution; $\delta_P$, polar contribution; $\delta_H$, hydrogen bonding contribution [82]; $^a$ Hansen solubility parameter; $^b$ Calculated by Materials Studio (molecular dynamics simulation) [61, 69]; 1-Ethyl-3-Methylimidazolium acetate ([EMIM]OAc)

Figure 3.1. 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 \( \chi \); therefore, the proper range of the solvent mixture composition can be derived from the free energy. Figure 3.2 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, \( \phi_1 \) and \( \phi_2 \), respectively. In Figure 3.2, the Gibbs free energy of mixtures containing 12% PAN in solvent mixtures is presented. As shown in Figure 3.2a, binary DMSO/IL solvent mixtures lead to negative values of \( \Delta G \) with ionic liquid concentrations of 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 \( \Delta G \) values. Figure 3.2b shows \( \Delta G \) for PAN in ternary solvents. Based on the free energy analysis, the theoretical solvent mixture composition most suitable for fabrication of 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 the ionic liquid, as depicted in Figure 3.2b. 12 wt% PAN was not soluble in the pure ionic liquid. Systems with 12% PAN in (20/80, 30/70 or 40/60) IL/DMSO solvent mixtures were homogeneous. A solution with 12% PAN in a (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.
Figure 3.2. The Gibbs free energy of mixing for 12 % PAN in (a) binary and (b) ternary solvent mixtures.
3.3.1.2. Cloud points and phase diagram

The phase diagram in Figure 3.3 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, i.e., the limit between the stable and unstable regions, where the polymer solution changes from homogeneous to turbid [113]. Ternary phase diagrams can give an indication of the final structure of membranes [101, 114]. 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 IL/DMSO solvent mixtures, phase separation is induced with a slightly smaller amount of water than with solutions in pure DMF or DMSO. The tendency of the polymer solutions to phase separate with the 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., the viscosity of the solution and the polymer concentration), a solution with 12% PAN in (20/80) IL/DMSO was chosen for posterior hollow fiber membrane fabrication, which was compared to hollow membranes fabricated using pure DMSO and DMF in terms of various properties.
3.3.2. Morphology

3.3.2.1. 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 3.4) and regular unique patterns on the inner surface (Figures 3.4 and 3.5). On the other hand, membranes prepared with pure DMSO, exhibited finger like morphology, but with different porosity and patterns in the inner surface. As the hollow fibers were fabricated for application in forward osmosis (FO), the walls of the hollow fiber membranes were designed to obtain the highest flux as a support in a FO system. The wall thickness of all hollow fiber membranes was less than approximately 100 μm.

Figure 3.3. Phase diagram and cloud point for PAN in different solvents or solvent mixtures and water as non solvent, obtained at 25 ±1 ºC.
3.3.2.2. Thin film composite (TFC) hollow fiber membranes

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 3.6).

Figure 3.4. FESEM images of hollow fiber membrane cross-sections and surfaces: HF-20IL 1, HF-20IL 2 and HF-20IL 3 (IL/DMSO), HF-DMSO (DMSO), and HF-DMF (DMF).
Figure 3.5. FESEM images of the inner surfaces of (a) HF-20IL 1 (IL/DMSO) and (b) HF-DMSO (DMSO) hollow fiber membranes.

Figure 3.6. FESEM images of outer surfaces and cross-sections of TFC hollow fiber membranes.
3.3.3. Viscosity and rheological measurement of the polymer solutions

The viscosity of the dope solutions with DMSO, DMF and IL/DMSO is shown in Figure 3.8a. 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 moduli were measured on a rheometer under oscillation. Figure 3.8 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 3.8b), 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’s capacity to dissipate energy or mobility, is 2.6 for the solution 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 the two moduli, and they were around 50 Pa (Figure 3.8c). 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 3.8d), the G″/G’ ratio is around 3.8, which is the largest one. The pore formation in membranes by phase inversion depends on the interplay between the thermodynamics and kinetics of the polymer solution. By immersion in water, the solvent–non-solvent exchange will drive the system to phase separation, reaching the unstable region of the phase diagram (Figure 3.3). 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, also leading 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 (the solubility parameter is closer to that of water) and facilitates the water-solvent exchange. These factors might have contributed to the regular and open pore structure shown in Figure 3.5. 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, and how fast and abrupt the water-solvent exchange takes place, as well as how viscous the polymer solution is.
Figure 3.7. (a) Viscosity of dope solutions and storage ($G'$) and loss ($G''$) modulus as a function of oscillation strain (%) at 1 Hz: 12 % PAN (b) in DMSO, (c) in (20/80) IL/DMF, and (d) in DMF.

3.3.4. Membrane characterization

To analyze the existence of any remaining ionic liquid in the membranes, Fourier transform infrared spectroscopy (FTIR) was performed. Figure 3.9 shows the peaks of PAN, of membranes with 20% ionic liquid and without the ionic liquid, and of pure ionic
liquid. Typical peaks for PAN appeared at 2939 cm\(^{-1}\) for C-H stretching vibration, at 2243 cm\(^{-1}\) for C≡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. In particular, the peak at 1559 cm\(^{-1}\) for the ionic liquid is strong and could not be seen in the membranes. We can affirm that no remaining 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 the fabricated hollow fiber membranes in water for a day. For each membrane, the results of the water permeance, the molecular weight cut-off (MWCO), the mechanical strength (stress and strain values at the breaking point), the Young’s modulus and the contact angle are summarized in Table 3.4. The water permeance was measured in a dead-end set-up and it was calculated by using equation (5).

A membrane prepared with ionic liquid, HF-20IL 2, had 2.5 times higher water permeance than that for the membrane prepared from solution in DMSO alone, HF-DMSO. Higher porosity is a reason for that (see the inner surface morphology in Figures 3.4 and 3.5).

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-20IL 1, HF-20IL 3 and HF-DMF were deformed while testing their water permeance, due to their mechanical properties. As their Young’s moduli showed low values in Table 3.4, which denotes that their elasticities are higher, these properties were affected on deforming the circular 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\(^{-1}\) PEG to 600 000 g mol\(^{-1}\) PEO is summarized in Table 3.5. The membrane prepared with the ionic liquid is only slightly more hydrophilic than the one without the ionic liquid (Table 3.4). 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; this membrane also had a higher Young’s modulus than the other membranes, indicating more rigidity.

Figure 3.8. FT-IR spectra of: hollow fiber with IL (red), hollow fiber without IL (blue), pure Ionic liquid (grey), and PAN (green).
Table 3.4. Results of water permeance, MWCO, mechanical strength, Young’s modulus, and contact angle.

<table>
<thead>
<tr>
<th>HF support membrane</th>
<th>Water permeance (Lm⁻²h⁻¹bar⁻¹)</th>
<th>MWCO (g mol⁻¹)</th>
<th>Mechanical strength</th>
<th>Young’s modulus</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stress (Mpa)</td>
<td>Strain (%)</td>
<td></td>
</tr>
<tr>
<td>HF-20IL 1</td>
<td>428 ± 10</td>
<td>60 000</td>
<td>4.8 ± 0.2</td>
<td>37 ± 1</td>
<td>1.17</td>
</tr>
<tr>
<td>HF-20IL 2</td>
<td>540 ± 30</td>
<td>54 000</td>
<td>5.8 ± 0.1</td>
<td>31 ± 1</td>
<td>1.69</td>
</tr>
<tr>
<td>HF-20IL 3</td>
<td>175 ± 10</td>
<td>67 000</td>
<td>3.9 ± 0.2</td>
<td>24 ± 5</td>
<td>1.12</td>
</tr>
<tr>
<td>HF-DMSO</td>
<td>209 ± 10</td>
<td>32 000</td>
<td>6.3 ± 0.3</td>
<td>43 ± 3</td>
<td>2.02</td>
</tr>
<tr>
<td>HF-DMF</td>
<td>22 ± 10</td>
<td>80 000</td>
<td>4.1 ± 0.2</td>
<td>14 ± 2</td>
<td>0.81</td>
</tr>
</tbody>
</table>

a Deformation of the hollow fiber was observed during the test. Feed solution: 0.1 wt% of 300, 1 500, 6 000, 10 000, 35 000 g mol⁻¹ PEG and 100 000 and 600 000 g mol⁻¹ PEO solutions

Table 3.5. PEG rejection by hollow fiber membranes.

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

Test conditions: 2 bar (pressure), Feed solution: 0.1 wt% of 300, 1 500, 6 000, 10 000, 35 000 g mol⁻¹ PEG and 100 000 and 600 000 g mol⁻¹ PEO solutions
3.3.5. Performance in forward osmosis tests

An interfacially polymerized polyamide layer was prepared on the outer surface of the hollow fiber membranes (Figure 3.6). Table 3.6 shows the performance results for hollow fiber membranes in a FO system, using sucrose solutions as a draw solution. The water flux values of the hollow fiber membranes prepared with the ionic liquid were slightly higher than for the others. For example, that of HF-20IL 1, which is a hollow fiber membrane prepared with ionic liquid, was about 2 LMH higher than those of the other membranes prepared with DMSO alone (HF-DMSO) and DMF alone (HF-DMF) in the condition of a 1 M sucrose draw solution. The reversible solute flux, which is the amount of permeated solutes from the draw solution to the feed solution through a membrane per membrane area and time, was measured both by refractometry and by vapor pressure osmometry, as shown in Table 3.6. No reversible sucrose flux was detected in the feed solution for any of the TFC hollow fiber membranes.

Table 3.6. Performance of hollow fiber membranes in forward osmosis tests.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>1M Sucrose</th>
<th>2M Sucrose</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water flux (LMH)</td>
<td>Solute flux (gMH)</td>
<td>Water flux (LMH)</td>
</tr>
<tr>
<td>HF-20IL 1</td>
<td>6.7 ± 0.5</td>
<td>0</td>
<td>5.6 ± 0.5</td>
</tr>
<tr>
<td>HF-20IL 2</td>
<td>6.5 ± 0.5</td>
<td>0</td>
<td>6.8 ± 0.5</td>
</tr>
<tr>
<td>HF-20IL 3</td>
<td>5.6 ± 0.5</td>
<td>0</td>
<td>7.0 ± 0.5</td>
</tr>
<tr>
<td>HF-DMSO</td>
<td>4.3 ± 0.5</td>
<td>0</td>
<td>5.3 ± 0.5</td>
</tr>
<tr>
<td>HF-DMF</td>
<td>4.4 ± 0.5</td>
<td>0</td>
<td>6.3 ± 0.5</td>
</tr>
</tbody>
</table>

Test conditions: 2 M and 1 M sucrose solutions as draw solutions, deionized water as a feed solution, 1 L min⁻¹ as the flow rate, 25 °C as the test temperature, cross-flow, pH 7, and the active layer of the HF membranes facing the feed solution.
3.4. 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.

Hollow fiber membranes were successfully fabricated using less toxic solvents and an ionic liquid. The hollow fiber membranes fabricated with the ionic liquid had a fully-developed finger-like structure and regular patterns on their inner surface. In contrast, membranes prepared without ionic liquid had a porous structure with macrovoids or pear-like cavities, but without regular patterns in their 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⁻¹ were measured for the membranes prepared with ionic liquid. The water permeance was as high as 540 Lm⁻² h⁻¹ 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 solutions. The water fluxes of the hollow fiber membranes fabricated with the ionic liquid were higher than those of the other membranes, and no reversible solute flux was measured.
Chapter 4. The effects of a co-solvent on fabrication of cellulose acetate membranes from solutions in 1-ethyl-3-methylimidazolium acetate

This chapter was published as: DooLi Kim, Ngoc Lieu Le, and Suzana P. Nunes, *Journal of membrane science*, 2016, 520, 540-549.

4.1. Introduction

Since Loeb and Sourirajan introduced cellulose acetate (CA) membranes for seawater desalination in the 1960’s [115, 116], CA-derived materials have been extensively studied for membrane-based applications because of their high biocompatibility, high fouling resistance, excellent hydrophilicity, and low cost. To fabricate CA membranes, various solvents such as acetone or acetone mixtures [115-117], N-methyl-2-pyrrolidone (NMP) [118, 119], formamide [120], dimethylformamide (DMF) [121] have been employed. Among them, NMP and DMF are commonly used because of the high solubility of CA in these solvents and good properties of the resultant membranes. However, they are classified as highly concerned solvents by European Chemicals Agency [122] and European Commission [13] because of their toxicity. Since the health and environmental concerns [2, 122] are increasing and the regulations of using toxic solvents become strict, many studies have explored greener solvents for preparing CA-based membranes.

As emerging environmentally friendly solvents, ionic liquids are of interest because of their inherent non-toxicity, negligible vapor pressure, chemical and thermal stability, recyclability and non-flammability [110]. In addition, solvent properties of ionic liquids...
can be modified through chemical changes in their cations or anions to dissolve both polar and non-polar compounds [33, 110]. To dissolve CA, imidazolium-based ionic liquids with different anions such as thiocyanate and methyl sulfate have been studied. The solubility of CA in these solvents varies according their anion and cation properties, which affect their viscosity and solubility parameters. For example, Xing et al. [46] found that with the same cation 1-butyl-3-methylimidazolium (BMIM), the dissolution of CA in the methyl sulfate ionic liquid ([BMIM][MeSO₄]) was much slower than that in the ionic liquid with the same cation but with the thiocyanate anion ([BMIM]SCN), because of the higher viscosity of [BMIM][MeSO₄]. On the other hand, 1-ethyl-3-methylimidazolium ([EMIM]), which has a shorter carbon chain, dissolved CA more effectively than the longer carbon chain BMIM with the same anion thiocyanate because of its lower viscosity [66]. Despite the improved solubility, the feasible solubility of CA in these solvents with an acceptable viscosity remains low (approximately 12 wt%) and hence its resultant membranes do not have adequate mechanical properties for practical applications. The low solubility of CA in these ionic liquids results from their weak interaction or low compatibility.

To improve the solubility of CA in ionic liquids, in this study, we propose a di-solvent system, where acetone was used as a co-solvent to fabricate CA flat sheet and hollow fiber membranes with the ionic liquid [EMIM]OAc. Acetone was chosen, due to its lower toxicity, compared to other common solvents used for membrane fabrication, such as DMF, DMAc, and NMP, according to Szekely et al. [5] and solvent guidance [4, 123, 124]. In addition, the acetone/CA miscibility is high even at high CA concentration. However, due to its high volatility, the use of acetone as a single solvent to fabricate CA membranes is infeasible because the resultant membranes are dense and have high
resistance to water transport. [EMIM]OAc was selected because its acetate anions are expected to have excellent interaction with acetate groups of CA. In addition, it has low toxicity and desirable biodegradability [55]. Therefore, this study aims to (1) investigate the thermodynamic and kinetic properties of the CA solution in the di-solvent [EMIM] OAc/acetone system; (2) analyze the effects of adding acetone as co-solvent on membrane morphologies and separation capability and (3) evaluate the opportunities of the di-solvent [EMIM]OAc/acetone system to fabricate membranes for practical applications.

4.2. Experiments

4.2.1 Materials

Cellulose acetate (CA, average Mn = ~50,000), 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc, ≥95.0 %), acetone (≥95.0 %), and N-methyl-2-pyrrolidone (≥99.0 %) were supplied by Sigma-Aldrich. Their chemical structures are shown in Figure 4.1. Polyethylene glycol (PEG) (Sigma-Aldrich) and polyethyleneoxide (PEO) (Sigma-Aldrich), with the molecular weights of 300, 1500, 6000, 10000, 35000, 100000 and 600000 g mol⁻¹, were used for the solute rejection evaluation and determination of the molecular weight cut-off (MWCO). Bovine serum albumin (BSA, ~66 kg mol⁻¹) and γ-globulin (~140 kg mol⁻¹) purchased from Sigma-Aldrich were dissolved in phosphate buffered saline solution (Fisher Scientific), which is formulated with 0.137 M sodium chloride, 0.003 M potassium chloride, and 0.012 M phosphate, for ultrafiltration tests.
Chemical structures of CA, [EMIM]OAc and acetone.

**Figure 4.1.** Chemical structures of CA, [EMIM]OAc and acetone.

### 4.2.2. Thermodynamics of polymer solutions

#### 4.2.2.1. Determination of the Hansen solubility parameter of [EMIM]OAc

The Hansen solubility parameter of [EMIM]OAc was determined by using the software HSPiP [82]. 44 solvents were chosen with their different dispersed interactions, polar cohesive forces, and hydrogen bonding interactions. The miscibility test of each solvent with [EMIM]OAc was conducted by mixing two solvents and observing their miscibility. Based on their results which were miscible or immiscible, each Hansen solubility parameter’s component which is related to the dispersive ($\delta_D$), dipole-dipole ($\delta_p$), and hydrogen bonding ($\delta_H$) interactions [82] was computed by the software. The Hansen solubility parameter was then calculated by the following equation:

$$\delta^2 = \delta_D^2 + \delta_p^2 + \delta_H^2$$  

(1)
4.2.2.2. Estimation of Gibbs free energy of mixing

The Gibbs free energy of mixing ($\Delta G_m$) is an informative parameter to predict the homogeneity of a polymer/solvent mixture [68]. In particular, if $\Delta G_m$ is negative, the polymer is expected to completely dissolve in the solvent. In contrast, if $\Delta G_m$ is much higher than zero, the mixture is unlikely to be homogenous. According to the Flory–Huggins theory, $\Delta G_m$ can be estimated by the following equation [79]:

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

(2)

Where $k$ is the Boltzmann constant, $T$ is the absolute temperature (K), and $\phi_i$ and $x_i$ are the volume fraction and number of segments of the $i^{th}$ component, respectively. $\chi$ is the Flory-Huggins parameter, which can be calculated from the following equation:

$$
\chi_{ij} = \frac{V_i \delta_i \delta_j^{1/2}}{RT} + 0.34
$$

(3)

where $V_i$ is the molar volume of the solvent (cm$^3$/mol), $R$ is the ideal gas constant (cm$^3$ Mpa K$^{-1}$ mol$^{-1}$). The value of 0.34 is an empirical constant absent in the original theory but found important for polymer systems [80-83]. $\delta$ is the solubility parameter of the solvent $i$ and polymer $j$ (MPa$^{1/2}$).

