

Exploring the performance-affecting factors of monocationic and dicationic phosphonium-based thermoresponsive ionic liquid draw solutes in forward osmosis

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ABSTRACT

Because of easy recovery, thermoresponsive phosphonium-based ionic liquids (ILs) can be used as a potential draw solute in forward osmosis (FO). Its phase separation behaviors and water-drawing potential are two main factors affecting FO performance. In this study, these two factors were investigated for the lower critical solution temperature (LCST) type mono-cationic and di-cationic phosphonium-based IL draw solutes with different anions, including p-toluenesulfonate (TSO), hydrogen maleate (Mal), and trimethylbenzenesulfonate (TMBS). In phase separation behaviors, the structure chemistry of cation/anion can affect the LCST cloud temperature point (T_{cloud}). High hydrophilicity of the anion leads to high LCST T_{cloud} of phosphonium-based IL aqueous solution. For the same anion, the LCST T_{cloud} of di-cationic phosphonium-based IL is lower than that of mono-cationic phosphonium-based IL. In water-drawing potential, it is related to the osmolality and the viscosity of IL aqueous solution. Mono-cationic phosphonium-based IL aqueous solution with high osmolality and low viscosity has high water-drawing potential and water flux in FO test. After FO process, diluted IL draw solution is phase separated into IL-rich layer and water-rich layer above LCST. Phosphonium-based IL with low osmolality can lead to low residual IL content in water-rich layer.

Keywords: Forward osmosis; Lower critical solution temperature; Liquid-liquid phase separation; Thermoresponsive phosphonium-based ionic liquids; Water-drawing potential

1. Introduction

Forward osmosis (FO) is considered as an emerging membrane-based separation technology for wastewater treatment and water desalination. It is an osmotic water separation process that water flow from the feed solution side toward a membrane-separating the draw solution side. For wastewater treatment, the FO process can be used for the concentration and volume reduction of process wastewater.

For water desalination applications, the FO process can be coupled with reverse osmosis (RO) process or other membrane processes to produce pure water permeate [1,2].

The osmotic difference between the feed solution and draw solute solution is the driving force for water flow in the FO process. It is strongly dependent on the water-drawing potential of the draw solute in draw solution side. For getting suitable water flux, an appropriate water-drawing potential of the draw solute is required [3].

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Many materials are studied as the draw solutes for the FO process [4,5], including the thermolytic solution [6], inorganic salts [7], organic salts [8], water-soluble polymers [9], hydrophilic magnetic nanoparticles [10], switchable polarity solvent [11], and volatile dimethyl ether [12], etc.

Although the draw solute for the FO process has been intensively studied, recovery of draw solute, or water from the diluted draw solute solution is still a challenging topic. Theoretically, when we want to recover draw solute or water from the diluted draw solution, the dehydration process from the hydrated draw solute must be occurred. Low energy requirement for this dehydration process is expected.

Ionic liquids (ILs), which are organic salts in the liquid state with expected high osmotic pressure, have been proposed as a novel draw solute. Moreover, ILs are known as designer solvents since the physio-chemical properties of ILs can be widely tuned by a combination of different cations and anions [13]. A typical IL is composed of an organic cation and an inorganic or organic anion. The cations can be N,N-dialkylimidazolium, alkylpyridinium, alkylphosphonium, etc. The anions include carboxylate, tetrafluoroborate, or large organic anions such as bis-(trifluoromethanesulfonyl) amide, etc. [14]. In recent years, thermoresponsive ILs were tried to use as the draw solute for the FO [15,16]. Thermoresponsive ILs show the dynamic change of water solubility (liquid–liquid phase separation) during the temperature change. thermoresponsive ILs can be upper critical solution temperature (UCST) type or lower critical solution temperature (LCST) type [17]. In UCST type, the IL and water are immiscible below the critical temperature. It becomes to be a miscible and homogenous phase when the system is heated above a critical temperature. As to LCST-type, a homogeneous phase of the IL/water mixture can undergo to a separated phase upon heating above a critical temperature. The benefit of the thermoresponsive IL draw solute, especially for LCST type, is that the hydrated thermoresponsive IL draw solute in diluted draw solution can be dehydrated by the mild temperature change and then most of the draw solute or water can be easily recovered through liquid–liquid phase separation. Hence, besides water drawing potential, when the LCST-type thermoresponsive IL is used as the draw solute of FO process, its phase separation characteristics must be understood.

