**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 latter 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.

Key words: cellulose acetate, ionic liquids, co-solvent, thermodynamics, kinetics, solubility parameter.

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 al found [13] 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 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 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.

Experiments

1.1 Materials

Cellulose acetate (CA, average $M_n = \sim 50,000$), 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 Figure 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, $\sim 66 \text{ kg mol}^{-1}$) and γ -globulin ($\sim 140 \text{ kg mol}^{-1}$) 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 0.012M phosphate, for ultrafiltration tests

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

1.2 Thermodynamics of polymer solutions

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:

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

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]:

$$\frac{\Delta G_m}{N_A} = kT \left[\chi \phi_1 \phi_2 + \frac{\phi_1}{X_1} \ln \phi_1 + \frac{\phi_2}{X_2} \ln \phi_2 \right] \quad (2)$$

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 i^{th} 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 ($\text{cm}^3 \text{Mpa K}^{-1} \text{mol}^{-1}$). 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 ($\text{MPa}^{1/2}$).

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.

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.

1.3 Kinetics of polymer solutions

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.

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) [13, 14].

$$T_r = \frac{(T - T_{min})}{(T_{max} - T_{min})} \times 100\% \quad (4)$$

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

1.4 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 μ m 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 1. The resultant membranes are marked as HF-12CA/[EMIM]OAc and HF-18CA/Ac/[EMIM]OAc, respectively.

Table 1. Spinning conditions

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

1.5 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:

$$\text{Pure water permeance, (Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}) = \frac{Q}{A \cdot \Delta P} \quad (5)$$

where Q is the water flux (L/h), A is the effective membrane area (m²), and ΔP 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:

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

where C_{perm} and C_{feed} are the concentrations of the permeate and feed solutions, respectively, which was analyzed by gel permeation chromatography (GPC) with a PL aquagel-OH 40 and 60 columns (1260 infinity GPC/SEC, Agilent technologies). Solute diameter was calculated by the Stokes radius equation [26, 27]:

For PEG

$$r = 16.73 \times 10^{-10} M^{0.557} \quad (7)$$

For PEO

$$r = 10.44 \times 10^{-10} M^{0.587} \quad (8)$$

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).

$$F(R) = A + B (\ln d) \quad (9)$$

$$\frac{\partial R(d_p)}{\partial d_p} = \frac{1}{d_p \ln \sigma_p \sqrt{2\pi}} \exp \left[-\frac{(\ln d_p - \ln \mu_p)^2}{2(\ln \sigma_p)^2} \right] \quad (10)$$

where μ_p is the mean of the effective pore size diameter at $R = 50 \%$. σ_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 [27] and ignoring the deformation of macromolecules under pressure and shear rate in the solution [28]. 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 equation (7) or (8).

Protein separation

Ultrafiltration performance was examined by filtration tests of BSA and γ -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).

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.

2. Results and discussion

2.1 Thermodynamics of polymer solutions

Hansen solubility parameter of [EMIM]OAc

The ternary diagram in Figure 2a shows 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 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 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.

Figure 2. Ternary diagram of the Hansen solubility parameter's components of [EMIM]OAc

Table 2. Solubility parameters of the polymer and solvents used in this study.

Compounds	δ_d	δ_p	δ_h	δ (Mpa ^{1/2})
Cellulose acetate [20]	18.6	12.7	11	25.1
[EMIM]OAc (by HSPiP)	22.2	15.9	16.9	32.1
Water [20]	15.5	16	42.3	47.8
Acetone [20]	15.5	10.4	7	19.9

Estimation of Gibbs free energy of mixing

Figure 3a shows ΔG_m of CA with solvents. The polymer solutions of CA (12 wt% and 18 wt%) in [EMIM]OAc had the ΔG_m values of $> \text{zero}$. 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 2). The addition of acetone into the CA/[EMIM]OAc systems decreased their ΔG_m values. Once the acetone amount reached 30 wt% approximately, ΔG_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 ΔG_m of CA in [EMIM]OAc. As a result, it facilitated a homogeneity of the system. Figure 3b shows the ΔG_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 ΔG_m is much higher than zero.

Figure 3. (a) The Gibbs free energy of mixing CA polymer in different solvent systems and (b) its ternary diagram.

The green region indicates the ΔG_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.

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 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 3. The size (diameter) of polymer molecules in single solvents.

Solutions	Z-Average (nm)
0.1 wt% CA/99.9 wt% [EMIM]OAc	19
0.1 wt% CA / 99.9 wt% Acetone	183
0.1 wt% CA / 99.9 wt% NMP	34

Phase diagram by cloud point tests

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

2.2 Kinetics of polymer solutions

Viscosity

Figure 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, 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 °C. Its value became similar to those of the other solutions. This indicates that 60 °C was the preferable temperature to fabricate the membrane prepared from the pure [EMIM]OAc.

Figure 5. Viscosity of CA solutions as a function of temperature at the shear rate of 10 s^{-1} .

Phase separation kinetics

Figure 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. 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.

Figure 6. The phase inversion kinetics of CA polymer solutions cast on a glass plate and coagulated in water

2.3 Membrane characterization

2.3.1 Flat sheet membranes

Membrane morphology

Figure 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 12/[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.

Figure 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).

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.

Pure water permeance, MWCO, pore size and pore size distribution

Figure 8a and Table 4 present the pure water permeance of CA membranes prepared from different solvent systems. The 12CA/[EMIM]OAc membrane had a water permeance of $130 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. Adding acetone to the solvent system increased the water permeance of the resultant membrane (12CA/Ac/[EMIM]OAc) 2.5 times to $330 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. 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 $4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$).

Figure 8. (a) Pure water permeance, (b) PEG rejection and (c) pore size distribution of the membranes prepared from different solvent systems.

Figure 8b shows the rejection of all studied membranes towards the neutral solutes PEG or PEO with different molecule weights. The comparison was done for membranes prepared under similar conditions, without additional pore-forming agents, which are frequently used for membrane fabrication. The CA/Ac membrane was not reported because it had practically no measurable water permeation, under these conditions. From the rejection results, the pore size distributions were illustrated in Figure 8c and their MWCOs were listed in Table 4. Figure 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. Pure water permeance, MWCO and protein separation of CA flat-sheet membranes

Membranes	Pure water permeance (L m ⁻² h ⁻¹ bar ⁻¹).	MWCO (kg mol ⁻¹)	Rejection (%)	
			BSA	γ -Globulin
12CA/[EMIM]OAc	130	77	-	96
12CA/Ac/[EMIM]OAc	330	74	-	98
12CA/NMP	100	70	-	98
18CA/Ac/[EMIM]OAc	110	57	91	98

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. 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 %.

Mechanical properties

Along with the separation capability of proteins, the mechanical properties are another major characteristics determining the potential practical applications of membranes. Table 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 5. Mechanical properties

Membranes	Stress at break (MPa)	Pressure resistance of HF modules (kPa)
12CA/[EMIM]OAc	1.62	
12CA/Ac/[EMIM]OAc	2.02	
12CA/NMP	1.96	
18CA/Ac/[EMIM]OAc	2.94	
HF-12CA/[EMIM]OAc		100
HF-18CA/Ac/[EMIM]OAc		250

2.3.2 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 9. Their hydraulic pressure tolerances are presented in Table 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 9. Morphologies of the hollow fiber membranes (a) HF-12CA/[EMIM]OAc and (b) HF-18CA/Ac/[EMIM]OAc

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 ΔG_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 γ -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.

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