4.2.2.3. Hydrodynamic diameter of polymer coils

The size of polymer coils in each solvent system (at the polymer concentration of 0.1 wt%) was measured by dynamic light scattering (Zetasizer, Malvern). In the cases of
complete dissolution, the bigger size of polymer coils indicates their higher compatibility in the solvent system and the higher thermodynamic stability of the solution.

4.2.2.4. Phase diagram by cloud point tests

Phase diagram of a polymer/solvent/non-solvent system was estimated through cloud point tests. A series of CA solutions were prepared in different compositions and concentrations. Their cloud points were determined by adding water as a non-solvent at room temperature until turbidity was observed. The amounts of CA, solvents, and water for each cloud point were plotted in a ternary diagram.

4.2.3. Kinetics of polymer solutions

4.2.3.1. Viscosity of polymer solutions

The viscosity of a polymer solution is an important factor for membrane fabrication especially when using ionic liquids as a solvent because comparing to common organic solvents, ionic liquids themselves generally have higher viscosity and produce more highly viscous polymer solutions due to their weaker interaction with polymer molecules. In this study, the viscosity of CA solutions was measured using a AR1500ex Rheometer, TA Instruments at the shear rate of 10 s⁻¹ with different temperatures.

4.2.3.2. Phase inversion kinetics

Phase inversion kinetics of polymer solutions was studied through light transmittance experiments. Polymer solutions were cast on a glass plate with the solution thickness of 1 mm and then immediately immersed in water as a non-solvent. Changes of
light transmittance were monitored at 600 nm (water has no absorbance peak at this wavelength) using a Cary 5000 UV-Vis-NIR, Agilent. The relative light transmittance ($T_r$) was determined by the following equation (4) [46, 66].

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

(4)

where $T_{\text{min}}$, $T_{\text{max}}$ and $T$ are the minimum, maximum, and the transmittance at a time, respectively.

4.2.4. Preparation of polymer solutions and fabrication of membranes

Five polymer solutions with different polymer concentrations and solvents were prepared, without further additives: 12 wt% CA/ 88 wt% [EMIM]OAc; 12 wt% CA/35 wt% acetone/53 wt% [EMIM] OAc (acetone: [EMIM]OAc = 40: 60); 18 wt% CA/33 wt% acetone/ 49 wt% [EMIM]OAc (acetone: [EMIM]OAc = 40: 60); 12 wt% CA/ 88 wt% acetone; and 12 wt% CA/88 wt% NMP. The value of 12 wt% is the maximum CA concentration in pure [EMIM]OAc that can produce a homogenous solution. The CA solution in NMP was used as a control. The polymer was dissolved in each solvent system at 60 °C for 1–3 days. For flat-sheet membrane fabrication, the polymer solutions of 3 mL were cast on a glass plate sized of 15 cm x 15 cm with 150 μm thickness at room temperature and then immediately immersed into the deionized water of room temperature as a non-solvent to induce the phase inversion and form membranes. The membranes are marked as 12CA/[EMIM]OAc, 12CA/Ac/[EMIM]OAc, 18CA/Ac/[EMIM]OAc, 12CA/Ac, and 12CA/NMP, respectively. For hollow fiber membrane fabrication, two polymer solutions of 12 wt% CA/88 wt% [EMIM]OAc and 18 wt% CA/33 wt% acetone/49
wt% [EMIM]OAc were prepared. The spinning conditions are listed in Table 4.1. The resultant membranes are marked as HF-12CA/[EMIM]OAc and HF-18CA/Ac/[EMIM]OAc, respectively.

Table 4.1. Spinning conditions.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>HF-12CA/[EMIM]OAc</th>
<th>HF-18CA/Ac/[EMIM]OAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope solution composition (wt %)</td>
<td>12 wt% CA/88 wt% [EMIM]OAc</td>
<td>18 wt% CA/88 wt% acetone/[EMIM]OAc (40/60)</td>
</tr>
<tr>
<td>Composition of bore fluid (wt %)</td>
<td>DI water</td>
<td></td>
</tr>
<tr>
<td>Coagulant bath</td>
<td>DI water</td>
<td></td>
</tr>
<tr>
<td>Air gap (cm)</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Flow rate of dope solution (mL/min)</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Flow rate of inner coagulant (mL/min)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Take up speed (m/min)</td>
<td>14.4</td>
<td>18.2</td>
</tr>
<tr>
<td>Temperature of the dope solution (°C)</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Temperature of the bore fluid and the coagulant bath (°C)</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

4.2.5. Membrane characterizations

Membrane morphologies were observed by field emission scanning electron microscopy (FESEM) (FEI Quanta 200, Quanta 600, and Nova Nano FESEM). To observe the cross-sectional images, the membranes were fractured in liquid nitrogen and then coated by iridium.

Pure water permeance of membranes was examined through filtration experiments and calculated by the following equation:
Pure water permeance, \((\text{Lm}^2\text{h}^{-1}\text{bar}^{-1}) = Q, A^{-1}, \Delta P^{-1}\) \(\text{(5)}\)

where \(Q\) is the water flux (L/h), \(A\) is the effective membrane area (m\(^2\)), and \(\Delta P\) is the applied pressure (bar).

Pore sizes or MWCOs of membranes were investigated by filtration tests with neutral solutes PEG and PEO in a dead-end cell with stirring speed of 450 rpm under 2 bar. Their rejection was evaluated by the following equation:

\[
\text{Solute rejection, } R(\%) = \left(1 - \frac{C_{\text{perm}}}{C_{\text{feed}}} \right) \times 100\%
\] \(\text{(6)}\)

where \(C_{\text{perm}}\) and \(C_{\text{feed}}\) are the concentrations of the permeate and feed solutions, respectively, which was analyzed by gel permeation chromatography (GPC) with a PL aquagel-OH 40 and 60 columns (1260 infinity GPC/SEC, Agilent technologies). Solute diameter was calculated by the Stokes radius equation [125, 126]:

For PEG
\[
r = 16.73 \times 10^{-10} M^{0.557}
\] \(\text{(7)}\)

For PEO
\[
r = 10.44 \times 10^{-10} M^{0.587}
\] \(\text{(8)}\)

where \(r\) is the Stokes radius (cm), and \(M\) is the molecular weight (g/mole or Da) of PEG and PEO. The relation between the solute diameter \((d = 2r)\) and its rejection is shown in the equation \((9)\) and the pore size probability of membranes is expressed by the equation \((10)\).

\[
F(R) = A + B (\ln d)
\] \(\text{(9)}\)
where \( \mu_p \) is the mean of the effective pore size diameter at \( R = 50 \% \). \( \sigma_p \) is the geometric standard deviation and defined as the ratio of \( d \) values at \( R = 84.13 \) and 50 % by neglecting the steric and hydrodynamic hindrance effects [126] and ignoring the deformation of macromolecules under pressure and shear rate in the solution [127]. From the plot of the equation (9), the mean pore size \( (d_s) \) was determined at \( R = 90 \% \) and the molecular weight cut-off (MWCO) was calculated by the equations (7) or (8).

4.2.6. Protein separation

Ultrafiltration performance was examined by filtration tests of BSA and \( \gamma \)-globulin solutions with the concentration of 1 mg mL\(^{-1} \) at pH 7 using a dead-end UF set-up (Amicon cell). These solutions were prepared in the phosphate buffered saline solution. Their rejection was calculated by the equation (6) based on their permeate and feed concentrations, which were analyzed by a UV spectrometer at 280 nm (Thermo scientific, Nanodrop 2000c).

4.2.7. Mechanical properties

The mechanical properties of the membranes were measured by dynamic mechanical analysis (Q800, TA instrument) at room temperature with the force rate of 0.05 N/min. For examining the pressure tolerance of hollow fiber membranes, hydraulic
pressure with the cross-flow water supply was applied in their shell side and gradually increased until the membranes collapsed.

4.3. Results

4.3.1. Thermodynamics of polymer solutions

4.3.1.1. Hansen solubility parameter of [EMIM]OAc

The ternary diagram in Figure 4.2a shows the relationship of the Hansen solubility parameter components of [EMIM]OAc in comparison with those of other solvents. The blue dots are the solvents miscible with [EMIM]OAc and red dots are the ones immiscible with it. Based on miscibility between [EMIM]OAc and other solvents, two green and yellow circles were computed, where [EMIM]OAc is located at their center (green and yellow dots). The green circle, though, fits more stochastically. The solvents confined in the circles have high probability of being miscible with [EMIM]OAc while those located out of them have low probability. Figure 4.2b shows its 3D images, where the green sphere shows the miscible probability of solvents with [EMIM]OAc (green dot). Solubility parameters of [EMIM]OAc were determined and tabulated in Table 4.2 along with those of other solvents used in this study. The difference in solubility parameters of CA and acetone is smaller than that of CA and [EMIM]OAc, which implies that acetone may have a stronger interaction with CA and dissolve it better. In addition, since the solubility parameters of acetone and [EMIM]OAc are lower and higher than CA, respectively, their mixture might have a closer solubility parameter with CA. Therefore, the motivation of this study is to use acetone as a co-solvent to improve the thermodynamics and kinetics of the CA/[EMIM]OAc system and hence the properties of the resultant membranes.
Table 4.2. Solubility parameters of the polymer and solvents used in this study.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>δD</th>
<th>δP</th>
<th>δH</th>
<th>δ (Mpa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose acetate [82]</td>
<td>18.6</td>
<td>12.7</td>
<td>11</td>
<td>25.1</td>
</tr>
<tr>
<td>[EMIM]OAc (by HSPiP)</td>
<td>22.2</td>
<td>15.9</td>
<td>16.9</td>
<td>32.1</td>
</tr>
<tr>
<td>Water [82]</td>
<td>15.5</td>
<td>16</td>
<td>42.3</td>
<td>47.8</td>
</tr>
<tr>
<td>Acetone [82]</td>
<td>15.5</td>
<td>10.4</td>
<td>7</td>
<td>19.9</td>
</tr>
</tbody>
</table>

4.3.1.2. Estimation of Gibbs free energy of mixing

**Figure 4.3a** shows $\Delta G_m$ of CA with solvents. The polymer solutions of CA (12 wt% and 18 wt%) in [EMIM]OAc had the $\Delta G_m$ values of > zero. These positive values imply that the CA polymer had a weak interaction with [EMIM]OAc. The result was consistent with the large difference in their Hansen solubility parameters (Table 4.2). The addition of
acetone into the CA/[EMIM]OAc systems decreased their $\Delta G_m$ values. Once the acetone amount reached 30 wt% approximately, $\Delta G_m$ turned to zero. Further adding acetone provided more negative values. It can be explained that the co-solvent acetone influenced the interaction between CA molecules and [EMIM]OAc and decreased the required $\Delta G_m$ of CA in [EMIM]OAc. As a result, it facilitated a homogeneity of the system. Figure 4.3b shows the $\Delta G_m$ relationship among 12 wt% CA, the solvents ([EMIM]OAc and acetone), and the non-solvent water. The solution with 100 % [EMIM]OAc is in the blue region and close to the black region where $\Delta G_m$ is much higher than zero.

The green region indicates the $\Delta G_m$ values below zero and the system shifted to this green region, when the acetone amount was higher than 30 wt%. In this study, therefore, the ratio of 40 wt% acetone and 60 wt% [EMIM]OAc was chosen for further studies.

![Figure 4.3](image)

**Figure 4.3.** (a) The Gibbs free energy of mixing CA polymer in different solvent systems and (b) its ternary diagram.
4.3.1.3. Hydrodynamic diameter of the polymer coils in solvents

Hydrodynamic diameter (Z-Average), which is the size of polymer coils in the solvent systems, was analyzed for the single solvents by dynamic light scattering and tabulated in Table 4.3. A large hydrodynamic diameter reflects that the polymer is dissolved in a good solvent. Among these systems, the size of polymer coils in pure acetone was the largest, which was attributed to excellent interaction between acetone molecules with acetate groups of CA. The coil size in [EMIM]OAc is practically 10-fold smaller, indicating poorer interaction, but still enough to dissolve.

Table 4.3. Polymer molecules size (diameter) in single solvents.

<table>
<thead>
<tr>
<th>Diluted polymer solution</th>
<th>Z-Average (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 wt% CA / 99.9 wt% [EMIM]OAc</td>
<td>19</td>
</tr>
<tr>
<td>0.1 wt% CA / 99.9 wt% Acetone</td>
<td>183</td>
</tr>
<tr>
<td>0.1 wt% CA / 99.9 wt% NMP</td>
<td>34</td>
</tr>
</tbody>
</table>

4.3.1.4. Phase diagram by cloud point tests

Figure 4.4 shows the phase diagram of CA polymer solutions in different solvent systems using water as the non-solvent. The amount of water uptake in polymer solution systems, before phase separation initiates, is depended on the solvent system and was quantified in the following order: acetone/[EMIM]OAc < [EMIM]OAc < NMP < acetone. This tendency was completely consistent with the trend in polymer size measured by dynamic light scattering (Table 4.3) for single solvents. Acetone/[EMIM]OAc is a solvent mixture in the limit of stability and phase separation can be induced with small amount of
the non-solvent, water. The fact that for the solvent quality of the mixture is lower than each single solvent (acetone or [EMIM]OAc) could be due to stronger interaction between acetone and acetate groups of [EMIM]OAc, rather than between acetone and acetate groups of CA. A strong interaction between the two solvents disfavors their interaction with the polymer. This leads to a fast phase inversion when the solution is brought in contact with water.

**Figure 4.4.** Phase diagram of CA solutions using water as a non-solvent at room temperature.

### 4.3.2. Kinetics of polymer solutions

#### 4.3.2.1. Viscosity

**Figure 4.5** shows the viscosity of CA polymer solutions using different solvent systems as a function of temperature. The results indicate that 12 wt% CA/[EMIM]OAc
has a high viscosity of 33 Pa s at 25 °C. The addition of acetone to the solution decreased the viscosity more than 16 times to approximately 2 Pa s, which is in the range of viscosity measured for 12 wt% CA/acetone. The reasons for the low viscosity values might be different in the 2 cases. Since the coils in acetone are large, the concentration at which coils begin to entangle is lower than in other cases. This concentration is proportional to the inverse of the cube of the radius of gyration. If the radius of gyration is 10-fold higher, the concentration corresponding to the change of dilute to semi-dilute regime can be 1000-fold lower. The 12 wt% solution in acetone is in the semi-dilute regime. But even with inter-coil entanglement, a good solvent acts as a plasticizer, leading to low viscosity. If the solvent is not a good one, the coils are compacted and the concentration at which they start to entangle is higher. For coils hydrodynamic diameter of 19 nm, the concentration, at which entanglement starts is around 5 wt%. Therefore, also the 12 wt% solution in [EMIM]OAc is in the semi-diluted regime with inter-coil entanglements. However, in contrast to the solution in acetone the polymer segment-segment friction is high due to the poor solvent quality. As a consequence, the viscosity is high. By taking in account Figure 4.4, when acetone is added to [EMIM]OAc, the solvent quality considerably decreases. If the coils shrink, the concentration, at which entanglement starts, increases. The addition of acetone to [EMIM]OAc brings the system below the semi-dilute regime and the shrunken coils flow with negligible entanglements. Viscosity becomes much lower than for solutions in pure [EMIM]OAc. In this way, it is possible to increase the polymer concentration 18 wt%, keeping the viscosity in levels convenient for membrane casting and hollow fiber spinning. Increasing temperature decreased the viscosity of all polymer solutions. Especially, the viscosity of the 12 wt% CA/[EMIM]OAc solution dropped significantly
with the increase in temperature and at 60 ºC. Its value became similar to those of the other solutions. This indicates that 60 ºC was the preferable temperature to fabricate the membrane prepared from the pure [EMIM]OAc.

Figure 4.5. Viscosity of CA solutions as a function of temperature at the shear rate of 10 s⁻¹.

4.3.2.2. Phase separation kinetics

Figure 4.6 shows the phase inversion kinetics of different CA solutions. The ones prepared from the mixture of acetone and [EMIM]OAc had faster phase separation than others, which almost finished in 75 s and 125 s for 12 wt% CA and 18 wt% CA, respectively. Increasing the CA concentration from 12 wt% to 18 wt% slowed down the speed of phase separation because the high amount of polymers led to the lower diffusion coefficients and hence restricted solvent exchange. It is important to note that the phase
separation of 18 wt% CA/Ac/[EMIM]OAc at the early stage ($T_r \leq 75\%$) was 10-fold slower than that of 12 wt% CA/Ac/[EMIM]OAc. The CA/acetone solution had a slow phase separation due to the good solvent quality. Higher water content can be present without starting the phase separation, as shown in Figure 4.4. For the solution in pure [EMIM]OAc the phase separation is slow, due to the high viscosity, which retards the solvent-non-solvent exchange. For other solutions, the transmittance decreases fast. The phase separation kinetics of polymer solutions affects their resultant membrane morphologies, which will be discussed in the next section.