In considering the phase separation behaviors of LCST-type thermoresponsive ILs, many LCST type phosphonium cations with different anions, especially the amino acid type anions, were studied by Fukaya et al. [18]. They considered that the LCST cloud point temperature (T_{cloud}) of the phosphonium-based IL aqueous solution is related to the hydrophilicity/hydrophobicity balance of the cation/anion [19]. In addition to hydrophilicity/hydrophobicity balance of the cation/anion, the intramolecular interaction in anion or cation and the aggregation characteristics of the IL in water are another two factors affecting the LCST phase separation behaviors. The IL aggregate is the immediate state of a phase separation from a homogeneous phase to phase separation. In our previous study, we found that the IL aggregate characteristics related to phase separation type and phase separation time. Higher degree of aggregation of IL in aqueous solution leads to lower LCST T_{cloud} and shorter macroscopic phase separation time [20].

As to the water-drawing potential of the thermoresponsive ILs, the osmolality and the viscosity of its aqueous solution are two main affecting factors [21]. Research has shown that the concentration of draw solution have a great influence on its osmolality and viscosity [22]. For draw solutions with the same concentration, their osmolality is also related to the degree of ionic dissociation of the IL in aqueous solution [14]. Higher degree of ionic dissociation of thermoresponsive IL in aqueous solution can lead to higher osmolality. As to the viscosity of the draw solution, it can affect the water-drawing efficiency of the thermoresponsive IL draw solute in FO process. If the viscosity of the draw solution is too high, the water movement and the diffusion of the draw solute in the draw solution will be restricted, then the water flow from the feed solution side into draw solutions side will be decreased. The resulting water-drawing ability of the thermoresponsive IL draw solutes will be reduced.

In this study, the phase separation behaviors and water-drawing potential of the LCST type mono-cationic and di-cationic phosphonium-based IL draw solutes with several anions having different hydrophilicity, including p-toluenesulfonate (TSO), hydrogen maleate (Mal), and trimethylbenzenesulfonate (TMBS) were investigated. Some of these ILs used as the draw solutes for the FO process were conducted. In comparison to mono-cationic ILs, di-cationic ILs are more hydrophobic ILs having two monocations combined into one cation with an alkyl chain linker [23]. Hence, the hydrophobic effect of mono-cationic, di-cationic phosphonium, and the anion on the performance of the FO were also discussed. The present study can provide a more detailed scientific information about the LCST type thermoresponsive ILs used as the draw solute in the FO process.

2. Experimental

2.1. Ionic liquids

The chemical structures of the cations and anions of the ILs used in this study are shown in Fig. 1.

2.2. Synthesis and characterization of mono-cationic and di-cationic phosphonium-based ILs

2.2.1. Mono-cationic phosphonium-based IL

[P₄₄₄₄][hydrogen maleate](P1Mal)

The detailed preparation process and characterization method can be seen in our previous paper [20].

[P₄₄₄₄][p-toluenesulfonate] (P1TSO)

Tetrabutylphosphonium p-toluenesulfonate was supplied by Sigma-Aldrich Co., (United States).

2.2.2. Di-cationic phosphonium-based ILs

In this study, 1,8-octanediyl-bis(tri-n-butylphosphonium) dibromide was first prepared. 1,8-octanediyl-bis(tri-n-butylphosphonium)di(p-toluenesulfonate) and 1,8-octanediyl-bis(tri-n-butylphosphonium)di(2,4,6-trimethyl-benzenesulfonate) were then synthesized from 1,8-octanediyl-bis(tri-n-butylphosphonium) dibromide. The detailed

