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The effects of a co-solvent on fabrication of cellulose acetate membranes from solutions in 1-ethyl-3-methylimidazolium acetate

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ABSTRACT

Ionic liquids have been considered green solvents for membrane fabrication. However, the high viscosity of their polymer solutions hinders the formation of membranes with strong mechanical properties. In this study, acetone was explored as a co-solvent with the ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) to dissolve cellulose acetate. The effects of acetone on the thermodynamic and kinetic aspects of the polymer solutions were studied and the physicochemical properties and separation capability of their resultant membranes were analyzed. The Hansen solubility parameters of [EMIM]OAc were measured by the software HSPiP and these data demonstrated that acetone was a suitable co-solvent to increase the solubility of cellulose acetate. The Gibbs free energy of mixing ΔG_m was estimated to determine the proper composition of the polymer solution with better solubility. The study of the kinetics of phase separation showed that the demixing rate of the CA polymer solution in acetone and [EMIM]OAc was higher than that for solutions in [EMIM]OAc only. The membranes prepared from the former solution had higher water permeance and better mechanical stability than those prepared from the later solution. Adding acetone as a co-solvent opened the opportunity of fabricating membranes with higher polymer concentrations for higher separation capability and better mechanical properties.

1. Introduction

Since Loeb and Sourirajan introduced cellulose acetate (CA) membranes for sea water desalination in the 1960's [1,2], 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 [1–3], N-methyl-2-pyrrolidone (NMP) [4,5], formamide [6], dimethylformamide (DMF) [7] 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 [8] and European Commission [9] because of their toxicity. Since the health and environmental concerns [8,10] 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 [11]. 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 [11,12]. 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 to their anion and cation properties, which affect their viscosity and solubility parameters. For example, Xing et at found [13] that with the same cation 1-butyl-3-methylimidazolium (BMIM), the dissolution of CA in the methyl sulfate ionic liquid ([BMIM][$MeSO_4$]) 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][$MeSO_4$]. On the other hand, 1-ethyl-3-methylimidazolium ([EMIM]), which has the a shorter carbon-chain, dissolved CA more effectively than the longer carbon chain BMIM with the same anion thiocyanate [14]. Despite of 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

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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. [15] and solvent guidance [16–18]. 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 [19]. 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.

2. Experiments

2.1. Materials

Cellulose acetate (CA, average Mn $=\sim$50,000), 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc, $\geq$ 95.0%), acetone ($\geq$ 95.0%), and N-methyl-2-pyrrolidone ($\geq$ 99.0%) were supplied by Sigma-Aldrich. Their chemical structures are shown in Fig. 1. Polyethylene glycol (PEG) (Sigma-Aldrich) and polyethyleneoxide (PEO) (Sigma-Aldrich), with the molecular weights of 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, $\sim$66 kg mol^{-1}) and γ-globulin ($\sim$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.

2.2. Thermodynamics of polymer solutions

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 HSP iP [20]. 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 (δ_D), dipole-dipole (δ_p), and hydrogen bonding (δ_H) interactions [20] was computed by the software. The Hansen solubility parameter was then calculated by the following equation:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (1)$$

2.2.2. Estimation of Gibbs free energy of mixing

The Gibbs free energy of mixing (ΔG_m) is an informative parameter to predict the homogeneity of a polymer/solvent mixture [21]. In particular, if ΔG_m is negative, the polymer is expected to completely dissolve in the solvent. In contrast, if ΔG_m is much higher than zero, the mixture is unlikely to be homogenous. According to the Flory–Huggins theory, ΔG_m can be estimated by the following equation [22]:

$$\frac{\Delta G_m}{N_A} = kT\left[\chi\phi_1\phi_2 + \frac{\phi_1}{X_1}\ln\phi_1 + \frac{\phi_2}{X_1}\ln\phi_2\right] \quad (2)$$

Where k is the Boltzmann constant, T is the absolute temperature (K), and ϕ_i and x_i are the volume fraction and number of segments of the ith component, respectively. χ is the Flory-Huggins parameter, which can be calculated from the following equation:

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

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 [20,23–25]. δ is the solubility parameter of the solvent i and polymer j ($MPa^{1/2}$).

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.

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.

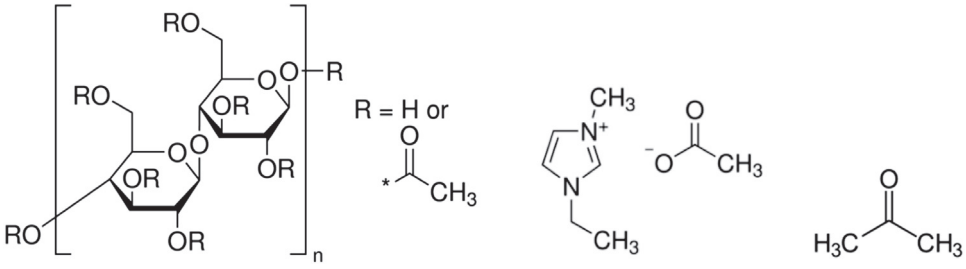

Fig. 1. Chemical structures of CA, [EMIM]OAc and acetone.