![Phase inversion kinetics of CA polymer solutions cast on a glass plate and coagulated in water.](image)

**Figure 4.6.** Phase inversion kinetics of CA polymer solutions cast on a glass plate and coagulated in water.
4.3.3. Membrane characterization

4.3.3.1. Membrane morphology of Flat sheet membranes

**Figure 4.7** shows the morphologies of the membranes fabricated from different CA solutions. Their cross-sectional images show that 12CA/Ac/[EMIM]OAc and 12CA/NMP membranes are thicker with large macrovoids, while 12CA/[EMIM]OAc, 12CA/Ac and 18CA/Ac/[EMIM]OAc membranes are thinner with sponge-like structure. The large macrovoids in 12CA/Ac/[EMIM]OAc and 12CA/NMP membranes correlate with their low viscosity. When the solution is cast and immersed in the coagulant bath, the cavities are initiated by abrupt intrusion of water breaking the incipient skin, which is being formed. More viscous solutions have a higher resistance to macro-void cavity formation. 12CA/Ac is an exception in this series as far as the correlation between viscosity and macrovoid is concerned. However other factors have to be taken into consideration. First acetone is the most volatile of all solvents used and the polymer concentration and viscosity in the top layer of the cast solution might rapidly increase even with very short evaporation times. Furthermore, acetone might diffuse faster out of the solution layer into the water bath.

Both points are supported by the fact that the final membrane is very thin. Since acetone is the best solvent for CA, phase separation will only be initiated when the solvent-water exchange proceeded to a large extent. The skin is formed then at a relative later, when large amount of water is already in the solution layer. The osmotic driving force for water intrusion is then lower at the moment that the skin is formed.

A quick scan over the surface morphologies of all studied membranes shows that the 12CA/Ac membrane had the densest top layer, since acetone is the most volatile of all
solvents and probably the fastest diffusion into the water bath. Details on their pore size will be discussed in the next section.

**Figure 4.7.** Cross-sectional and surface morphologies of the following membranes: (a) 12 wt% CA/[EMIM]OAc; (b) 12 wt% CA/Ac/[EMIM]OAc (12 % CA/35 % Ac/53 % [EMIM]OAc); (c) 12 wt% CA/Ac; (d) 12 wt% CA/NMP; (e) 18 wt% CA/Ac/[EMIM]OAc (18 wt% CA/33 wt% Ac/49 wt% [EMIM]OAc).
4.3.3.2. Pure water permeance, MWCO, pore size and pore size distribution

**Figure 4.8a** and **Table 4.4** present the pure water permeance of CA membranes prepared from different solvent systems. The 12CA/[EMIM]OAc membrane had a water permeance of 130 L m$^{-2}$ h$^{-1}$ bar$^{-1}$. Adding acetone to the solvent system increased the water permeance of the resultant membrane (12CA/Ac/[EMIM]OAc) 2.5 times to 330 L m$^{-2}$ h$^{-1}$ bar$^{-1}$. A comparison between the membranes prepared from the solvent mixture (12CA/Ac/[EMIM]OAc) and from the commonly used solvent NMP (12CA/NMP) shows that, although both had similar structures with large macrovoids, the former had 3.3 times higher water permeance than the latter. The 12CA/NMP membrane had much denser morphology than 12CA/Ac/[EMIM]OAc. On the other hand, the membrane prepared from the pure acetone had no measurable water permeation, during the long testing period up to 7 bar (the data were not included) due to its extremely dense top layer. Increasing the polymer concentration led to the membranes with lower water permeances but the 18CA/Ac/[EMIM]OAc membrane had much higher water permeance than 18CA/NMP (110 vs 4 L m$^{-2}$ h$^{-1}$ bar$^{-1}$).

![Figure 4.8a](image)

**Figure 4.8.** (a) Pure water permeance, (b) PEG rejection and (c) pore size distribution of the membranes prepared from different solvent systems.
**Figure 4.8b** shows the rejection of all studied membranes towards the neutral solutes PEG or PEO with different molecule weights. The CA/Ac membrane was not reported because it had practically no measurable water permeation. From the rejection results, the pore size distributions were illustrated in **Figure 4.8c** and their MWCOs were listed in **Table 4.4**. **Figure 4.8c** shows that the 12CA/NMP had smaller pore size than other membranes prepared from similar CA concentration. It also had the smallest MWCO value. On the other hand, there was no significant difference in pore size distribution between the 12CA/[EMIM]OAc and 12CA/Ac/[EMIM]OAc membranes. Increasing the CA content in the polymer solution led to the 18CA/Ac/[EMIM]OAc membrane with a smaller mean pore size and lower MWCO, with a decrease from 74 kg mol\(^{-1}\) to 57 kg mol\(^{-1}\).

**Table 4.4.** Pure water permeance, MWCO and protein separation of CA flat-sheet membranes.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Pure water permeance (L m(^{-2}) h(^{-1}) bar(^{-1}))</th>
<th>MWCO (kg mol(^{-1}))</th>
<th>Rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>BSA</td>
</tr>
<tr>
<td>12CA/[EMIM]OAc</td>
<td>130</td>
<td>77</td>
<td>-</td>
</tr>
<tr>
<td>12CA/Ac/[EMIM]OAc</td>
<td>330</td>
<td>74</td>
<td>-</td>
</tr>
<tr>
<td>12CA/NMP</td>
<td>100</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>18CA/Ac/[EMIM]OAc</td>
<td>110</td>
<td>57</td>
<td>91</td>
</tr>
</tbody>
</table>
4.3.3.3. Protein separation

The proteins bovine serum albumin (BSA) (~66 kg mol\(^{-1}\)) and γ-globulin (~140 kg mol\(^{-1}\)) were used to evaluate the protein separation capability of the membranes and the results were listed in Table 4.4. With the polymer concentration of 12 wt\%, all membranes had MWCOs of larger than 70 kg mol\(^{-1}\) and hence cannot reject BSA molecules. The BSA rejection may depend on not only physical factors such as the pore size and tortuosity of membranes but also the electrostatic interaction between the membranes and the protein molecules due to their charges. Even though the membranes had larger pore size than the diameter of BSA, they can reject BSA to some extent but all rejection values were lower than 50 %. On the other hand, all membranes prepared from 12 wt\% CA solutions achieved high separations of γ-globulin with the rejection > 96 %, due to its high molecular weight. Increasing the polymer concentration to 18 wt\% narrowed the surface pore size and decreased its MWCO to a lower value than that of BSA. As a result, the membrane was able to reject BSA up to 91 %.

4.3.3.4. Mechanical properties

Along with the separation capability of proteins, the mechanical properties are another major characteristics determining the potential practical applications of membranes. Table 4.5 presents the mechanical properties of the membranes prepared from the different solvent systems and polymer concentrations. The mechanical strength of membranes is governed by their porous structures. The 12CA/[EMIM]OAc membrane had the lowest stress at break among those prepared from 12 wt\% solutions. Increasing the
polymer concentration to 18 wt% evidently improved the mechanical strength because of the increased polymer content in the membrane.

Using [EMIM]OAc as single solvent for the CA only provides a polymer solution with the maximum concentration of 12 wt%. Polymer solutions with higher concentrations were too viscous to fabricate membranes. As a result, the membranes prepared from pure [EMIM]OAc had low mechanical properties and a narrow range of separation capability caused by larger surface pore size and higher MWCO. Adding acetone as the co-solvent in the CA/[EMIM]OAc polymer solution system not only improved the thermodynamic properties of the polymer solution, enhanced mechanical strength and decreased MWCO but also opened the ability to fabricate membranes with higher polymer concentrations from ionic liquid solutions. By this way, better opportunities for using ionic liquids as green solvents to fabricate mechanically strong and separation-effective membranes for practical applications were added with this work.

**Table 4.5. Mechanical properties.**

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Stress at break (MPa)</th>
<th>Pressure resistance of HF modules (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12CA/[EMIM]OAc</td>
<td>1.62</td>
<td></td>
</tr>
<tr>
<td>12CA/Ac/[EMIM]OAc</td>
<td>2.02</td>
<td></td>
</tr>
<tr>
<td>12CA/NMP</td>
<td>1.96</td>
<td></td>
</tr>
<tr>
<td>18CA/Ac/[EMIM]OAc</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>HF-12CA/[EMIM]OAc</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>HF-18CA/Ac/[EMIM]OAc</td>
<td></td>
<td>250</td>
</tr>
</tbody>
</table>
4.3.3.5. Hollow fiber membranes

The importance of polymer concentrations on mechanical strength of practical membranes as well as the importance of adding acetone as the co-solvent with [EMIM]OAc to form CA membranes are even more evident when hollow fiber membranes are prepared instead of flat-sheet. We employed two polymer solutions, 12 wt% CA in [EMIM]OAc (abbreviated as HF-12CA/[EMIM]OAc) and 18 wt% CA in the mixture of acetone and [EMIM]OAc (abbreviated as HF-18CA/Ac/[EMIM]OAc) to fabricate hollow fiber membranes, which are frequently the more convenient configuration for practical applications. Their membrane morphologies are shown in Figure 4.9. Their hydraulic pressure tolerances are presented in Table 4.5. Clearly, the hollow fiber membrane HF-18CA/Ac/[EMIM]OAc had 2.5 times higher pressure tolerance than the membrane HF-12CA/[EMIM]OAc.

Figure 4.9. Morphologies of the hollow fiber membranes (a) HF-12CA/[EMIM]OAc and (b) HF-18CA/Ac/[EMIM]OAc.
4.4. Conclusion

CA flat-sheet and hollow-fiber membranes were fabricated with pure [EMIM]OAc and with a mixture of [EMIM]OAc and acetone. Thermodynamic and kinetic effects were investigated related to the membrane formation. First of all, the Hansen solubility parameter of [EMIM]OAc was obtained from the software HSPiP and then based on these data, the $\Delta G_m$ of each polymer solution system was estimated. The results showed that adding acetone into the CA/[EMIM]OAc system increased its solubility. The studies on phase diagram and dynamic light scattering gave an indication of the thermodynamic instability of the polymer solution in a mixture of the two solvents. A kinetic investigation indicated that the phase separation rate of the CA polymer solution in the mixture of acetone and CA/[EMIM]OAc was faster than in pure [EMIM]OAc.

Membranes prepared from 18CA/Ac/[EMIM]OAc, 12CA/Ac and 12CA/[EMIM]OAc had uniform symmetrical sponge-like structure, while 12CA/NMP and 12/Ac/[EMIM]OAc had finger-like cavities. The membrane 12CA/Ac/[EMIM]OAc had higher water permeance than the membranes with [EMIM] OAc or NMP only. The water permeance of 18CA/Ac/[EMIM]OAc was much higher (about 27 times) than that of 18CA/NMP. All membranes fabricated from 12 wt % polymer had large pore size or high MWCO and hence could not reject BSA efficiently. However, they still can reject $\gamma$-globulin at > 96 %. Increasing the polymer concentration to 18 wt % narrowed the pore size and enabled the membrane to reject BSA at 91 %.

Both the flat-sheet and hollow fiber membranes prepared from the polymer concentration of 18 wt% had stronger mechanical properties than those prepared from that of 12 wt%. Therefore, adding acetone as a co-solvent with [EMIM]OAc opens an
opportunity of fabricating CA membranes with high polymer concentrations, which were more selective and had stronger mechanical properties than those obtained from analogous solutions in pure [EMIM]OAc, NMP or acetone for practical applications.
Chapter 5. Green membrane manufacture for peptide separations

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5.1. Introduction

Biomedical separations [128], food processing [129], water desalination [130], and purification [131] heavily count on nanostructured polymeric membranes. For industrial membrane manufacture, an important step is the casting of polymer solutions. Polysulfone (PSU) and polyethersulfone (PES) are among the most successful polymers in this field. However, despite of the success of membrane technology, membrane manufacture itself is now under scrutiny. Solution casting uses relatively harmful solvents, such as dimethylformamide, N-methyl pyrrolidone, and dimethyl acetamide [132]. These solvents are now included in the Registration, Evaluation, Authorization, and Restriction of chemicals (REACH) of the European Chemicals Agency (EACH)[133], with perspectives to be banned in the near future and not be applicable anymore for membrane industrial fabrication, at least in Europe. It has been recently reported that the membrane manufacture industry produces 50 billion liters of wastewater containing toxic solvents per year [134]. Finding green alternatives for membrane manufacture is urgently needed [5, 6]. This is the main motivation of this work. We report here a process in which PES is fully dissolved in an ionic liquid, without addition of any other organic solvent.
Ionic liquids are considered green solvents [33] from the perspective of enabling processes with no generation of harmful volatile organic chemicals (VOC) [135], even if aspects related to the synthesis, life cycle and toxicity in wastewater of some of them have been seen as less environmentally friendly than mostly claimed [111, 136]. For a sustainable membrane fabrication, ionic liquids should be recycled.

The role of ionic liquids in membrane technology has been limited and considered mostly in a different way. The membrane research using ionic liquids takes advantage of their ion conductivity, for instance in fuel cells [137], or their preferential interaction with CO$_2$ for gas separation [138-141]. A successful strategy is the use of ionic liquid supported in porous membranes (SILMs) as medium for gas CO$_2$ [135] or SO$_2$ [142], separation from other gases. Ionic liquids have been also polymerized as membrane material for gas separation [141, 143]. These applications rely on the fact that polymers hardly dissolved in ionic liquids. Few examples of polymer dissolution in ionic liquids have been previously reported. Therefore, ionic liquids have been seldom used for membrane fabrication. The few reports used cellulose in [EMIM]OAc[144], cellulose acetate in 1-Ethyl-3-methyl-imidazolium-thiocyanate [EMIM]SCN and 1-Buthyl-3-methyl-imidazolium-thiocyanate [BMIM]SCN [145, 146], mixture of polybenzimidazole and polyimide in 1-Ethyl-3-methyl-imidazolium acetate [EMIM]OAc [147], and polyimidazole in [EMIM]OAc [93].

Ionic liquids have been additionally used in combination with other solvents [65, 78].
5.2. Methods

5.2.1. Materials

PES (Ultrason®, average Mn = 75,000), 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP, ≥ 98.0 %), DMF (≥ 99.8 %), DMAc (≥ 99.5 %) and NMP (≥ 99.0 %) were supplied by Sigma-Aldrich. The structures of the polymer and the ionic liquid are shown in Figure 5.1. Polyethylene glycol (PEG) and polyethyleneoxide (PEO) (Sigma-Aldrich) with molecular weights 300; 1500; 6000; 10 000; 35 000; 100 000; and 600 000 g mol⁻¹ were used for the solute rejection evaluation and determination of the molecular weight cut-off (MWCO). Bovine serum albumin (BSA), 1,4-dithiothreitol (DTT), ammonium bicarbonate, and trifluoroacetic acid were also obtained from Sigma-Aldrich. Iodoacetamide was obtained from GE Healthcare. Sequencing-grade modified trypsin was supplied by Promega. Acetonitrile was purchased from Fisher-Scientific.

![Polyethersulfone](image1.png)

![EMIM]DEP](image2.png)

Figure 5.1. Chemical structures of PES and [EMIM]DEP.
5.2.2. Solution thermodynamics

The Hansen solubility parameter ($\delta$) for the ionic liquids [EMIM] DEP and [EMIM] OAc were determined by using the HSPiP software (4th edition 4.1.07) [148]. The total solubility parameter is given by equation (1):

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$$

(1)

where $\delta_D$ is the contribution due to the van der Waals interactions, $\delta_P$ is relative to polar cohesive forces and $\delta_H$ is due to hydrogen bonds. Miscibility tests were performed in 44 solvents with known solubility parameters to evaluate the $\delta$ values for the ionic liquid.

The phase of a specific polymer/solvent solution can be theoretically estimated by calculating the Gibbs free energy of mixing, $\Delta G_m$, based on $\chi$ and $\delta$. $\Delta G_m$ should be negative if only one phase is present with the polymer fully dissolved. $\Delta G_m$ can be calculated [65, 149] with equation (2):

$$\frac{\Delta G_m}{N_A} = kT [\chi \phi_1 \phi_2 + \frac{\phi_1}{X_1} \ln \phi_1 + \frac{\phi_2}{X_2} \ln \phi_2]$$

(2)

where, $\chi$ is the Flory-Huggins parameter; $\chi$ can be estimated from the difference between the total Hansen solubility parameters of the polymer and ionic liquid, determined as mentioned above; $k$ is the Boltzmann constant; $N_A$ is the Avogadro number; $\phi_1$ and $\phi_2$ are the volume factions of solvent and polymer, respectively; $X_1$ and $X_2$ are the corresponding number of segments of each component. From $\Delta G_m$ values, the system compositions with the highest miscibility can be delimited, as conducted by other systems [65].