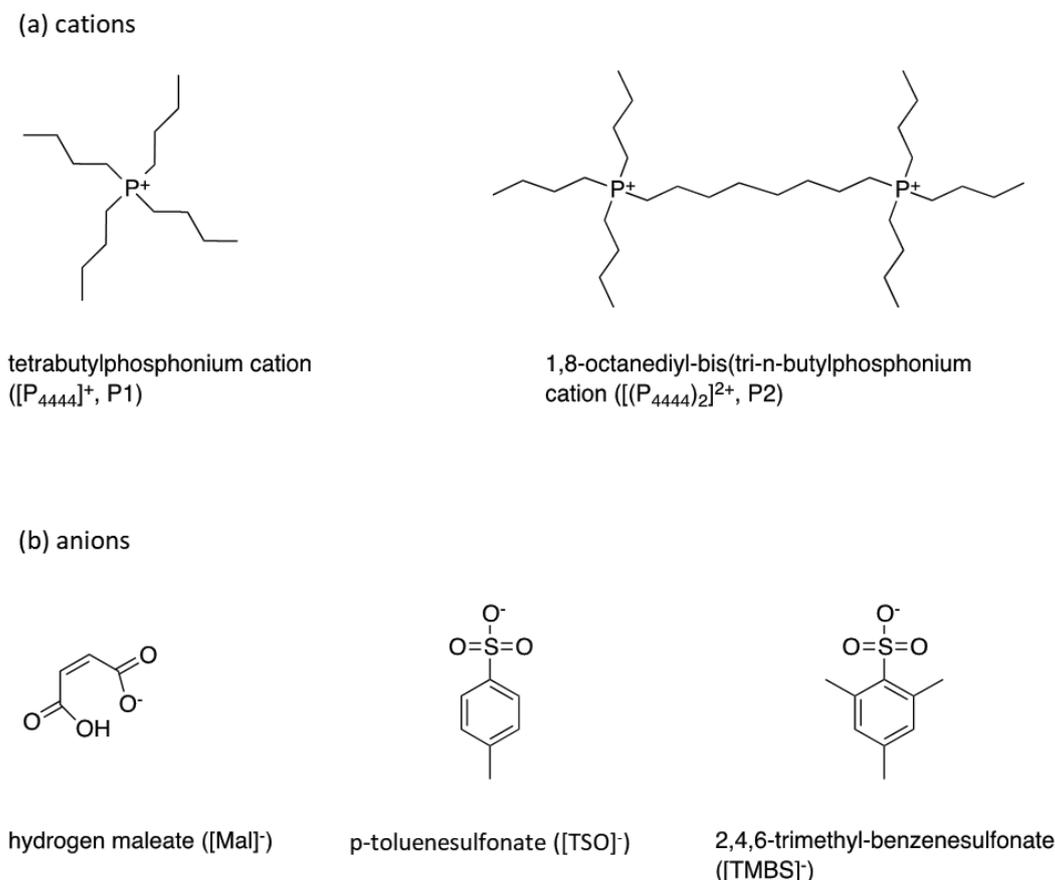


Fig. 1. Chemical structures of (a) cations and (b) anions of the IL used in this study.

preparation procedure of each compound is described as follow.

2.2.2.1. 1,8-octanediyl-bis(tri-n-butylphosphonium) dibromide (P2Br)

First, 80.0 g (0.4 mol) of tributylphosphine (Strem Chemical, U.S.A) and 48.9 g (0.18 mol) of 1,8-dibromooctane (Acros, U.S.A) were put into a 500 mL round bottom bottle. Then, 150 mL of anhydrous acetone was added and stirred at 40°C for 48 h. After the reaction finished, the resulting reaction solution was slowly dripped into 1.5 L of ether. The white solid powder was obtained after filtration, and then it was washed several times with ether. The washed white solid was dried and 117 g of product P2Br was obtained.

