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

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ABSTRACT

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

1. Introduction

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

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

Hollow fiber membranes are important for their large effective area, and high packing density in modules [24]. Manufacturing hollow fibers is more challenging than flat-sheet requiring a stricter viscosity control. Few studies on hollow fiber membrane fabrication based on ionic liquid polymer solutions have been reported. Xing et al. [21] successfully spun hollow fiber membranes from the highly viscous polymer solution (approximately 100 Pa.s at 1 1/s and 23 °C) of 12 wt% CA in [EMIM]SCN. Our group has fabricated hollow fiber membranes based on CA/[EMIM]OAc with/without cosolvent [18] and polyacrylonitrile (PAN)/[EMIM]OAc/co-solvent [20]. Here we first successfully fabricated hollow fiber membranes from highly viscous PES/[EMIM]DEP solutions and characterized them concerning the separation capacity of biotechnological product, and mechanical properties.

Second, we demonstrated the feasibility of another PES /ionic liquid

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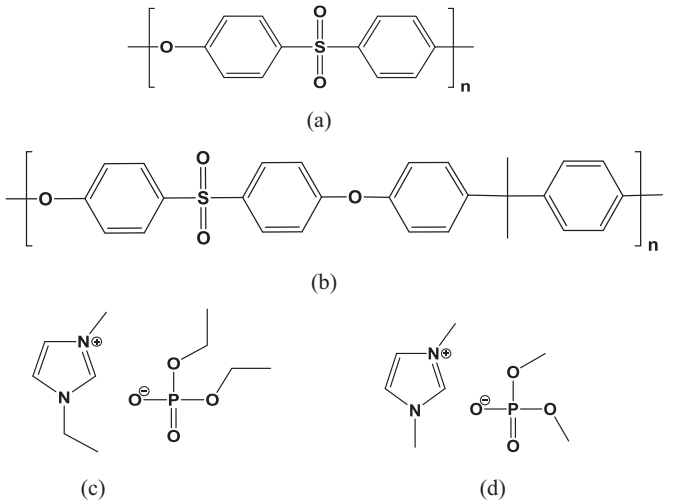

Fig. 1. Chemical structures of (a) PES, (b) PSf, (c) [EMIM]DEP, and (d) [MMIM]DMP.

system for membrane preparation. Finally, we use density functional theory to explain why PES solubility allows efficient membrane preparation, while polysulfone (PSf) with very similar chemical structure cannot be dissolved in the same solvents.

2. Methodology

2.1. Materials

Polyethersulfone (PES, average Mw = 75,000 provided from BASF) was purchased from BASF (Ultrason®). Polysulfone (PSf, average Mw = 81,000) was purchased from Solvey (Udel P-3500). 1-ethyl-3-methylimidazolium diethylphosphate ([EMIM]DEP, ≥ 98.0%), 1, 3-dimethylimidazolium 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 Fig. 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.

2.2. Density functional theory (DFT) calculation

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

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

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

2.3. Experimental polymer solution characterization

2.3.1. Binary systems (polymer/solvent)

Parallel to the computational estimation, experimental measurements of the polymer coil size were provided by intrinsic viscosity ([η]), 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 Eq. (3):

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

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

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

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

where, C* is the concentration which the polymer coils start to entangle. [η] is the intrinsic viscosity (cm^3/g), M is the polymer molecular weight (g mol^{-1}), N_A is the Avogadro number (6.022×10^{23} mol^{-1}), R_g is the radius of gyration (cm), respectively. From the intrinsic viscosity in Eq. (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.

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.

2.4. Membrane preparation

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

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