Phase diagrams for PES/solvent/water ternary systems were estimated by measuring the cloud points for each solution with addition of water. The experiments were
conducted at room temperature. PES solutions of various concentrations were prepared in different solvents. Water was added to each solution until it became turbid. The detected cloud points for a specific PES/solvent/water system delineate the binodal curve, which denotes the boundary between the stable (one phase) region and the meta-stable region of the phase diagram.

The coil size distribution of PES in each solvent was measured by dynamic light scattering (Zetasizer, Malvern). 0.1 wt% PES solutions in [EMIM]DEP, NMP, DMAc, and DMF were prepared and filtered through membranes with 0.45 mm pores before analysis. The experiments were done using He-Ne laser with wavelength 633 nm.

5.2.3. Solution kinetics

The kinetics of the phase separation, when different casting solutions are immersed in water, was evaluated by transmittance measurement using a Cary 5000 UV-Vis-NIR, Agilent, equipment. 16 wt% PES solutions in [EMIM]DEP, NMP, DMAc, and DMF were cast on a glass plate forming a 150μm-thick layer, which was immersed in a glass cuvette containing water. Changes of transmittance, starting from the moment of immersion in water until reaching a constant value, were monitored as a function of time at 600 nm[145, 146]. Values of relative light transmittance ($T_r$) were calculated by equation (3).

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

where, $T$ is transmittance at a given time; $T_{\text{min}}$ is the minimum transmittance; and $T_{\text{max}}$ is the maximum measured transmittance.
The rheological properties of polymer solutions were evaluated in an AR1500ex Rheometer (TA Instruments) at different temperatures at 1 Hz and 10 % oscillation strain. The viscosity of each polymer solution was measured at 10 s$^{-1}$ shear rate.

5.2.4. Membrane preparation

Four binary solutions were prepared with PES in [EMIM]DEP. The following PES concentrations were chosen: 8, 12, 14, and 16 wt% PES. Additionally, 16 wt% PES solutions were prepared in NMP, DMAc and DMF. PES was dissolved in the ionic liquid at 90 ºC and in NMP, DMAc, and DMF at 60 ºC, stirring for a day. The polymer solutions were cast on a glass plate using a doctor blade with 150 μm gap and immersed into a deionized water bath to induce phase inversion and pore formation.

5.2.5. Membrane characterizations

The membrane morphology was observed on FEI Quanta 200, 600, and Nova Nano Field Emission Scanning Electron Microscopes (FESEM). To avoid pore collapse, the membranes were freeze-dried. For the cross-section, freeze-dried membranes were fractured in liquid nitrogen and then sputter coated with iridium.

Water permeance and rejection of neutral solutes (PEG) were measured under 2 bar in a dead-end filtration cell, calculated with the following equations:

\[ \text{Water permeance (L m}^2 \text{ h}^{-1} \text{ bar}^{-1}) = Q \times A \times \Delta P^{-1} \]  

\[ \text{PEG rejection, } R (\%) = (1 - \frac{C_{\text{perm}}}{C_{\text{feed}}}) \times 100 \% \]
where $Q$ is the permeated pure water rate (L h$^{-1}$); $A$ is the effective membrane area (m$^2$); $\Delta P$ is the pressure; $C_{perm}$ and $C_{feed}$ are the concentrations of the permeate and feed solutions, respectively. The rejection was analyzed by gel permeation chromatography (GPC) with PL aquagel-OH 40 and 60 columns, (1260 infinity GPC/SEC, Agilent technologies). The molecular weight cut-off (MWCO) is the molecular weight corresponding to 90 % rejection. The feed solution composition for the PEG rejection contained 0.1 wt% 6000 PEG, 0.1 wt% 10,000 PEG, 0.1 wt% 35,000 PEG, 0.1 wt% 100,000 PEO, 0.1 wt% 600,000 PEO and the membranes were tested at 2 bar.

The solute (PEG and PEO) diameter was calculated using the Stokes radius equation[125, 150], from values of molecular weight (Equation 6 and 7):

For PEG

$$a = 16.73 \times 10^{-10} M^{0.557}$$

(6)

For PEO

$$a = 10.44 \times 10^{-10} M^{0.587}$$

(7)

where $a$ is the Stokes radius (in cm) and $M$ is the molecular weight of PEG and PEO (g mole$^{-1}$). The rejections were plotted as a function of the Stokes diameters ($d = 2a$) corresponding to each molecular weight.

5.2.6. Protein digestion and peptide analyses

Bovine serum albumin (BSA) (Sigma-Aldrich) was digested into peptides and their rejection was evaluated in membrane filtration experiments, using a dead-end filtration cell. In summary, 500 µg of BSA dissolved in 8 M Urea Tris-HCl pH 8.5 were reduced by the addition of 10 mM DTT and incubated for 1 hour at 37 °C. Proteins were alkylated by the
addition of 40 mM iodoacetamide and incubated in the dark for 1 hour at 37 °C. 10 mM DTT were added to the sample, which was then incubated in the dark for another 15 minutes. The sample was diluted 10 times in 50 mM ammonium bicarbonate at pH 8.5 to reduce urea concentration to < 1 M. To digest the proteins, trypsin was added in a 1:50 (trypsin: protein) ratio and incubated overnight at 37 °C. The digestion was stopped by the addition of trifluoroacetic acid to a final concentration of 2 %. The sample was cleaned via reverse phase purification with Sep-Pak C18 cartridges (Waters), dried in a speedvac, re-suspended in 50 µl of 3 % acetonitrile 0.1 % trifluoroacetic acid in MQ water and used as feed. The peptide concentration was measured with Nanodrop at 280 nm wavelength.

To measure the rejection of the peptides, feed solutions containing 40 µg of peptides were filtrated by the membranes fabricated from PES/[EMIM]DEP solutions using a sterilized Amicon cell (Millipore) under 2 bar. Feed and permeates were weighed, dried in a speedvac, and resuspended in 30 µl of 3 % acetonitrile (Fisher-Scientific) 0.1 % trifluoroacetic acid in MQ water. 2 µl per sample (feed and permeate) were loaded into the LC/MS (Ultimate 3000 UHPLC/Q-Exactive, Thermo Scientific) with an Acclaim PepMap RSLC 75 µm x 15 cm nanoViper column. Peak files were compared against UniProt database through MASCOT [151]. MASCOT search results were combined and analyzed with Scaffold [152]. Spectral counts from Scaffold were used to calculate the BSA peptide rejection (%) for each membrane as function of the peptides identified in the feed solution.

5.2.7. Ionic liquid recovery

The waste containing a mixture of [EMIM]DEP and water from the coagulant bath, after fabricating membranes was treated to recycle [EMIM]DEP. Few steps were carried
out to increase the concentration of [EMIM]DEP. First, the water was evaporated in rotavapor (Buchi, Rotavapor R-215) at 90 ºC (heating); 5 ºC (cooling); 80 rpm (rotating speed), under 250 mbar (vacuum) for 2 hrs. In a second step the solution was submitted to vacuum at 130 ºC. Third, magnesium sulfate (MgSO₄) was added to the solution to capture the remaining water and then centrifuged. The recycled ionic liquid concentration was quantified in all steps by refractometry (AR2008 Digital Abbe Refractometer, KRÜSS) using a calibration curve in all steps.

5.3. Results

5.3.1. Solution thermodynamics

The Hansen solubility parameter (δ) of the ionic liquids [EMIM]DEP and [EMIM]OAc was estimated with the HSPiP software based on miscibility tests between the ionic liquids and 44 solvents (Table 5.1S). The δ value for PES was previously reported by Hansen.[148] The estimated differences between values for PES and ionic liquids, |δₑ - δₑ[EMIM]DEP| and |δₑ - δₑ[EMIM]OAc|, were 4.9 and 8.7, respectively, indicating that [EMIM]DEP is indeed a better solvent for PES than [EMIM]OAc. |δₑ - δₑ[EMIM]DEP| is 5.4. This difference is already large enough to disfavor solubilization. From δ values for PES, [EMIM]DEP, [EMIM]OAc and other solvents, the Flory-Huggins parameters, χₑ/ₑ[EMIM]DEP; χₑ/ₑ[EMIM]OAc; and χₑ/ₑDMF or DMAC or NMP, were calculated and applied to obtain ΔGₘ for different concentrations. Figure 5.2 compares ΔGₘ values for different systems at 25 ºC and 90 ºC. ΔGₘ for PES/[EMIM]DEP is positive in all range of concentrations, but it is lower than for PES/[EMIM]OAc and for PSU/[EMIM]DEP. The values for PES in NMP, DMAc, and DMF are negative. For
non-charged organic solvents, $\Delta G_m$ can be calculated from $\delta$ and $\chi$ values, which mainly take into consideration interaction contributions of van der Waals forces, polarity, and hydrogen bonds. The $\Delta G_m$ estimation in the case of ionic liquids is a relatively rough approximation, since additional strong coulombic interactions are not taken into account and ionic liquids are more complex systems than ordinary organic solvents. But the relative values shown in Figure 5.2 are a good indication of the quality of different solvents for PES and PSU. By comparing Figures 5.2a and b, the effect of temperature on the solubility of PES in ionic liquids can be seen. $\Delta G_m$ decreases as the temperature is increased from 25 to 90 ºC, a clear indication that the solubility is higher at higher temperatures.

Figure 5.3 shows the phase diagrams for different PES/solvent/water systems obtained by measuring their cloud points. The 2 phases region increases in the following order of PES/NMP < PES/DMAc < PES/DMF ≤ [EMIM]DEP. The estimated $\Delta G_m$ for 16 wt% PES solutions increases in the same sequence. An indication of the solvent quality for a specific polymer is given also by the size of the coil in a diluted solution measured by DLS. The values of coil size for 0.1 wt% PES solutions in NMP, DMAc, and DMF are 17, 15, and 13 nm, respectively (Table 5.1). A better polymer-solvent interaction leads to coil expansion, which is consistent with the sequence of $\Delta G_m$ values measured for higher polymer concentration. The coil size in [EMIM]DEP was 15 nm, which is in the same range as in DMAc and even larger than in DMF.
5.3.2. Solution kinetics

The membrane morphology is highly influenced by the solution thermodynamics and by the kinetics of phase separation. The kinetics was investigated for 16 wt% PES solutions, by measuring the transmittance reduction when the solution is immersed in water. The results are shown in Figure 5.4. The phase separation kinetics for solutions in NMP, DMAc and DMF is very similar, with abrupt turbidity increase in the first 10 s, after immersion in water. For solutions in [EMIM]DEP, the turbidity increase is slower. This could be a consequence of higher solution viscosity, which delays the water-solvent exchange. The curves delineated by the cloud points (Figure 5.3) can be considered coincident with the binodal curve separating the stable (one phase) region of the phase diagram and the metastable region. The metastable region is separated from the instable (2 phases) region by spinodal curves [153]. If the water-solvent exchange is fast, the solution will be quenched into the 2 phases region and phase separation will follow the spinodal decomposition mechanism [153], starting with continuous oscillations of concentration. If the water-solvent exchange is slow, the system might stay relatively long in the metastable region, between binodal and spinodal curves. In this case, nucleation and growth will be the predominant mechanism [154]. This might be favored in PES/[EMIM]DEP solutions immersed in water, while spinodal decomposition might prevail in other solvents.

Independently of the phase separation mechanism, after entering the 2-phases region the system will separate in a dilute phase which gives rise to the pores and a continuous matrix with high polymer concentration. When the concentration of this
phase is high enough, the mobility of the phase separated systems is so low that the morphology is immobilized, kinetically trapped.

**Figure 5.2.** (a) $\Delta G_m$ estimated for PES and PSU solutions in different solvents and polymer concentrations at 25 °C and (b) at 90 °C.

**Figure 5.3.** Phase diagram measured by cloud point test at 25 °C.
Table 5.1. Coil diameters (Z-average) and polydispersity measured by DLS for 0.1 wt% PES solutions in different solvents; calculated Rg and C* values.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diameter Z-Average(nm)</th>
<th>PDI</th>
<th>Rg(nm)</th>
<th>C*(wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP</td>
<td>17.3 ± 0.2</td>
<td>0.18</td>
<td>6.6</td>
<td>10.0</td>
</tr>
<tr>
<td>DMAc</td>
<td>15.7 ± 0.2</td>
<td>0.19</td>
<td>6.0</td>
<td>15.4</td>
</tr>
<tr>
<td>DMF</td>
<td>13.3 ± 0.3</td>
<td>0.18</td>
<td>5.1</td>
<td>22.6</td>
</tr>
<tr>
<td>[EMIM]DEP</td>
<td>15.3 ± 0.3</td>
<td>0.23</td>
<td>6.0</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Figure 5.4. Relative light transmittance, Tr, (600 nm wavelength) of 16 wt% PES solutions in different solvents cast as a 150 μm-thick layer as a function of time, after immersion in water.

As long as the viscosity of the concentrated phase is still low enough, the morphology evolves, the dilute phase changes in size and form, giving rise to larger pores before further water-solvent exchange proceeds and the system solidifies.
In addition to the microporous morphology guided by phase separation, membranes frequently have large finger-like cavities, which are highly influenced by solution viscosity and will be discussed later.

5.3.3. Solution rheology

The viscosity of 16 wt% PES solutions in the different solvents and in different concentrations for solutions in [EMIM]DEP was investigated as a function of temperature; the results are shown in Figure 5.5a. The viscosity of 16 wt% PES solutions in [EMIM]DEP is up to 500–fold higher than in other solvents (NMP, DMAc or DMF) at room temperature (25 °C). An abrupt decrease is observed as the temperature increases. The viscosity values become similar as the temperature approaches 70 °C. The influence of concentration is directly related to the extent of entanglement between coils. Above the scaling critical concentration ($C^*$) the coils begin to entangle, entering the semi-diluted regime (Figure 5.5b, inset). $C^*$ can be estimated from values of the radius of gyration [155], $R_g$, using equation (8):

$$C^* = \frac{M}{\frac{4}{3} \pi N_A R_g^3}$$

where $M$ is the polymer molecular weight.
Figure 5.5. (a) Viscosity at shear rate 10 s⁻¹ as a function of temperature for PES/[EMIM]DEP solutions with different concentrations; the red curve corresponds to 16 wt% PES solutions in DMF, NMP or DMF, which are practically coincident at this scale; (b) Storage modulus $G'$ at 1 Hz and oscillation strain 10 % as a function of temperature for 8-16 wt% PES/[EMIM]DEP and 16 wt% PES/DMF solutions; curves for 16 wt% PES in NMP and DMAc coincide with that in DMF; inset: representation of polymer coils in solutions with concentrations below and above $C^*$; (c) $G''/G'$ ratios as a function of temperature measured at 1 Hz and oscillation strain 10 % for PES/[EMIM]DEP solutions with temperature range, the viscosity has a strong dependence on different concentrations and 16 wt% PES solutions in NMP, DMF, and DMAc.
The z-average diameters in **Table 5.1**, obtained by DLS, are a measure of the hydrodynamic diameters ($D_H = 2R_H$) of the polymer coils in different solvents. In theta solvents, $R_g = 0.77 R_H$, where $R_H$ is the hydrodynamic radius\[156\]. Therefore, $c^*$, for PES/[EMIM]DEP, could be estimated as being around 15.4 wt% (**Table 5.1**).

**Figure 5.5b** shows how the values of the storage modulus $G'$ changes as a function of temperature for solutions with different PES concentration in [EMIM]DEP. $G'$ is a measure of elasticity. The absolute values of $G'$ are higher for the 16 wt% PES solution than for 8 wt%. 16 wt% is above $c^*$. 8 wt % is far below $C^*$ and therefore with poor entanglement between coils. The ratio between the loss modulus $G''$ and $G'$, as a function of temperature, is shown in **Figure 5.5c**. It indicates the solution capacity to dissipate energy, behaving more like a liquid and less like a gel at high ratios. $G''/G'$ is particularly high for 16 wt% PES solutions in NMP and decreases in this sequence: NMP > DMAc ≥ DMF > [EMIM]DEP ($G''/G' = 193, 105, 79, 2$, respectively at 25 ºC). The gel character of PES solutions in [EMIM]DEP is therefore higher than in other solvents. As the temperature increases, the $G''/G'$ ratios for different solvents become more similar. 16 wt% PES solutions in NMP are also above $C^*$ (estimated as 10 wt% for PES in NMP in **Table 5.1**). However, NMP is a better solvent for PES than [EMIM]DEP with lower $\Delta G_m$. NMP acts as plasticizer, reducing the friction between polymer-polymer segments. This leads to low viscosity (**Figure 5.5a**) and low elasticity.