2.2.2.2. 1,8-octanediyl-bis(tri-n-butylphosphonium) di(p-toluenesulfonate) (P2TSO)

P2Br was converted to 1,8-octanediyl-bis(tri-n-butylphosphonium)dihydroxide) by using an ion exchange resin (hereinafter called P2OH for short). 6.40 g (32 wt.% in H₂O; 3.7 mmol) of P2OH and 1.41 g (7.4 mmol) of p-toluenesulfonic acid monohydrate (Alfa, U.K) were dissolved in 10.0 g of deionized water and stirred at room temperature for 12 h. After the reaction finished, the reaction

mixture was extracted with 10.0 mL of ethyl acetate two times. The organic layer was vacuum concentrated at 30°C, and yield 3.3 g (90%) of the product P2TSO was obtained. The product P2TSO was determined by ¹H NMR (400 MHz, δ , D₂O) (Varian Unity Inova 500 MHz NMR, Agilent, United States): 0.81 (t, 18H, CH₃CH₂-), 1.09 (m, 4H, -CH₂-), 1.1–1.5 (m, 32H, -CH₂-), 1.9–2.1 (t, 16H, PCH₂-), 2.25 (s, 6H, Ar-CH₃), 7.21 (d, 4H, Ar-H), and 7.58 (d, 4H, Ar-H). ¹³C NMR (400 MHz, δ , D₂O): 13.8 (CH₃CH₂CH₂CH₂P-), 18.9 (CH₃CH₂CH₂CH₂P-), 21.3 (2C, Ar-CH₃), 23.4 (di-branch -CH₂-), 25.6, 25.8 (CH₃CH₂CH₂CH₂P-), 25.6 (di-branch PCH₂-), 26.1, 29.3 (di-branch -CH₂-), 128.2 (4C, aromatic -CH-), 130.0 (aromatic -CH-), 139.4 (aromatic -C-), and 142.0 (aromatic -C-).

2.2.2.3. 1,8-octanediyl-bis(tri-n-butylphosphonium) di(2,4,6-trimethyl-benzenesulfonate) (P2TMBS)

P2Br was converted to 1,8-octanediyl-bis(tri-n-butylphosphonium)dihydroxide) by using an ion exchange resin (herein after called P₂OH). 31.08 g (32 wt.% in H₂O; 18.0 mmol) of P₂OH and 8.50 g (36.0 mmol) of 2,4,6-trimethylbenzene-sulfonic acid dihydrate (Alfa) were dissolved in 50.0 g of deionized water and stirred at room temperature for 12 h. After the reaction finished, the reaction mixture was extracted with 50 mL of ethyl acetate two times. The organic layer was vacuum concentrated at 30°C, and yield 15.4 g (92%) of the product P2TMBS was obtained.

The product P2TMBS was determined by ^1H NMR (400 MHz, δ , D_2O) (Varian Unity Inova 500 MHz NMR, Agilent): 0.80 (t, 18H, CH_3CH_2-), 1.09 (m, 4H, $-\text{CH}_2-$), 1.1–1.5 (m, 32H, $-\text{CH}_2-$), 1.9–2.0 (t, 16H, PCH_2-), 2.12 (s, 6H, $\text{Ar}-\text{CH}_3$), 2.25 (s, 12H, $\text{Ar}-\text{CH}_3$), and 6.88 (s, 4H, $\text{Ar}-\text{H}$). ^{13}C NMR (400 MHz, δ , D_2O): 13.8 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{P}-$), 18.9 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{P}-$), 21.9 ($\text{Ar}-\text{CH}_3$), 22.6 ($\text{Ar}-\text{CH}_3$), 23.4 (di-branch $-\text{CH}_2-$), 25.6 (di-branch PCH_2-), 25.6, 25.8 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{P}-$), 26.1, 29.3 (di-branch $-\text{CH}_2-$), 131.1 (aromatic $-\text{CH}-$), 137.4 (aromatic $-\text{C}-$), 139.0 (aromatic $-\text{CH}-$), and 140.3 (aromatic $-\text{C}-$).

2.3. Osmolality and solution viscosity measurement

The osmolality of a sample was determined by freezing point osmometry (OSMOMAT 030, GONOTEC, Germany). The viscosity of phosphonium-based ILs aqueous solution at different concentrations was measured by Brookfield viscometer.

2.4. LCST determination

Different concentrations of the phosphonium-based ILs aqueous solution were prepared. Each solution was stepwise heated from 25°C to 100°C , every 5°C for 10 min. When the distinct two-phase stratification was observed, the temperature point was defined as the cloud temperature point (T_{cloud}) of LCST.