Membranes were prepared from 16 wt% PES solutions in different solvents and different concentrations in [EMIM]DEP. Their morphologies were investigated by field emission scanning electron microscopy (FESEM) and shown in **Figure 5.6**.
Membranes prepared from 16 wt% casting solutions in NMP, DMAc, and DMF have finger-like porous structures. Membranes cast from solutions in [EMIM]DEP are sponge-like, regardless of the polymer concentration (from 8 to 16 wt%, Figure 5.6 and 5.1S), different than in other solvents. Pores could be hardly observed (Figure 5.2S), even at high magnification when [EMIM]DEP was used as solvent. This morphology is favored by the high viscosity of the casting solution (20-550 Pa s, as seen in Figure 5.5a), which promotes a slow phase separation. When the water-ionic liquid exchange takes place, after immersion in the coagulation bath, the system might long remain metastable. Phases diluted in polymer do not evolve to form large pores. The ionic liquid diffuses into the bath and water comes into the polymer concentrated layer immobilizing the morphology as seen in the final membrane. With other solvents the solution viscosity is lower than 10 Pa s. Phase separation is fast (see Figure 5.4). By immersion in water, the system is quenched into the 2-phases region of the phase diagram. This favors pore formation by spinodal decomposition [157]. Moreover, high viscosity hinders the formation of finger-like cavities or macrovoids in solutions with ionic liquid. Macrovoids are caused by the abrupt intrusion of water into the solution layer, promoted by local instabilities of interface tension at the border between polymer solution and water. Low viscosity facilitates the uncontrolled water invasion [158-160]. Macrovoids are seen in Figure 5.6 for membranes prepared from solutions in NMP, DMAc and DMF, which have much lower viscosity than those in the ionic liquid.
Figure 5.6. FESEM images of membrane cross-sections: membranes prepared from 16 wt% PES solutions in [EMIM]DEP, NMP, DMAc, and DMF.

5.3.4. Membrane performance

The water permeances of the nanoporous membranes cast from PES/[EMIM]DEP solutions were measured and compared with membranes cast from solutions in NMP, DMAc and DMF. Although the pores of membranes fabricated from PES/[EMIM]DEP are smaller, their water permeance is higher than that of membranes cast from solutions in the other solvents, as shown in Figure 5.7a. The water permeances of the membranes fabricated from 16 wt%, 14 wt%, 12 wt%, and 8 wt% PES solutions in [EMIM]DEP were 20, 30, 65, and 140 L m$^{-2}$ h$^{-1}$ bar$^{-1}$. Comparing the membranes prepared with the same PES concentration (16
wt%) in different solvents, the permeances of those cast from solutions in [EMIM]DEP were 2 times higher than in NMP, 6-fold higher than in DMAc, and 20-fold higher than in DMF.

The membranes cast from PES/[EMIM]DEP solutions had nanosized pores. As shown in Figure 5.7b and Table 5.2S, the MWCO of membranes cast from 8, 12, 14, and 16 wt% PES solutions were 30, 5, 1.3, and 1.25 kg mol⁻¹, respectively. These values correspond to 5.2, 1.9, 0.9, and 0.88 nm solutes sizes respectively, as estimated using the Stokes radius equations (6) and (7). For comparison, membranes prepared from 16 wt% PES in NMP, DMAc and DMF are able to reject only larger solutes with the following sizes: 5.3, 5.1 and 5.5 nm. The pore size distribution estimated for different membranes is shown in Figure 5.7c, confirming that membranes prepared under comparable conditions using [EMIM]DEP had smaller pore sizes than when using NMP, DMAc or DMF.

The MWCO’s of the membranes prepared in this work were compared with PES membranes previously reported in the literature [161-174]. The MWCO-permeation trade-off plot is shown in Figure 5.8a. The membranes prepared from PES/[EMIM]DEP solutions are able to reject smaller solutes (1250 g mol⁻¹) than most other membranes, while keeping superior water permeance [13, 161-169, 171-174]. As a whole in the range of MWCO below 70 kg mol⁻¹ only one literature data on permeance (187 L m⁻² h⁻¹ bar⁻¹) is reported higher than in our case (for MWCO 10 kg mol⁻¹) [166], which resulted from optimization by non-solvent addition in the dope solution, using a short air gap.
Figure 5.7. (a) Water permeance as a function of time, measured for membranes prepared from PES/[EMIM]DEP solutions with different polymer concentrations and 16 wt% PES solutions in NMP, DMF, and DMAc; (b) PEG (and PEO) rejections for the same membrane.
Figure 5.8. (a) MWCO-permeation trade-off plot of the membranes fabricated in this study (in red) and membranes previously reported in the literature (Table 5.3S) and (b) BSA peptides rejection versus peptides molecular weight, measured with membranes cast from PES/[EMIM]DEP solutions with different polymer concentrations.
5.3.5. Peptides separation

The membranes cast from PES/[EMIM]DEP were applied in the separation of peptides with molecular weights ranging from 800 to 3500 g mol$^{-1}$. After peptide analyses by proteomics, the rejections were calculated. The peptide rejection for each membrane can be found in Figure 5.8b. All BSA peptides larger than 1150 g mol$^{-1}$ were rejected more than 95 % by the membrane cast from 16 wt% PES in [EMIM]DEP with MWCO 1250 g mol$^{-1}$ (estimated with PEG). Peptides with molecular weight larger than 2000 g mol$^{-1}$ were rejected almost 100 %. In the case of the membrane from 14 wt% PES, 95 % rejection of peptides with molecular weight 1450 g mol$^{-1}$ and 100 % rejection of peptides with size over 2050 g mol$^{-1}$ were measured. Membranes from 12 wt% and 8 wt% of PES had MWCO’s 5000 and 30 000 g mol$^{-1}$, respectively, and were able to reject even peptides slightly smaller than their measured MWCO’s. As a whole, their rejection of smaller peptides was lower than for membranes from 14 and 16 wt% PES. The membrane separation of charged solutes can be affected by size exclusion and Donnan exclusion effects. In nanofiltration (NF) membranes, the size exclusion effect is however predominant; Donnan exclusion effects are predominant in the separation of peptides with ultrafiltration (UF) membranes [175]. Membranes from 16 wt% and 14 wt% have MWCO’s of 1,250 and 1,300 g mol$^{-1}$. Separation by size exclusion might be the preferential mechanism in this case. However, membranes from 12 wt% and 8 wt% solutions have pores in the range of ultrafiltration and, might be more affected by Donnan exclusion effects. This might be one of the reasons why some peptides, which are smaller than the pre-estimated MWCO, could be rejected.
5.3.6. Recovery of [EMIM]DEP

We evaluated the possibility of recovery of ionic liquid from the membrane fabrication bath. The concentration of [EMIM]DEP in the all recovery steps is shown in Figure 5.9. The starting concentration of [EMIM]DEP in the waste solution was of 1.4 %. The solution was first concentrated by rotary evaporation, leading to the [EMIM]DEP concentration of 87.4 %. The additions of vacuum and heat increased the concentration to 95.5%. MgSO$_4$ was used to absorb the remaining water, leading to a final concentration of 99 %.

![Figure 5.9. Concentration of [EMIM]DEP at different steps of [EMIM]DEP recovery.](image-url)
5.4. Conclusion

We identified an ionic liquid that is able to completely dissolve PES. We propose the PES/[EMIM]DEP system for membrane manufacture by solution casting and immersion in water. The new process is fully absent of volatile solvents and therefore constitutes a new route for PES membrane manufacture. The process is environmentally friendly and healthier than classical membrane manufactures currently implemented in the industry, as long as a further step of ionic liquid recovery from the water bath could be provided. The proposed casting solution uses only chemicals accepted as non-hazardous and attend any criteria to keep the process out, for instance of the REACH list of concerned chemicals. The method guarantees the continuity of production of PES membranes even if future environmental policies would ban the currently used solvents, such as NMP, DMF, and DMAc, from industrial production.

We evaluated the thermodynamic conditions and the kinetics of phase separation for the new system. $\Delta G_m$ is positive, when estimated taking into account solubility parameters, but low enough to promote a homogeneous solution, while higher values were calculated for PSU/[EMIM]DEP. The viscosity and G’ are higher than for PES solutions in NMP, DMF and DMAc. The values are highly dependent of concentration in the range of 8 to 16 wt%, which is relevant for membrane fabrication. Nanoporous sponge-like membranes with unusually fine structure were obtained. By controlling the polymer concentration, membranes with MWCO’s of 30, 5, 1.3, and 1.25 kg mol$^{-1}$ were obtained with high water permeance. The membranes were applied in the separation of a peptide mixture with molecular
weights in the range of 800 to 3500 g mol\(^{-1}\), which could be effectively separated. Now concerning recycling, the ionic liquid could be recovered from the membrane fabrication bath, by simple steps, based on evaporation. The new manufacturing process is not only environmentally advantageous, but leads to PES membranes with performance characteristics that were previously not available.
Chapter 6. Polyethersulfone (PES) flat sheet and hollow fiber membranes from solutions in ionic liquids

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6.1. Introduction

Polyethersulfone (PES) is an excellent material for membrane fabrication with broad application for instance in desalination, biomedical devices and water treatment [176]. PES membranes have been playing an important role in purification of biotechnology products [128], such as typical proteins, peptides, and DNA, pharmaceutical products [177], food [129], daily [178], and water [130, 131]. 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 [65]. Alternatives to replace these solvents are needed [6]. A few candidates are under consideration as greener solvents, such as supercritical fluids and ionic liquids [33, 179]. 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 [21, 33].

Many studies of cellulose dissolution in ionic liquid have been investigated [53-56]. The use of ionic liquids for membrane manufacture is still relatively restricted. Examples
are: 1-ethyl-3-methylimidazolium acetate [EMIM]OAc for polybenzimidazole [61],
cellulose acetate (CA) [63], cellulose [64], and polyacrylonitrile [65]; 1-ethyl (or butyl)-3-
methylimidazolium thiocyanate ([EMIM]SCN and [BMIM]SCN) for CA [46, 66].
Recently we reported the fabrication of PES flat-sheet membranes using 1-ethyl-3-
methylimidazolium diethylphosphate ([EMIM]DEP) [67]. 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 [101]. 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. [66]
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
[63] and polyacrylonitrile (PAN)/[EMIM]OAc/co-solvent [65]. 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.
6.2. Methodology

6.2.1. 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, ≥ 98.0 %), 1, 3-dimethyl- imidazolium dimethylphosphate ([MMIM]DMP), and dimethyl formamide (DMF, ≥ 99.8 %) were supplied by Sigma-Aldrich. Polymers and ionic liquids used in this study are illustrated in Figure 6.1. 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.

6.2.2. Density functional theory (DFT) calculation

All quantum chemical calculations employ the Gaussian 09 software package [180]. Structures are optimized with the M062X hybrid meta exchange-correlation functional [181] using a 6-31G* basis set. The interaction energy between polymer and ionic liquid is calculated as:

\[ E_{\text{int}} = E_{\text{polymer+IL}} - (E_{\text{polymer}}+E_{\text{IL}}), \]  

with \( E_{\text{polymer+IL}}, E_{\text{polymer}}, \) and \( E_{\text{IL}} \) 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 [182].

![Chemical structures](image)

Figure 6.1. Chemical structures of (a) PES, (b) PSf, (c) [EMIM]DEP, and (d) [MMIM]DMP.

6.2.3. Experimental polymer solution characterization

6.2.3.1. 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):

\[
\eta = \lim_{c \to 0} \left( \frac{\eta_{rel}}{c} - 1 \right) = \lim_{c \to 0} \eta_{red}
\]

where, \( \eta_{rel} \) is the relative viscosity (defined as \( \eta_{rel} = \) polymer solution dynamic viscosity / solvent dynamic viscosity), \( \eta_{red} \) 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) [183]:

\[
C^* = \frac{1}{[\eta]}
\]

\[
C^* = \frac{4}{3} \frac{M}{\pi N_A R_g^3}
\]

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 x 10\(^{23}\) 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.
6.2.3.2. 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.

6.2.4. Membrane fabrication

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 ºC under the pressure of 2 bars. The polymer solutions were spun with the spinning conditions listed in Table 6.1 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 6.1. Spinning conditions for hollow fiber membranes**

<table>
<thead>
<tr>
<th>Sample code</th>
<th>18PES/DMF-2/25</th>
<th>12PES/IL-2/70</th>
<th>12PES/IL-5/70</th>
<th>12PES/IL-5/90</th>
<th>12PES/IL-30/90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope solution composition (wt%)</td>
<td>18 wt% PES/DMF</td>
<td>12 wt% PES/[EMIM]DEP</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition of bore fluid (wt%)</td>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coagulant bath</td>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air gap (cm)</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Flow rate of dope solution (ml/min)</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow rate of inner coagulant (ml/min)</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Take up speed (m/min)</td>
<td>Free fall</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of the dope solutions (°C)</td>
<td>25</td>
<td>70</td>
<td>70</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Temperature of the bore fluid and the coagulant bath (°C)</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.2.5. 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:

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

where \( Q \) is the permeated pure water rate (L h\(^{-1}\)), \( A \) is the effective membrane area (m\(^2\)), and \( \Delta P \) 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):

\[
\text{PEG rejection, } R \text{ (\%)} = (1 - \frac{C_{\text{perm}}}{C_{\text{feed}}}) \times 100 \%
\]
where \( C_{\text{perm}} \) and \( C_{\text{feed}} \) 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 [125, 150]:

For PEG

\[
r = 16.73 \times 10^{-10} M^{0.557}
\]

(8)

For PEO

\[
r = 10.44 \times 10^{-10} M^{0.587}
\]

(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).

\[
F(R) = A + B (\ln d)
\]

(10)

\[
\frac{\partial R(d_p)}{\partial d_p} = \frac{1}{d_p \ln \sigma_p} \exp \left[ \frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right]
\]

(11)

where \( \mu_p \) is the mean effective pore size diameter at \( R = 50 \% \) and \( \sigma_p \) 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 [126] and ignoring the deformation of macromolecules under pressure and shear rate in the solution [127]. 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 \( R = 90 \% \).
6.2.6. 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).

6.2.7. 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.

6.3 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 6.1, 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 the total energy (or electron) distribution and result in not being miscible with ionic liquids which have electrostatic force such as strong hydrogen force and Coulombic force.
6.3.1. 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 6.2), which then are used for further analysis. For the monomers, the interaction energy turns out to be -13.1 kcal mol\(^{-1}\) for PES1/[EMIM]DEP and -5.4 kcal mol\(^{-1}\) for PSf1/[EMIM]DEP, while for the dimers it is -13.1 kcal mol\(^{-1}\) for PES2/[EMIM]DEP and -7.9 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 kcal mol\(^{-1}\), respectively, and that for the PSf monomer and dimer to -8.3 and -6.9 kcal mol\(^{-1}\). To understand the nature of the interaction, the energy contributions are decomposed in each case, see the results given in Table 6.2. 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.
Figure 6.2. Lowest energy structures of monomers (PES1 and PSf1) and dimers (PES2 and PSf2) surrounded by ionic liquid cations and anions: (a) [EMIM]+ and DEP– and (b) [MMIM]+ and DMP–.
Table 6.2. Energy decomposition analysis.

<table>
<thead>
<tr>
<th>Polymer/ Ionic liquid</th>
<th>E_{int}</th>
<th>E_{elec}</th>
<th>E_{dispersion}</th>
<th>E_{induction}</th>
<th>E_{exchange}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES1/[EMIM]DEP</td>
<td>-13.1</td>
<td>-33.6</td>
<td>-11.9</td>
<td>-16.4</td>
<td>46.9</td>
</tr>
<tr>
<td>PES2/[EMIM]DEP</td>
<td>-13.1</td>
<td>-24.3</td>
<td>-16.1</td>
<td>-7.9</td>
<td>34.2</td>
</tr>
<tr>
<td>PSf1/[EMIM]DEP</td>
<td>-5.4</td>
<td>-11.5</td>
<td>-8.2</td>
<td>-4.3</td>
<td>17.9</td>
</tr>
<tr>
<td>PSf2/[EMIM]DEP</td>
<td>-7.3</td>
<td>-14.9</td>
<td>-14.4</td>
<td>-5.4</td>
<td>26.4</td>
</tr>
<tr>
<td>PES1/[MMIM]DMP</td>
<td>-15.5</td>
<td>-36.8</td>
<td>-9.6</td>
<td>-18.0</td>
<td>46.1</td>
</tr>
<tr>
<td>PES2/[MMIM]DMP</td>
<td>-20.8</td>
<td>-37.7</td>
<td>-20.0</td>
<td>-10.8</td>
<td>46.5</td>
</tr>
<tr>
<td>PSf1/[MMIM]DMP</td>
<td>-8.3</td>
<td>-17.0</td>
<td>-12.6</td>
<td>-6.5</td>
<td>26.8</td>
</tr>
<tr>
<td>PSf2/[MMIM]DMP</td>
<td>-6.9</td>
<td>-16.9</td>
<td>-12.2</td>
<td>-4.8</td>
<td>26.1</td>
</tr>
</tbody>
</table>

6.3.2. Polymer solutions characterization

6.3.2.1. 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 6.3). 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 ≥ PES/[EMIM]DEP ≥ 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.
6.3.2.2. Phase diagram (ternary system, polymer/solvents/water)

Figure 6.3 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 ≈ PES/[EMIM]DEP ≤ PES/DMF.

Table 6.3. Intrinsic viscosity ([η]), entanglement concentration (C*), radius of gyration (Rg), hydrodynamic diameter obtained from the intrinsic viscosity (Dh([η]−1)) and DLS (Dh(DLS)), and solvent density.