2.5. FO test

A FO device was assembled for lab-scale tests, as shown in Fig. 2. A FO module was a plate and frame type. A flow channel design was dual-channel circulation type. A film was TW30-1812 with an effective area of 64 cm^2 (commercially available from Dow Co., U.S.A). Solutions were, respectively, introduced into the feed part and draw solution part by a pump and circulated in the feed part and draw solution part at a cross-flow rate of 25 cm/s . The weight of the feed part, the weight of the draw solution part, and the conductivity (Eutech Cyberscan CON 1500) at different time were logged by the computerized data acquisition system for each minute.

The FO water flux J_w was calculated by measuring the weight of the feed side:

$$J_w = \frac{\Delta m_{\text{feed}} / \rho_{\text{feed}}}{A_{\text{eff}} \times \Delta t} \quad (1)$$

where Δm_{feed} is the weight changes of the feed side; ρ_{feed} is the density of feed solution; A_{eff} is the effective membrane surface area and Δt is the measuring interval time.

3. Results and discussion

3.1. LCST behavior of mono-cationic and di-cationic phosphonium-based ILs

The LCST T_{cloud} of thermoresponsive IL aqueous solution is affected by the hydrophilicity/hydrophobicity balance of anion/cation part of the thermoresponsive IL. High hydrophilic thermoresponsive IL aqueous solution has high LCST T_{cloud} [19]. The LCST T_{cloud} of several mono-cationic and di-cationic phosphonium-based ILs at different IL concentrations in weight % (wt.%) is shown in Fig. 3.

The results of Fig. 3 reveal that the LCST T_{cloud} of the P1T5O aqueous solutions is higher than 50°C and the LCST T_{cloud} of the P1Mal aqueous solutions is around 25°C . The LCST T_{cloud} of the mono-cationic P1T5O aqueous solution is much higher than that of mono-cationic P1Mal aqueous solution at the same IL concentration. High LCST T_{cloud} of P1T5O aqueous solution is resulted from high hydrophilicity of the T5O anion [21]. On the other hand, in comparison to the mono-cationic phosphonium-based IL, P1T5O, the results in Fig. 3 also indicate that the lower LCST T_{cloud} is observed for di-cationic P2T5O aqueous solution. An increase in the alkyl chain length of cation in ILs can increase the hydrophobic character of ILs. Hence, the hydrophilicity of dicationic phosphonium-based IL will decrease and easy formation of interconnection aggregates in di-cationic IL solution. Lower LCST T_{cloud} value is then observed [24,25]. In di-cationic phosphonium-based ILs, the methyl groups in TMBS anion can decrease anionic hydrophilicity. Therefore, the LCST T_{cloud} of the P2TMBS

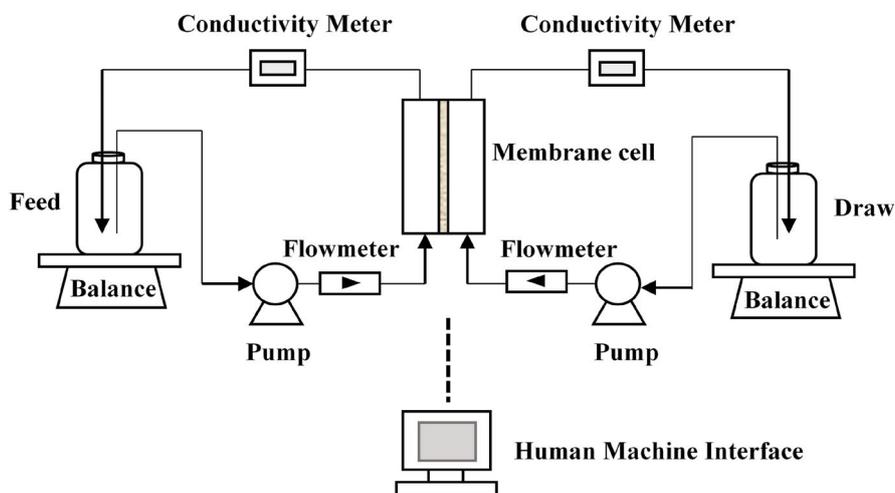


Fig. 2. Schematic diagram of plate type FO device.