<table>
<thead>
<tr>
<th>PES/solvents</th>
<th>Intrinsic viscosity ([η])</th>
<th>C*</th>
<th>Rg</th>
<th>Rh</th>
<th>Dh</th>
<th>Dh(DLS)</th>
<th>Solvent density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm³/g)</td>
<td>(g/cm³)</td>
<td>(nm)</td>
<td>(nm)</td>
<td>(nm)</td>
<td>(nm)</td>
<td></td>
</tr>
<tr>
<td>[EMIM]DEP</td>
<td>58.5</td>
<td>0.017</td>
<td>12.0</td>
<td>15.6</td>
<td>31.2</td>
<td>15.1</td>
<td>1.1458</td>
</tr>
<tr>
<td>[MMIM]DMP</td>
<td>96.4</td>
<td>0.010</td>
<td>14.2</td>
<td>18.5</td>
<td>36.9</td>
<td>18.2</td>
<td>1.2532</td>
</tr>
<tr>
<td>DMF</td>
<td>52.0</td>
<td>41.6 b</td>
<td>0.019</td>
<td>11.6</td>
<td>15.0</td>
<td>30.0</td>
<td>13.1</td>
</tr>
</tbody>
</table>

---

a Measured for PES (Mw = 75 kg mol⁻¹) at 25 ºC
b Measured for PES (Mw = 70 kg mol⁻¹) at 23 ºC; [η] = 63.3 cm³/g (Mw = 113 kg mol⁻¹)
c Measured by DLS (Dh(DLS)) at 25 ºC
d Measured with a pycnometer at 22± 1 ºC
6.3.2.3. 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 6.4. 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 (\( R_{hyd} = \frac{8\eta LQ}{\pi r^4} \)) [185] in non-ideal fluid dynamics, the hydraulic resistance (\( R_{hyd} \), the pressure drop) in a tube is proportional to viscosity (\( \eta \)). Thus, the
hydraulic resistance can be reduced up to 200 times (8 × 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 (\( \eta \)) and solvent (\( \eta_0 \)) is shown in Figure 6.4b and Table 6.4. The normalization discounts the pure solvent contribution. At 25 ºC 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 6.3 PES in [MMIM]DMP starts to entangle from \( C^* \) equal to 0.01 g/cm\(^3\) (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 6.4](image)

**Figure 6.4.** (a) Viscosity of polymer solutions at different temperatures and (b) ratios between solution and the solvent viscosities.
Table 6.4. Table 6.4. Viscosity of concentrated PES solutions ($\eta$) and solvents ($\eta_0$) and their ratios at 25 ºC.

<table>
<thead>
<tr>
<th>PES concentration (wt %)</th>
<th>Solvents</th>
<th>$\eta$ (Pa.s)</th>
<th>$\eta_0$ (Pa.s)</th>
<th>$\eta / \eta_0$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>[EMIM]DEP</td>
<td>97.1</td>
<td>0.384</td>
<td>250</td>
</tr>
<tr>
<td>12</td>
<td>[MMIM]DMP</td>
<td>59.7</td>
<td>0.189</td>
<td>320</td>
</tr>
<tr>
<td>12</td>
<td>DMF</td>
<td>0.1</td>
<td>0.00077</td>
<td>130</td>
</tr>
<tr>
<td>16</td>
<td>DMF</td>
<td>0.3</td>
<td>0.00077</td>
<td>390</td>
</tr>
<tr>
<td>18</td>
<td>DMF</td>
<td>0.6</td>
<td>0.00077</td>
<td>780</td>
</tr>
</tbody>
</table>

6.3.3. Flat sheet membranes characterization

Figure 6.5 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 6.5. 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 6.5 and Figure 6.6. When [EMIM]DEP and [MMIM]DMP were the used solvents, the membranes water permeances were 55 and 43 Lm⁻²h⁻¹bar⁻¹, respectively. In Figure 6.6 and Table 6.5, 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 6.6b shows that when using [EMIM]DEP, membranes with particularly narrow pore size distribution are obtained, with a mean pore size around 2 nm.

After analyzing the PEG rejection results of Table 6.5, 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 6.6. 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. 100 % DNA with 6366 g mol⁻¹ molecular weight was removed by membranes prepared from solutions in ionic liquids.
Figure 6.6. (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 6.5. Performance of flat-sheet membranes prepared from 12 wt% PES solutions in different solvents; measurements at 2 bar and 25 °C.

<table>
<thead>
<tr>
<th>Casting solvent</th>
<th>Water permeance</th>
<th>PEG rejection (%)</th>
<th>MWCO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.3</td>
<td>1.5</td>
</tr>
<tr>
<td>[EMIM]DEP</td>
<td>55 ± 5</td>
<td>16.7</td>
<td>40.9</td>
</tr>
<tr>
<td>[MMIM]DMP</td>
<td>43 ± 3</td>
<td>7.5</td>
<td>17.9</td>
</tr>
<tr>
<td>DMF</td>
<td>135 ± 5</td>
<td>17.2</td>
<td>32.8</td>
</tr>
</tbody>
</table>

*Units for water permeance (Lm$^{-2}$h$^{-1}$bar$^{-1}$) and molecular weight and MWCO (kg mol$^{-1}$)
Table 6.6. DNA separation by flat sheet membranes.

<table>
<thead>
<tr>
<th></th>
<th>Rejection (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DNA</td>
<td>DNA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(M&lt;sub&gt;w&lt;/sub&gt; = 3153 g mol&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>(M&lt;sub&gt;w&lt;/sub&gt; = 6366 g mol&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td></td>
</tr>
<tr>
<td>12 wt% PES/[EMIM]DEP</td>
<td>98.8</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>12 wt% PES/[MMIM]DMP</td>
<td>92.2</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>12 wt% PES/DMF</td>
<td>7.0</td>
<td>27.2</td>
<td></td>
</tr>
</tbody>
</table>

6.3.4. 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 6.7. On the other hand, 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 6.7. 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 6.7 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 6.7 and Figure 6.1S. 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 6.1S).
Figure 6.7. Morphology of manufactured hollow fiber membranes.
Table 6.7. Summary of hollow fiber preparation conditions and resulting dimensions.

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

The pure water permeance of all hollow fiber membranes is summarized in Table 6.8. 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 6.7, the pure water permeance was increased from 22.4 to 45.8 Lm⁻²h⁻¹bar⁻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 6.8 and Table 6.8. 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 6.8, 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 6.8. The rejection values were higher, when measured with the PEG mixture. Especially, the difference of the PEG rejection between the single PEGs and PEG mixtures was 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.

![Graph showing PEG rejection and pore distribution](image)

**Figure 6.8.** PEG rejection and the pore distribution of tested hollow fiber membranes.
**Table 6.8.** 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.

<table>
<thead>
<tr>
<th>Hollow fibers</th>
<th>Water permeance</th>
<th>PEG rejection (%) (mixture / single)</th>
<th>MWCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>18PES/D MF-2/25</td>
<td>87.6</td>
<td>18 / - 33 / - - / 7 79 / 14 88 / -</td>
<td>100 / 11 / 37</td>
</tr>
<tr>
<td>12PES/IL-2/70</td>
<td>22.4</td>
<td>51 / - 94 / 72 - / 89 100 / 96</td>
<td>1.4 / 3.5</td>
</tr>
<tr>
<td>12PES/IL-5/70</td>
<td>17.8</td>
<td>45 / - 98 / 82 - / 94 100 / 96</td>
<td>1.3 / 2.5</td>
</tr>
<tr>
<td>12PES/IL-5/90</td>
<td>25.9</td>
<td>48 / - 94 / 77 - / 87 100 / 96</td>
<td>1.4 / 3.9</td>
</tr>
<tr>
<td>12PES/IL-30/90</td>
<td>45.8</td>
<td>37 / - 95 / 11 - / 34 100 / 97</td>
<td>1.4 / 5.7</td>
</tr>
</tbody>
</table>

*Units for water permeance (Lm⁻²h⁻¹bar⁻¹) and molecular weight and MWCO (kg mol⁻¹)*

**Table 6.9** 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 further application.
Table 6.9. Membrane mechanical properties.

<table>
<thead>
<tr>
<th>PES solutions</th>
<th>Mechanical strength</th>
<th></th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tensile strength at break (MPa)</td>
<td>Elongation at break (%)</td>
<td></td>
</tr>
<tr>
<td>Flat sheet</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 wt% PES/[EMIM]DEP</td>
<td>2.2</td>
<td>18</td>
<td>0.4</td>
</tr>
<tr>
<td>12 wt% PES/[MMIM]DMP</td>
<td>1.8</td>
<td>13</td>
<td>0.2</td>
</tr>
<tr>
<td>12 wt% PES/DMF</td>
<td>3.5</td>
<td>65</td>
<td>0.8</td>
</tr>
<tr>
<td>18 wt% PES/DMF</td>
<td>7.0</td>
<td>131</td>
<td>1.5</td>
</tr>
<tr>
<td>Hollow fiber</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18PES/DMF-2/25</td>
<td>6.0</td>
<td>84</td>
<td>1.4</td>
</tr>
<tr>
<td>12PES/IL-2/70</td>
<td>2.3</td>
<td>40</td>
<td>0.3</td>
</tr>
<tr>
<td>12PES/IL-5/70</td>
<td>3.0</td>
<td>46</td>
<td>0.3</td>
</tr>
<tr>
<td>12PES/IL-5/90</td>
<td>4.0</td>
<td>51</td>
<td>0.5</td>
</tr>
<tr>
<td>12PES/IL-30/90</td>
<td>2.8</td>
<td>25</td>
<td>0.4</td>
</tr>
</tbody>
</table>

6.4. 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 $\text{PES}/[\text{MMIM}]\text{DMP} \geq \text{PES}/[\text{EMIM}]\text{DEP} \geq \text{PES}/\text{DMF}$. It is consistent with the results of DFT calculation. From the thermodynamic point of view, the ionic liquids, $[\text{MMIM}]\text{DMP}$ and $[\text{EMIM}]\text{DEP}$, are better solvents for PES than DMF.

(3) The polymer solutions in $[\text{MMIM}]\text{DMP}$ and $[\text{EMIM}]\text{DEP}$ 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 $[\text{EMIM}]\text{DEP}$ and $[\text{MMIM}]\text{DMP}$ 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 $[\text{EMIM}]\text{DEP}$ and $[\text{MMIM}]\text{DMP}$ 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/$[\text{EMIM}]\text{DEP}$ and 12 wt% PES/$[\text{MMIM}]\text{DMP}$, respectively. DNA with 6366 g mol$^{-1}$ was completely removed by membranes prepared from solutions in ionic liquids.
Chapter 7. Poly (ether imide sulfone) membranes from solutions in ionic liquids

This chapter was submitted as: DooLi Kim and Suzana P. Nunes, *Journal of polymer science A: polymer chemistry*, 2017

7.1. Introduction

Membrane technology has been used in various fields such as biomedical separations [186-189], desalination [190], wastewater treatment [191], and energy conversion [192-194]. 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 processes. 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) [4, 5, 123, 124].

Ionic liquids can be considered as green solvents [179] from a perspective of no generation of harmful volatile organic chemicals (VOCs) [33]. Research on ionic liquids as green solvents for polymer dissolution has increased, especially since the confirmation that they can dissolve biopolymers, such as cellulose [54, 74, 195] and chitin [196], which are hardly dissolved in any other organic solvent. They have been reported for production of biofuel and for membrane fabrication [63, 64, 66]. The use of ionic liquids to dissolve
synthetic polymers with sulfone or imide groups and their use for membrane fabrication have been gradually reported [61, 67]. Ionic liquids have been also used as additives in polymer solutions [65, 78].

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. [197] and Peng et al. [198] as hollow fiber membranes for gas separation. Jalal et al. [170] fabricated EXTEM™ ultrafiltration membranes for liquid separation. Recently Mazinani et al. [199] 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 to use of ionic liquids for EXTEM™ solubilization and membrane preparation. Interestingly, we found out that high concentration 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.
7.2. Methodology

7.2.1. 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 Figure 7.1S. [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 7.1. 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 \(\gamma\)-globulin (~140 kg mol\(^{-1}\)) were supplied from Sigma-Aldrich.

![Chemical structures](image)

**Figure 7.1.** Chemical structures of (a) EXTEM™, (b) [EMIM]SCN, (c) [BMIM]SCN, and (d) [EMIM]OAc.
7.2.2. Polymer solution thermodynamics

7.2.2.1. The Gibbs free energy of mixing ($\Delta G_m$)

For non-charged organic solvents $\Delta G_m$ can be calculated from solubility parameters ($\delta$) and Flory-Huggins parameters ($\chi$), 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 mixture [68]. If $\Delta G_m$ is negative, the polymer solubility is favored in the specific solvent. In contrast, if $\Delta G_m$ is significantly higher than zero, the mixture is unlikely to be homogenous. According to the Flory–Huggins theory, $\Delta G_m$ can be estimated by the following equation [79]:

$$
\frac{\Delta G_m}{N_A} = kT \left[ \chi \phi_1 \phi_2 + \frac{\phi_i}{x_i} \ln \phi_i + \frac{\phi_j}{x_j} \ln \phi_j \right]
$$

(1)

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

$$
\chi_{ij} = \frac{V_i \delta_i \delta_j^{1/2}}{RT} + 0.34
$$

(2)

where $V_i$ is the molar volume of the solvent (cm$^3$ mol$^{-1}$), $R$ is the ideal gas constant (cm$^3$ MPa K$^{-1}$ mol$^{-1}$). The value of 0.34 is an empirical constant absent in the original theory and later introduced for polymer systems [80-83]. $\delta$ is the solubility parameter of the solvent i and polymer j (MPa$^{1/2}$).
Few studies have attempted to calculate the δ of ionic liquids [91, 145, 146, 200, 201]. Here the δ values of EXTEM™, [EMIM]SCN, and [BMIM]SCN were determined using the HSPiP [82] 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 parameters [82] were computed by the software. The total solubility parameters (δ) were then calculated by the following equation:

\[ \delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \]  

(3)

The δ contributions for [EMIM]OAc were previously reported [63, 67].

7.2.3. Polymer solutions characterization

7.2.3.1. Diluted polymer solutions

In the cases of homogenous polymer solutions, larger polymer coils indicate higher solubility. From the intrinsic viscosity ([η]), the size of the polymer coils was estimated. To measure [η], 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 using an Ubbelohde viscometer (Lauda iVisc). [η] can be calculated by equation 4:

\[ [\eta] = \lim_{c \to 0} \left( \frac{\eta_{rel} - 1}{c} \right) = \lim_{c \to 0} \eta_{red} \]  

(4)
where \( \eta_{\text{rel}} \) is the relative viscosity (defined as \( \eta_{\text{rel}} = \text{dynamic viscosity} / \text{solvent viscosity} \)), 
\( \eta_{\text{red}} \) is the reduced viscosity (defined as \( \eta_{\text{red}} = (\eta_{\text{rel}} - 1) / C \)), 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):

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

\( C^* \) is related to \( R_g \) by equation 6:

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

where \( M \) is the molecular weight of EXTEM\textsuperscript{TM}, \( N_A \) is the Avogadro number (6.022 x 10\textsuperscript{23} mol\textsuperscript{-1}), respectively. From \( R_g \), the hydrodynamic radius (\( R_h \)) and diameter (\( D_h \)) can be estimated (\( R_h = 0.77 R_g \)) [156]. \( D_h \) 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\textsuperscript{TM} 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\textsubscript{4}) vapor for 3 hours.

7.2.3.2. Semi-diluted polymer solutions

The rheology of EXTEM\textsuperscript{TM} solutions was investigated using a AR1500ex Rheometer, TA Instruments, at shear rate of 10 s\textsuperscript{-1} in the temperature range of 25 to 90 °C.
7.2.3.3. Cloud point and phase diagrams

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.

7.2.3.4. Kinetics of phase separation

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) [66] using a Cary 5000 UV-Vis-NIR, Agilent. The relative light transmittance \( T_r \) was determined by equation 7.[63, 67]

\[
T_r = \frac{(T - T_{\text{min}})}{(T_{\text{max}} - T_{\text{min}})} \times 100\%
\]  

(7)

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

7.2.4. 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 into deionized water 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 samples were prepared by freeze-dry to avoid pore collapse. The membrane samples were fractured in liquid nitrogen, and then coated by iridium for cross-sectional images.

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

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

where $Q$ is the water flux (L/h), $A$ is the effective membrane area ($m^2$), and $\Delta P$ 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:

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

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

The solute diameter was calculated by the following Stokes radius equation 10 and 11 [125, 126]:

For PEG

$$r = 16.73 \times 10^{-10} M^{0.557}$$  \hspace{1cm} (10)
For PEO

\[ r = 10.44 \times 10^{-10} M^{0.587} \]  

(11)

where \( r \) is the Stokes radius (cm), and \( M \) is the molecular weight (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 \( \mu_p \) is the mean effective pore diameter at \( R = 50 \% \). \( \sigma_p \) 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 [126] and ignoring the deformation of macromolecules under pressure and shear rate in the solution [127]. The molecular weight cut-off (MWCO, \( R = 90 \% \)) was calculated by equation 12.

7.2.5. Proteins and DNA separation

Water permeance and rejection of all membranes were examined by filtration of DNA, BSA, and \( \gamma \)-globulin solutions (1 g mL\(^{-1}\)) through the membranes, using a dead-end ultrafiltration set-up (Amicon cell). The feed solutions for BSA, and \( \gamma \)-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 rejection 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).
7.3. Results

7.3.1. Binary polymer solutions in ionic liquids

7.3.1.1. Solubility parameters

The difference between solubility parameters is a first indication of potential solvents for EXTEM™. Table 7.1 shows the solubility parameters of all components used in this study and the polymer-solvent difference. The solubility of EXTEM™ in different solvents would then decrease in the following order: DMF > [BMIM]SCN > [EMIM]OAc > [EMIM]SCN.