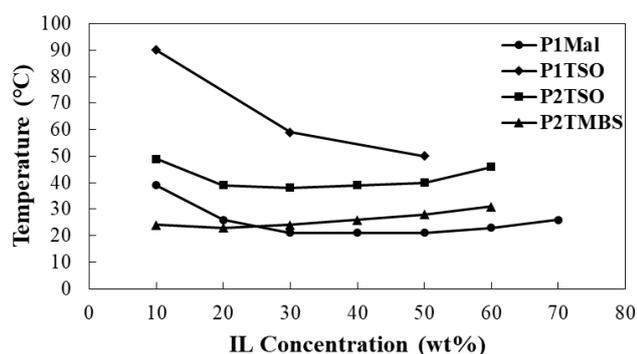


Fig. 3. T_{cloud} of several mono-cationic or di-cationic phosphonium-based ILs at different IL concentrations.

aqueous solution is lower than that of the P2TSO aqueous solution. The results of Fig. 3 reveal that the LCST T_{cloud} of P1Mal aqueous solution and P2TMBS aqueous solution are approximately similar. It is interesting to point out that the different phase separation characteristics of these two phosphonium-based ILs aqueous solution. The low LCST T_{cloud} values of P2TMBS aqueous solution is mainly resulted from more hydrophobic dication. However, the unexpected low LCST T_{cloud} value of P1Mal aqueous solution can be explained that the occurrence of strong intra-hydrogen bond at the anionic hydrogen maleate above LCST. The more hydrophobic P1Mal aggregates were then easily formed and phase separation can be triggered at lower temperature [20]. That is to say, when one of the anion/cation structures in phosphonium based ILs is apt to form hydrophobic IL aggregates, lower LCST T_{cloud} of phosphonium-based IL aqueous solution can be obtained.

3.2. FO performance study

In considering the practical requirement for the separation of draw solute or water from the diluted draw solution with lower energy consumption, three phosphonium-based IL draw solutes with lower T_{cloud} value (<50°C), P1Mal, P2TMBS, and P2TSO were further investigated in the following FO performance study. The investigation topics include water-drawing potential, water flux and residual IL in water-rich layer after phase separation by temperature change.

3.3. Water-drawing potential analysis

As described in introduction section, the osmolality and the viscosity of the IL draw solution are two factors affecting water-drawing potential of IL draw solute in aqueous solution. ILs with high hydrophobicity have low osmolality because of the formation of hydrophobic IL aggregate [21]. In di-cationic IL, increasing in the number of carbon chains of the cation can enhance its hydrophobicity and formation of IL interconnection aggregates [24,25]. Hence, in comparison to mono-cationic P1Mal, the osmolality of the di-cationic P2TSO will be lower at the same concentration of IL aqueous solution, as shown in Fig. 4. Similarly, the osmolality of the IL decreased with increasing anionic

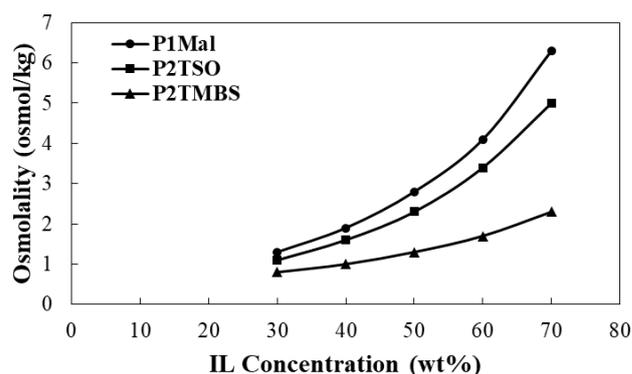


Fig. 4. Osmolality of the phosphonium-based IL aqueous solution at different concentrations.

hydrophobicity. The experimental result in Fig. 4 indicate that the osmolality of P2TMBS is lower than that of P2TSO.