Table 7.1. Solubility parameters of the polymer and solvents used in this study.

|                  | δ_D | δ_P | δ_H | δ (MPa^1/2) | |δEXTEM™ - δSolvent|
|------------------|-----|-----|-----|-------------|----------------|
| EXTEM™^a         | 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        |                |

^aCalculated using HSPiP and ^bfrom Ref.[82]

7.3.1.2. Gibbs free energy of mixing

Values of Gibbs free energy of mixing (ΔG), which are calculated using Flory-Huggins parameters estimated from solubility parameters, are illustrated in Figure 7.2. Values close to zero or below are indication of homogeneous systems. The ΔG for EXTEM™/[BMIM]SCN and DMF was below zero. It denotes that the EXTEM™
solutions in [BMIM]SCN and DMF are thermodynamically stable and homogenous. In case of EXTEM™/[EMIM]OAc and EXTEM™/[EMIM]SCN, the values of $\Delta G$ were positive, but not far from zero, still enough for solubilization. EXTEM™ 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 ionic liquids. By increasing temperature from 25 to 90 °C, all $\Delta G$ values slightly decreased, following equation 2 for $\chi$. As the temperature increases, $\chi$ decreases and the interaction between polymers and solvents increases (lower $\Delta G$).

Figure 7.2. $\Delta G$ estimation for EXTEM™ in different ionic liquids at 25 (dash lines) and 90 °C (solid lines).
7.3.1.3. Polymer coil size in diluted solutions

Intrinsic viscosity ([η]) leads to the calculation of molecular weight and coil size. The respective values for EXTEM™ in different solvents are shown in Table 7.1S and Table 7.2. The values of [η] for EXTEM™ decreases in the following order: [BMIM]SCN > [EMIM]OAc > DMF > [EMIM]SCN and the hydrodynamic diameter (Dh) calculated from [η] was consistent with the Dh calculated from TEM images shown in Figure 7.3 and Table 7.2. Interestingly, micellized EXTEM™ polymer coils were observed from homogenously dissolved EXTEM™ polymer solutions in different ionic liquids by TEM Because of that, the hydrodynamic diameter could be measured and calculated from the TES images as depicted in Figure 7.3.

Table 7.2. Critical concentration (C*) and the radius of gyration (Rg) calculated from [η] of all diluted polymer solutions and TEM.

<table>
<thead>
<tr>
<th>EXTEM™/solvents</th>
<th>[η] (cm³/g)</th>
<th>C* (g/cm³)</th>
<th>Rg (nm)</th>
<th>Rh (nm)</th>
<th>Dh (nm)</th>
<th>Dhm (nm)</th>
<th>Solvent density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXTEM™/[EMIM]SCN</td>
<td>18.5</td>
<td>0.054</td>
<td>9</td>
<td>11</td>
<td>22</td>
<td>18</td>
<td>1.1181</td>
</tr>
<tr>
<td>EXTEM™/[EMIM]OAc</td>
<td>39.9</td>
<td>0.025</td>
<td>11</td>
<td>15</td>
<td>29</td>
<td>31</td>
<td>1.0992</td>
</tr>
<tr>
<td>EXTEM™/[BMIM]SCN</td>
<td>52.5</td>
<td>0.019</td>
<td>12</td>
<td>16</td>
<td>32</td>
<td>47</td>
<td>1.0707</td>
</tr>
<tr>
<td>EXTEM™/DMF</td>
<td>33.7</td>
<td>0.030</td>
<td>11</td>
<td>14</td>
<td>27</td>
<td>-</td>
<td>0.9474</td>
</tr>
</tbody>
</table>

*a Estimated from viscosity measurements; b Estimated from TEM images; c Measured at room temperature (22 ± 1 °C)
3.2. Rheology of semi-diluted polymer solutions

The viscoelastic properties of all EXTEM™ solutions were studied and illustrated in Figure 7.4. To fabricate membranes and understand the membrane structure, the viscoelastic properties are important, especially for semi-crystalline polymers, such as EXTEM™. X-ray diffraction (XRD) in Figure 7.1S shows a strong crystalline peak at 21.5 degrees. Figure 7.4a shows that 20 wt% EXTEM™ solutions in [EMIM]SCN and [EMIM]OAc have the highest viscosities. When the total viscosity is normalized by the solvent one (\( \eta / \eta_0 \)) as shown in Figure 7.4b, we see that the main contribution to the high viscosity of the EXTEM™ solution in [EMIM]OAc is the solvent viscosity itself. For the 20 wt% EXTEM™ 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 EXTEM™ 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 7.4d** 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 EXTEM™. 20 wt% solutions 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.

### 7.3.3. Ternary Phase diagram

The phase diagrams of different EXTEM™/solvent/water systems in **Figure 7.5** were obtained by measuring their cloud points. The 2 phases region of the diagram increases in the following order: \(\text{EXTEM}^{\text{TM}}/\text{[EMIM]}\text{OAc} < \text{EXTEM}^{\text{TM}}/\text{[BMIM]}\text{SCN} \approx \text{EXTEM}^{\text{TM}}/\text{DMF} < \text{EXTEM}^{\text{TM}}/\text{[EMIM]}\text{SCN}\). The marked points were obtained by adding water until the turbidity starts. The cloud points for the \(\text{EXTEM}^{\text{TM}}/\text{[EMIM]}\text{OAc}\) system were hardly detected, due to low turbidity.

The values of \([\eta]\) and \(D_h\) for binary EXTEM™/solvent systems increase in the following order: \(\text{EXTEM}^{\text{TM}}/\text{[EMIM]}\text{SCN} < \text{EXTEM}^{\text{TM}}/\text{DMF} < \text{EXTEM}^{\text{TM}}/\text{[EMIM]}\text{OAc} < \text{EXTEM}^{\text{TM}}/\text{[BMIM]}\text{SCN}\), which corresponds to the order of increasing solvent quality and is consistent with the result of the ternary phase diagram.
Figure 7.4. 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 (δ) at shear rate of 20 s⁻¹.
Figure 7.5. Phase diagram of EXTEM™ solutions using water as a non-solvent at room temperature.

7.3.4. Kinetics of phase separation

The non-solvent induced phase separation of EXTEM™ 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 7.6. The phase separation for membranes prepared from solutions in ionic liquids is slow. 20 wt% EXTEM™ solutions in [BMIM]SCN and [EMIM]OAc becomes turbid after 50 and 25 s, respectively. The turbidity reaches its maximum only after 40 (EXTEM™/[EMIM]SCN), 75 (EXTEM™/[BMIM]SCN, and 50 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. The 20 wt% EXTEM™/DMF system becomes turbid 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). An important factor in determining the kinetics of phase separation, leading to SD or NG, might be the solution viscosity. As shown in Figure 7.4, solutions in ionic liquid have significantly higher viscosity than in DMF.

![Figure 7.4](image)

**Figure 7.4.** Kinetics of phase separation of EXTEM™ solutions cast on a glass plate and immersed in water.

### 7.3.5. Membrane characterization

The membranes fabricated from EXTEM™/[EMIM]SCN solutions have sponge-like structure with fine pores, promoted by NG mechanism. In contrast, the finger-like cavities can be seen in membranes prepared in DMF. The cavities resulted from 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. 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, the membranes prepared from these ionic liquids were very brittle with low elasticity (Figure 7.4), which might be caused by crystallinity (Figure 7.1S). They were not further characterized in terms of pore size, separation performance and permeance.

![Cross-sectional and surface morphologies](image)

Figure 7.7. 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.
All membranes prepared from the solution 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 7.8 and Table 7.3. 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.

The PEG rejection of the ionic liquid based membranes was higher in all range of molecular weight of PEG than that of membranes fabricated from DMF.

Figure 7.8. (a) Water permeance and (b) PEG rejection of different membranes.
### Table 7.3. Water permeance and MWCO of EXTEM™ membranes.

<table>
<thead>
<tr>
<th>EXTEM™ Membranes</th>
<th>Water permeance (L m⁻² h⁻¹ bar⁻¹)</th>
<th>MWCO (kg mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% in [EMIM]SCN</td>
<td>230 ± 20</td>
<td>7.3</td>
</tr>
<tr>
<td>22 wt% in [EMIM]SCN</td>
<td>120 ± 20</td>
<td>5.2</td>
</tr>
<tr>
<td>24 wt% in [EMIM]SCN</td>
<td>90 ± 10</td>
<td>5.3</td>
</tr>
<tr>
<td>20 wt% in DMF</td>
<td>170 ± 15</td>
<td>9.7</td>
</tr>
<tr>
<td>24 wt% in DMF</td>
<td>3 ± 2</td>
<td>5.3</td>
</tr>
</tbody>
</table>

### 7.3.6. DNA and protein separation

All membranes rejected more than 97 and 99 % of BSA and γ-Globulin, respectively (Table 7.4). 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.

### Table 7.4. Results of DNA and protein separation.

<table>
<thead>
<tr>
<th>EXTEM™ Membranes</th>
<th>DNA (Mw = 3.4 kg mol⁻¹)</th>
<th>DNA (Mw = 6.4 kg mol⁻¹)</th>
<th>BSA (Mn = ~69 kg mol⁻¹)</th>
<th>γ-Globulin (Mn = ~140 kg mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt% in [EMIM]SCN</td>
<td>-</td>
<td>-</td>
<td>97.7</td>
<td>99.4</td>
</tr>
<tr>
<td>22 wt% in [EMIM]SCN</td>
<td>84.4</td>
<td>94.1</td>
<td>98.3</td>
<td>99.7</td>
</tr>
<tr>
<td>24 wt% in [EMIM]SCN</td>
<td>92.7</td>
<td>93.1</td>
<td>98.1</td>
<td>99.2</td>
</tr>
<tr>
<td>20 wt% in DMF</td>
<td>-</td>
<td>-</td>
<td>99.7</td>
<td>99.4</td>
</tr>
<tr>
<td>24 wt% in DMF</td>
<td>-</td>
<td>-</td>
<td>99.7</td>
<td>99.4</td>
</tr>
</tbody>
</table>
7.3.7. Ionic liquid recovery

The use of ionic liquids as solvents for membrane separation would only be sustainable if recovery and recycling would be possible. Waste water of 500 ml after the phase separation was taken from the coagulant bath to recover the [EMIM]SCN. After the membrane preparation, the concentration of [EMIM]SCN in the bath was 1.6 %. Through 3 steps of recovery, the final ionic liquid concentration could be increased to 96 % as plotted in Figure 7.9. The purity of the ionic liquid for casting solution preparation was $\geq 95 \%$. Therefore, it can be fully recovered for reuse.

$\text{Figure 7.9. Ionic liquid recovery.}$
7.4. Conclusion

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

1) The order of EXTEMTM solubility in different solvents is DMF > [BMIM]SCN > [EMIM]OAc > [EMIM]SCN, all forming thermodynamically stable solutions.

2) Membranes cast from EXTEMTM in [EMIM]SCN were mechanically more stable than those cast from [EMIM]OAc and [BMIM]SCN.

3) [η] for EXTEMTM solutions in different solvents decreased in the following order: [BMIM]SCN > [EMIM]OAc > DMF > [EMIM]SCN.

4) Membranes cast from EXTEMTM 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% EXTEMTM 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.
8.1. Conclusion

The following conclusions can be taken:

1. Hydrophilic ionic liquids can be greener solvents comparing to aprotic solvents such as DMF, DMAc, and NMP.
2. These studies give information related to physical properties of polymer-ionic liquid solutions such as solubility parameters, their thermodynamic comparability between polymer and ionic liquids, and kinetic properties of polymer solutions such as viscoelasticity and viscosity, as shown in Table 8.1.
3. Some polymer-ionic liquid solutions can be thermodynamically stable, similar to polymer solutions in aprotic solvents.
4. Kinetics of the polymer-ionic liquid solutions plays a crucial role in the membrane structure formation.
5. Using ionic liquids as solvents for membrane fabrication delays the phase separation and induces nucleation and growth mechanism. This results in membranes with a sponge-like structure and with well distributed nano-sized pores.
6. Membranes fabricated from ionic liquid solutions can perform better than those fabricated form aprotic solvents in terms of rejection of linear polymers, protein, peptides, and DNA. Furthermore, after the polyamide (PA) interfacial polymerization, the membranes from ionic liquids can be applied in forward osmosis (FO) system successfully.
7. Ionic liquids used in this thesis can be successfully recycled by simple purification steps up to 99%.

8.2. Future perspectives

The following research topics, regarding to the fabrication of greener membranes from ionic liquid solutions, would be interesting to explore:

- Identifying other commercial or synthesized polymers, that could be dissolved in ionic liquids to fabricate green membranes.
- Surface modification of the greener membranes and the use of additives for better membrane performance such as mechanical properties, water flux, and rejection.
- Application of the greener membranes in diverse separation processes.
- Biofouling studies on the ionic liquid based membranes.
- Estimation of the interaction energy between polymers and ionic liquids in more accurate ways.
- Ionic liquid recovery in a more energy efficient way
- Studies on the toxicity of ionic liquids such as acute and chronic toxicity, biodegradability, and life cycle.
Table 8.1. Summary of the discovery included in this thesis.

<table>
<thead>
<tr>
<th>The composition of polymer solutions and ionic liquids</th>
<th>Dissolution</th>
<th>$\delta$ (MPa$^{1/2}$)</th>
<th>$\Delta G$ and $E_{int}$ (DFT)$^a$</th>
<th>Density (g/cm$^3$)</th>
<th>$D_h$ by DLS (nm)</th>
<th>Intrinsic viscosity$^c$ ($[\eta]$) (cm$^3$g$^{-1}$)</th>
<th>Dynamic viscosity (Pa.s)</th>
<th>Membrane structure, water permeance (LM$^{-2}$H$^{-1}$bar$^{-1}$)/MWCO (kg mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN/[EMIM]OAc/DMSO</td>
<td>Yes</td>
<td>-</td>
<td>Negative ($\Delta G$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Fully developed finger-like and connected 540 ± 30(HF) / 54</td>
</tr>
<tr>
<td>PAN/[EMIM]OAc</td>
<td>No</td>
<td>-</td>
<td>Slightly positive ($\Delta G$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>N/A</td>
</tr>
<tr>
<td>PAN/DMSO</td>
<td>Yes</td>
<td>-</td>
<td>Negative ($\Delta G$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Finger-like and connected 209 ± 10 (HF) / 32</td>
</tr>
<tr>
<td>PAN/DMF</td>
<td>Yes</td>
<td>-</td>
<td>Negative ($\Delta G$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Finger-like and connected 22 ± 10 (HF) / 80</td>
</tr>
<tr>
<td>PAN</td>
<td>-</td>
<td>25.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[EMIM]OAc</td>
<td>-</td>
<td>32.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>DMSO</td>
<td>-</td>
<td>26.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DMF</td>
<td>-</td>
<td>24.8</td>
<td>-</td>
<td>0.9474</td>
<td>-</td>
<td>0.00077</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NMP</td>
<td>-</td>
<td>23</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CA/[EMIM]OAc</td>
<td>Yes</td>
<td>-</td>
<td>Slightly positive ($\Delta G$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Sponge-like and connected 130 / 77</td>
</tr>
<tr>
<td>CA/Ac/[EMIM]OAc</td>
<td>Yes</td>
<td>-</td>
<td>Negative ($\Delta G$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Sponge-like and connected 330 / 74</td>
</tr>
<tr>
<td>CA/Ac</td>
<td>Yes</td>
<td>-</td>
<td>Negative ($\Delta G$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Sponge-like and closed or disconnected, N/A</td>
</tr>
<tr>
<td>CA/NMP</td>
<td>Yes</td>
<td>-</td>
<td>Negative ($\Delta G$)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Finger-like and connected 100 / 70</td>
</tr>
<tr>
<td>CA</td>
<td>-</td>
<td>25.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ac (aceton)</td>
<td>-</td>
<td>19.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PES/[EMIM]DEP</td>
<td>Yes</td>
<td>--</td>
<td>Slightly positive ($\Delta G$) and -13.1 (DFT)$^a$</td>
<td>15.3 ± 0.3</td>
<td>58.5</td>
<td>97.1$^d$</td>
<td>-</td>
<td>Sponge-like and connected 55 ± 5(FS) / 5.1, 45.8 (HF) / 1.4</td>
</tr>
<tr>
<td>PSf/[EMIM]DEP</td>
<td>No</td>
<td>-</td>
<td>Positive ($\Delta G$) and -5.4 (DFT)$^a$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>N/A</td>
</tr>
<tr>
<td>Polymer</td>
<td>Compatibility</td>
<td>Polymer Name</td>
<td>ΔG (DFT)</td>
<td>Density (g/cm³)</td>
<td>Dh (nm)</td>
<td>Intrinsic Viscosity (η) (cm²/g⁻¹)</td>
<td>Dynamic Viscosity (Pa.s)</td>
<td>Membrane Structure, Water Permeance (LM²H⁻¹bar⁻¹) / MWCO (kg mol⁻¹)</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
<td>--------------</td>
<td>----------</td>
<td>----------------</td>
<td>--------</td>
<td>---------------------------------</td>
<td>----------------------</td>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>PES/ [MMIM]DMP</td>
<td>Yes</td>
<td>-</td>
<td>Slightly positive (ΔG)</td>
<td>18.2</td>
<td>96.4</td>
<td>59.7</td>
<td>Spong-like and connected</td>
<td>43 ± 3 (FS) / 7.9</td>
</tr>
<tr>
<td>PSi/ [MMIM]DMP</td>
<td>No</td>
<td>-</td>
<td>Positive (ΔG)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>PES/ DMF</td>
<td>Yes</td>
<td>-</td>
<td>Negative (ΔG)</td>
<td>13.3 ± 0.3</td>
<td>52.0</td>
<td>0.1</td>
<td>Finger-like and connected</td>
<td>135 ± 5 (FS) / 10.3</td>
</tr>
<tr>
<td>PES/ NMP</td>
<td>Yes</td>
<td>-</td>
<td>Negative (ΔG)</td>
<td>17.3 ± 0.2</td>
<td></td>
<td></td>
<td>Finger-like and connected</td>
<td></td>
</tr>
<tr>
<td>PES/ DMAc</td>
<td>Yes</td>
<td>-</td>
<td>Negative (ΔG)</td>
<td>15.7 ± 0.2</td>
<td></td>
<td></td>
<td>Finger-like and connected</td>
<td></td>
</tr>
<tr>
<td>PES</td>
<td>No</td>
<td>-</td>
<td>Positive (ΔG)</td>
<td>23.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EMIM] DEP</td>
<td>No</td>
<td>-</td>
<td>-</td>
<td>28.3</td>
<td>1.1458</td>
<td>0.384</td>
<td>Recovery: 99%</td>
<td></td>
</tr>
<tr>
<td>[MMIM] DMP</td>
<td>No</td>
<td>-</td>
<td>-</td>
<td>32.5</td>
<td>1.2532</td>
<td>0.189</td>
<td></td>
<td></td>
</tr>
<tr>
<td>The composition of polymer solutions and ionic liquids</td>
<td>Dissolution</td>
<td>Δ (MPa¹/²)</td>
<td>ΔG</td>
<td>Density (g/cm³)</td>
<td>Dh (nm)</td>
<td>Intrinsic viscosity (η) (cm²/g⁻¹)</td>
<td>Dynamic viscosity (Pa.s)</td>
<td>Membrane structure, water permeance (LM²H⁻¹bar⁻¹) / MWCO (kg mol⁻¹)</td>
</tr>
<tr>
<td>EXTEM™/[EMIM] SCN</td>
<td>Yes</td>
<td>-</td>
<td>Slightly positive (ΔG)</td>
<td>18.4</td>
<td>18.5</td>
<td>Sponge-like and connected</td>
<td>90 ± 10 (FS) / 5.3</td>
<td></td>
</tr>
<tr>
<td>EXTEM™/[BMIM] SCN</td>
<td>Yes</td>
<td>-</td>
<td>Slightly positive (ΔG)</td>
<td>47</td>
<td>52.5</td>
<td>N/A (too brittle)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EXTEM™/[EMIM] OAc</td>
<td>Yes</td>
<td>-</td>
<td>Slightly positive (ΔG)</td>
<td>31.4</td>
<td>39.9</td>
<td>N/A (too brittle)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EXTEM™/ DMF</td>
<td>Yes</td>
<td>-</td>
<td>Negative (ΔG)</td>
<td>(22.5)</td>
<td>33.7</td>
<td>Finger-like and connected</td>
<td>3 ± 2 (FS) / 5.3</td>
<td></td>
</tr>
<tr>
<td>EXTEM™</td>
<td>No</td>
<td>-</td>
<td>-</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EMIM] SCN</td>
<td>No</td>
<td>-</td>
<td>-</td>
<td>33.5</td>
<td>1.1181</td>
<td>0.023</td>
<td>Recovery: 99%</td>
<td></td>
</tr>
<tr>
<td>[BMIM] SCN</td>
<td>No</td>
<td>-</td>
<td>-</td>
<td>28.9</td>
<td>1.0707</td>
<td>0.052</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[EMIM] OAc</td>
<td>No</td>
<td>-</td>
<td>-</td>
<td>32.1</td>
<td>1.0992</td>
<td>0.094</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

δ: solubility parameter (Hildebrand), HF: hollow fiber membranes, and FS: flat sheet membranes

* Eint (interaction energy) calculated by DFT with monomer and a pair of ionic liquid, a Measured with a pycnometer at 22± 1 °C, b Measured for PES (Mw = 75 kg mol⁻¹) at 25 °C, c The polymer concentration of membranes is 12 wt%, d Dh: hydrodynamic diameter, e The EXTEM™ concentration is 24 wt
Appendix A

Table 5.1S. Hansen solubility parameters ($\delta$) for PES, PSU, and different solvents $\delta_D$, $\delta_P$ and $\delta_H$ are van der Waals, polarity, and hydrogen bond contributions to $\delta$.

<table>
<thead>
<tr>
<th></th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$\delta$ (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU$^b$</td>
<td>20</td>
<td>8</td>
<td>8</td>
<td>23</td>
</tr>
<tr>
<td>PES$^b$</td>
<td>19</td>
<td>11</td>
<td>8</td>
<td>23</td>
</tr>
<tr>
<td>[EMIM]DEP$^a$</td>
<td>20</td>
<td>13</td>
<td>15</td>
<td>28</td>
</tr>
<tr>
<td>[EMIM]OAc$^a$</td>
<td>22</td>
<td>16</td>
<td>17</td>
<td>32</td>
</tr>
<tr>
<td>NMP$^b$</td>
<td>18</td>
<td>12</td>
<td>7</td>
<td>23</td>
</tr>
<tr>
<td>DMF$^b$</td>
<td>17</td>
<td>14</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>DMAc$^b$</td>
<td>17</td>
<td>12</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>Water$^b$</td>
<td>16</td>
<td>16</td>
<td>42</td>
<td>48</td>
</tr>
</tbody>
</table>

$^a$Calculated with HSPiP, $^b$From a reference [148]
Appendix B

**Table 5.2S.** Rejections of PEG (and PEO) of different molecular weights, measured for PES membranes cast from solutions in [EMIM]DEP with different polymer concentrations and from 16 wt% PES solutions in NMP, DMAc and DMF; MWCO estimated from the measuring data.

<table>
<thead>
<tr>
<th>Molecular weight (kg mol(^{-1}))</th>
<th>Solute rejection (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 wt% [EMIM]DEP</td>
</tr>
<tr>
<td>600</td>
<td>100</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>35</td>
<td>99± 0.2</td>
</tr>
<tr>
<td>10</td>
<td>48± 0.4</td>
</tr>
<tr>
<td>6</td>
<td>16± 0.1</td>
</tr>
<tr>
<td>1.5</td>
<td>4± 0.5</td>
</tr>
<tr>
<td>0.3</td>
<td>1± 0.2</td>
</tr>
</tbody>
</table>

| MWCO (kg mol\(^{-1}\)) | 30 | 5 | 1.3 | 1.25 | 31 | 29 | 33 |
Table 5.3S. Water permeance and MWCO of PES membranes reported in the literature.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Membrane type</th>
<th>Water permeance (L m$^{-2}$ h$^{-1}$ bar$^{-1}$)</th>
<th>MWCO (kg mol$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 % PES/[EMIM]DEP</td>
<td>Flat sheet</td>
<td>140</td>
<td>30</td>
<td>This study</td>
</tr>
<tr>
<td>12 % PES/[EMIM]DEP</td>
<td>Flat sheet</td>
<td>65</td>
<td>5</td>
<td>This study</td>
</tr>
<tr>
<td>14 % PES/[EMIM]DEP</td>
<td>Flat sheet</td>
<td>25</td>
<td>1.3</td>
<td>This study</td>
</tr>
<tr>
<td>16 % PES/[EMIM]DEP</td>
<td>Flat sheet</td>
<td>20</td>
<td>1.25</td>
<td>This study</td>
</tr>
<tr>
<td>18 % PES/f-MWCNT/PVP/DMF</td>
<td>Flat sheet</td>
<td>24</td>
<td>35</td>
<td>[164]</td>
</tr>
<tr>
<td>18 % PES/15 % Methanol/67 % NMP</td>
<td>Hollow fiber</td>
<td>187</td>
<td>10</td>
<td>[174]</td>
</tr>
<tr>
<td>PES/PEG/NMP</td>
<td>Hollow fiber</td>
<td>28</td>
<td>45</td>
<td>[161]</td>
</tr>
<tr>
<td>32 % PES/DMF</td>
<td>Flat sheet</td>
<td>9.4</td>
<td>1.9</td>
<td>[162]</td>
</tr>
<tr>
<td>30 % PES/NMP</td>
<td>Flat sheet</td>
<td>22.2</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>NFPES10 (Nadir, Germany)</td>
<td>Flat sheet</td>
<td>15.4</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>N30F (Nadir, Germany)</td>
<td>Flat sheet</td>
<td>3.8</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>20 % PES/DMF</td>
<td>Flat sheet</td>
<td>5</td>
<td>35</td>
<td>[163]</td>
</tr>
<tr>
<td>20 % PEG/PEG/DMF</td>
<td>Flat sheet</td>
<td>25</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>NTR7450 (modified PES, Nitto-Denko)</td>
<td>Flat sheet</td>
<td>5.7</td>
<td>0.7</td>
<td>[165]</td>
</tr>
<tr>
<td>15 % PES/DMF</td>
<td>Flat sheet</td>
<td>9</td>
<td>2</td>
<td>[166]</td>
</tr>
<tr>
<td>15 % PES/NMP</td>
<td>Flat sheet</td>
<td>1.7</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>17.5 % PES/82.5 % NMP</td>
<td>Flat sheet</td>
<td>2.6</td>
<td>&gt; 69</td>
<td>[167]</td>
</tr>
<tr>
<td>17.5 % PES/82.5 % DMSO</td>
<td>Flat sheet</td>
<td>5.7</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>17.5 % PES/82.5 % DMF</td>
<td>Flat sheet</td>
<td>3.6</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>15 % PES/85 % NMP</td>
<td>Flat sheet</td>
<td>5.6</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>15 % PES/85 % DMSO</td>
<td>Flat sheet</td>
<td>11.9</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>15 % PES/85 % DMF</td>
<td>Flat sheet</td>
<td>7.7</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>PES (HFK-131, Koch)</td>
<td>Flat sheet</td>
<td>53</td>
<td>10</td>
<td>[169] [202]</td>
</tr>
<tr>
<td>16 % PES/2 % PVP/82 % DMAc</td>
<td>Flat sheet</td>
<td>74</td>
<td>80.5</td>
<td>[168]</td>
</tr>
<tr>
<td>16 % PES/2 % PVP/10 % AA/72 % DMAc</td>
<td>Flat sheet</td>
<td>44</td>
<td>35.9</td>
<td></td>
</tr>
<tr>
<td>16 % PES/2 % PVP/10 % HEMA/72 % DMAc</td>
<td>Flat sheet</td>
<td>59</td>
<td>34.1</td>
<td></td>
</tr>
<tr>
<td>18 % PES/NMP</td>
<td>Flat sheet</td>
<td>850</td>
<td>600</td>
<td>[171]</td>
</tr>
<tr>
<td>18 % PES/0.03 % ZrO$_2$/NMP</td>
<td>Flat sheet</td>
<td>1580</td>
<td>600</td>
<td>[172]</td>
</tr>
<tr>
<td>PES/PVP (LD Hydranautics)</td>
<td>Hollow fiber</td>
<td>600</td>
<td>150</td>
<td>[173]</td>
</tr>
<tr>
<td>PES/PVP/DMAc</td>
<td>Flat sheet</td>
<td>350</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>PES/TiO2/PVP/DMAc</td>
<td>Flat sheet</td>
<td>450</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>
Appendix D

Figure 5.1S. FESEM images of membranes cross-sections, cast from PES/[EMIM]DEP solutions with the following polymer concentrations: 8, 12 and 14 wt%.

Appendix E

Figure 5.2S. FESEM images of membranes surfaces (top and bottom), cast from 8 wt% PES/[EMIM]DEP and 16 wt % PES/DMF solutions.
Appendix F

Table 6.1S. Solubility parameters.

<table>
<thead>
<tr>
<th></th>
<th>$\delta_D$</th>
<th>$\delta_P$</th>
<th>$\delta_H$</th>
<th>$\delta$ (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[EMIM]DEP$^a$</td>
<td>20</td>
<td>13.5</td>
<td>14.8</td>
<td>28.3</td>
</tr>
<tr>
<td>[MMIM]DMP$^a$</td>
<td>22.3</td>
<td>16.2</td>
<td>17.2</td>
<td>32.5</td>
</tr>
<tr>
<td>PES $^b$</td>
<td>19</td>
<td>11</td>
<td>8</td>
<td>23.4</td>
</tr>
<tr>
<td>PSf $^b$</td>
<td>20</td>
<td>8</td>
<td>8</td>
<td>23</td>
</tr>
<tr>
<td>DMF$^b$</td>
<td>17</td>
<td>14</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>Water $^b$</td>
<td>15.5</td>
<td>16</td>
<td>42.3</td>
<td>47.8</td>
</tr>
</tbody>
</table>

$^a$Calculated with HSPiP. $^b$From Hansen, C. M. Hansen solubility parameters: a user’s handbook. CRC Press LLC: N.W., Boca Raton, USA, 2000

Appendix G

Table 6.2S. Spinning conditions for hollow fiber membranes spun from 18 wt% PES/DMF.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope solution composition (wt%)</td>
<td>18 wt% PES/DMF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition of bore fluid (wt%)</td>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coagulant bath</td>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air gap (cm)</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow rate of dope solution (mL/min)</td>
<td>9</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Flow rate of inner coagulant (mL/min)</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Take up speed (m/min)</td>
<td>Free fall</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of the dope solution (°C)</td>
<td>70</td>
<td>70</td>
<td>70</td>
<td>25</td>
<td>70</td>
<td>70</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Temperature of the bore fluid and the coagulant bath (°C)</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample No.</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Outer diameter (mm)</td>
<td>1010</td>
<td>930</td>
<td>950</td>
<td>870</td>
<td>780</td>
<td>900</td>
<td>850</td>
<td>770</td>
</tr>
<tr>
<td>Wall thickness (mm)</td>
<td>190</td>
<td>210</td>
<td>155</td>
<td>165</td>
<td>130</td>
<td>140</td>
<td>140</td>
<td>119</td>
</tr>
</tbody>
</table>

**Figure 6.1S.** Morphologies of the hollow fiber membranes spun from 18 wt% PES/DMF solutions.
Appendix H

**EXTEM™ Molecular weight evaluation**

By using the Mark–Houwink–Sakurada equation, the molecular weight of EXTEM was determined from the intrinsic viscosity values. The value of 0.5 was applied for the Mark–Houwink parameters, \( a \):

\[
[\eta] = K M^a
\]

**Table 7.1S.** EXTEM™ molecular weight evaluation.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Intrinsic viscosity ([\eta]) (cm(^3) g(^{-1}))</th>
<th>(M^a) (g mol(^{-1}))</th>
<th>(M^b) (g/mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(etherimid sulfone)</td>
<td>31.9</td>
<td></td>
<td>85,000</td>
</tr>
<tr>
<td>(EXTEM™)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyetherimide</td>
<td>23.8</td>
<td>55,000</td>
<td></td>
</tr>
<tr>
<td>(Ultem™)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polysulfone</td>
<td>33.5</td>
<td>81,000</td>
<td></td>
</tr>
<tr>
<td>(Udel®)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)provided by manufacturer  
\(^b\)determined from \([\eta]\) (applied with the average between \(K\) values for Ultem™ and Udel®)
Appendix I

Solvent viscosity and density

Table 7.2S. Density and viscosities of all solvents.

<table>
<thead>
<tr>
<th>At 25 °C</th>
<th>Kinetic viscosity (mm²/s)</th>
<th>Density (g/cm³)</th>
<th>Dynamic viscosity (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiments&lt;sup&gt;a&lt;/sup&gt;</td>
<td>References&lt;sup&gt;b&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>[EMIM]SCN</td>
<td>20.6</td>
<td>1.1181</td>
<td>1.114</td>
</tr>
<tr>
<td>[EMIM]OAc</td>
<td>85.9</td>
<td>1.0992</td>
<td>1.027</td>
</tr>
<tr>
<td>[BMIM]SCN</td>
<td>48.3</td>
<td>1.0707</td>
<td>1.07</td>
</tr>
<tr>
<td>DMF</td>
<td>0.8</td>
<td>0.9474</td>
<td>0.944</td>
</tr>
</tbody>
</table>

<sup>a</sup>Density measured with a pycnometer at 22± 1 °C

<sup>b</sup>Density supplied by Sigma Aldrich, measured at 25 °C

According to Ref. [203], the viscosities of [EMIM]OAc and [BMIM]OAc significantly decline upon addition of water at 25 °C. When the water amount in [EMIM]OAc increased from 2.3% to 4.8%, the corresponding viscosity declined from 122 to 81 mPa.s. Water included in ionic liquids affects their viscosity significantly. The water effect was not considered in this viscosity results.
Appendix J

Crystallinity of EXTEM™

Based on the XRD analysis, the membranes prepared from EXTEM™ in different solvents have sharp peaks of crystallinity and can be considered a semi-crystalline polymer.

**Figure 7.1S.** XRD results for membranes fabricated from 20 wt% EXTEM™ in different solvents.
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