Because ionic dissociation of thermoresponsive ILs in aqueous solution can lead to increasing solution conductivity [26]. It is interesting to investigate the solution conductivity of these three phosphonium-based ILs. The aqueous solution conductivity of three phosphonium-based ILs at different concentrations is shown in Fig. 5. Highest solution conductivity is observed for P1Mal and lowest solution conductivity for P2TMBS. The solution conductivity results in Fig. 5 show the same behavior with osmolality results shown in Fig. 4.

The aqueous solution viscosity of the thermoresponsive IL draw solution can affect the water-drawing efficiency of thermoresponsive IL in aqueous solution. The aqueous solution viscosity of these three phosphonium-based ILs at different concentrations is shown in Fig. 6. The results in Fig. 6 shows that the aqueous solution viscosity of di-cationic phosphonium-based IL is higher than that of mono-cationic phosphonium-based IL at high IL concentration. Below the concentration of 50 wt.%, the aqueous solution viscosity of three phosphonium-based IL are approximately the same. The results of Figs. 4 and 6 indicate that mono-cationic P1Mal has highest water-drawing potential owing to its highest osmolality and the lowest aqueous solution viscosity. As to these two di-cationic phosphonium-based ILs, di-cationic P2TSO has higher water-drawing potential.

3.4. Water flux

The water flux for three phosphonium-based IL draw solutions at the concentration of 70 and 50 wt.% is shown in Fig. 7. The feed solution is deionized water. As to almost the same aqueous solution viscosity of P2TSO and P2TMBS at the concentration of 70 wt.% and the higher osmolality for P2TSO, we can see that the water flux of P2TSO is higher than that of P2TMBS, shown in Fig. 7a. In Fig. 7a, it is also observed that the water flux of P1Mal with 3.5 LMH is higher than that of P2TSO and P2TMBS. Higher water flux of P1Mal is resulted from higher water-drawing potential (higher osmolality and lower aqueous solution viscosity). In Fig. 7b, at the concentration of 50 wt.%, the same water flux (around 2.5 LMH) is observed for P1Mal and P2TSO.

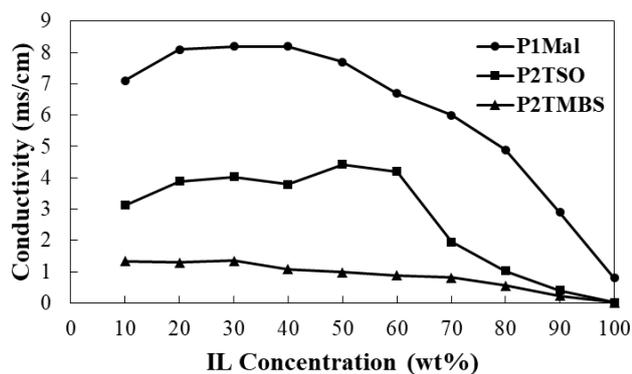


Fig. 5. Conductivity of the phosphonium-based IL aqueous solution at different concentrations

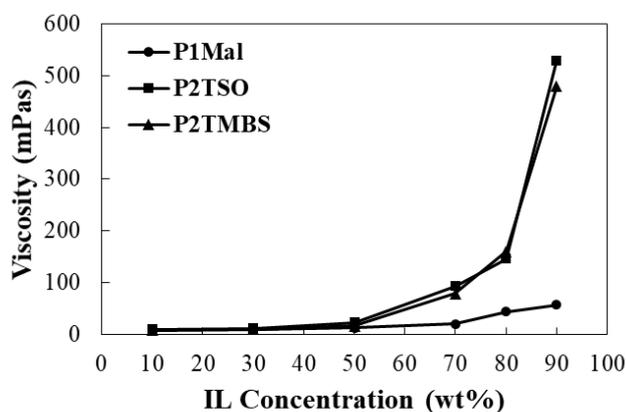


Fig. 6. Viscosity of the phosphonium-based IL aqueous solution at different concentrations.

This is due to the almost same osmolality and aqueous solution viscosity. However, the water flux of P2TMBS (lowest osmolality) is below 2 LMH.

3.5. Residual ionic liquid in water-rich layer

At the end of FO process, the diluted phosphonium ionic liquid draw solution is phase separated into two distinct ionic liquid-rich layer and water-rich layer at temperature above LCST. For getting pure water, the residual ionic liquid in water-rich layer can be removed by further membrane separation process. Table 1 lists the residual ionic liquid content in water-rich layer of three phosphonium ionic liquids at the aqueous solution concentration of 50 wt.% and different temperatures. It can be seen that lower residual ionic liquid content in water-rich layer is observed at higher temperature. In Table 1, it is also seen that the phosphonium based ionic liquid with high osmolality has high residual ionic liquid content. The residual ionic liquid content for P1Mal and P2TSO are almost the same value. In contrast, very low residual ionic liquid content is observed for P2TMBS. Hence, there is a trade-off between high water flux and lower residual ionic liquid content in water-rich layer.

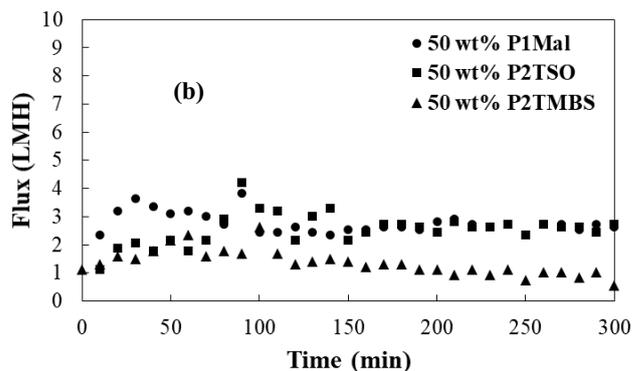
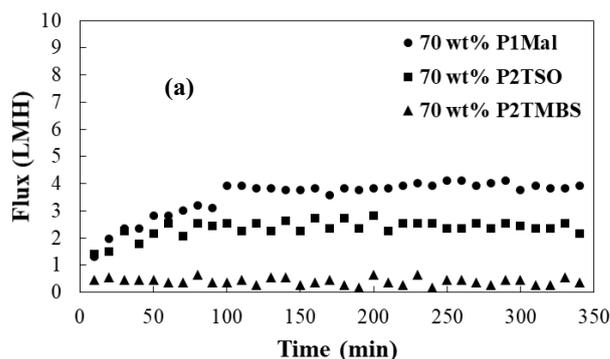


Fig. 7. (a and b) Water flux for FO process utilizing 70 and 50 wt.% phosphonium-based IL aqueous solution as draw solution and feed part was deionized water at 25°C.

Table 1

Residual ionic liquid content in water-rich layer for three phosphonium ionic liquid draw solutes at concentration of 50 wt.% and different temperatures

Temperature	P1Mal (wt.%)	P2TMBS (wt.%)	P2TOS (wt.%)
25°C	21.5	5.3	— ^a
30°C	18.5	3.8	— ^a
35°C	16.1	2.4	16.1
40°C	15.2	1.5	13.5

^ano phase separation

4. Conclusion

In this study, the phase separation behaviors and water-drawing potential of LCST type mono-cationic and di-cationic phosphonium-based IL draw solutes with different anions were investigated. In phase separation behaviors, the hydrophilicity and structure chemistry of cation/anion can affect the LCST T_{cloud} . High hydrophilic phosphonium-based IL aqueous solution has high LCST T_{cloud} . When the cation or anion structure of the phosphonium-based ILs is apt to form hydrophobic IL aggregates, lower LCST T_{cloud} can be obtained. For the same anion, the LCST T_{cloud} of di-cationic phosphonium-based IL is lower than that of mono-cationic phosphonium-based IL. In water-drawing potential, mono-cationic phosphonium-based IL with high osmolality and the low aqueous solution viscosity has high

water-drawing potential. In FO test, higher water flux and high residual IL content in water-rich layer are observed for phosphonium-based IL draw solutes with higher osmolality. In contrast, very low residual IL content is observed for phosphonium-based IL draw solute with low osmolality (P2TMBS). There is a trade-off between high water flux and lower residual IL content in water-rich layer.

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