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Insight into the water recovery characteristics of tetrabutylphosphonium hydrogen maleate ionic liquid draw solute in forward osmosis process

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ABSTRACT

In forward osmosis (FO) water desalination process, water recovery from diluted draw solute solution is an important issue. In this study, the water recovery characteristics of the thermo-responsive tetrabutylphosphonium hydrogen maleate [[P_{4444}][hydrogen maleate]] ionic liquid draw solute and its lower critical solution temperature (LCST) phase separation type were investigated. Above LCST, the hydrated thermo-responsive ionic liquid draw solute can be dehydrated. In [[P_{4444}][hydrogen maleate]] ionic liquid, it was considered that the dehydrated hydrogen maleate anion can form the intramolecular hydrogen bond, and then macroscopic phase separation was triggered. For water recovery economically, the LCST macroscopic phase separation and two distinct phases should be completed in a definite time. The macroscopic phase separation time to two distinct phases is dependent on temperature and the water content. Shorter time was observed at higher temperature and water content. In FO test with the [[P_{4444}][hydrogen maleate]] draw solute, an average water flux of 3.43 LMH is maintained at 25°C in our experimental condition. The J_s/J_w of 2.23 g/L was observed. The technical advantage is that the ionic liquid layer can be directly reused, and the recovery of water is conducted from the water-rich supernatants.

Keywords: Forward osmosis; Lower critical solution temperature; Macroscopic phase separation; Thermo-responsive ionic liquid; Water desalination

1. Introduction

Forward osmosis (FO) process is considered as an emerging membrane-based desalination technology for seawater and brackish wastewater. The operation principle of the FO is the osmotic pressure difference between the draw solute solution and the feed solution, separated by a membrane, which allows the water flow from the feed solution side toward the draw solute solution side [1,2]. Many materials are studied as the draw solute for the FO process [3,4], including the thermolytic solution [5], inorganic salts [6], organic salts [7], water soluble polymers [8], hydrophilic magnetic nanoparticles [9], switchable polarity solvent [10], volatile dimethyl ether [11], etc.

Although the draw solute for the FO process has been intensively studied, the water recovery from the diluted draw solute solution is still a challenging issue. Many recovery methods are reported in the literature. They include thermal recovery method [12], hydraulic pressure membrane recovery method [13], magnetic field recovery method [14], precipitation recovery method [15], etc. For FO recovery process, the high recovery of draw solute does not equal to the high water

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recovery. For example, a recovery study from diluted draw solution by ultrafiltration membrane was reported in a study by Ge et al. [8]. It was found that high recovery of draw solute can be obtained but the recovered water flux decreases with increasing concentration of the diluted draw solution.

In theory, when we want to recover water from the diluted draw solute solution, the dehydration from the hydrated draw solute must be triggered. The precipitation recovery method and the thermal recovery method are two examples of water recovery through dehydration. In copper sulfate draw solute solution, the water can be recovered by the precipitation reaction of copper sulfate with barium hydroxide [15]. The water recovery of the switchable polarity solvent draw solute solution is a good example of thermal recovery method. The water can be mechanically separated from the switchable polarity solvent by addition of carbon dioxide under mild heating [10]. The membrane distillation is also studied to recover water through dehydration from the diluted draw solute solution [16].

In recent years, the thermo-responsive compound has been highly expected as the draw solute for FO process because it can recover water through dehydration by the temperature change [4,17]. The thermo-responsive polymers are studied as the draw solutes for the FO process by some researchers [18,19]. However, the high solution viscosity makes it separate difficultly. In addition to the thermo-responsive polymers, the low viscosity thermo-responsive ionic liquids were tried to use as the draw solutes for the FO process [20]. Ionic liquid is a liquid organic salt at room temperature. It composes of organic cation and 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. [21]. Ionic liquid can be hydrophilic or hydrophobic depending on its static water solubility. However, the thermo-responsive ionic liquid shows dynamic change of water solubility (liquid–liquid phase separation) by the temperature change [22]. Similar to hydrophilic ionic liquid, the thermo-responsive ionic liquid aqueous solution can also dissociate to produce ionic species at initial water concentration ranges and has the initial increase in solution conductivity and osmotic strength [23]. In FO application, such increasing osmosis strength can compensate the decreasing osmotic strength of the draw solute solution by water dilution. These properties make the thermo-responsive ionic liquid be advantageously used as the draw solute for the FO process.

Thermo-responsive ionic liquid aqueous solution can be the upper critical solution temperature (UCST) type or the lower critical solution temperature (LCST) type [22]. In UCST type, the ionic liquid and water are immiscible below the critical temperature. As to LCST type, a homogeneous phase of the ionic liquid/water mixture can undergo a separated phase upon heating above a critical temperature. The LCST phase separation behavior of aqueous solution for many thermo-responsive ionic liquids, especially for the [P_{4444}]-based ionic liquid, is deeply investigated by the Kohno and Ohno [24]. Up to now, only a few thermo-responsive ionic liquid papers for FO application are reported in literature. Zhong et al. [25] studied the UCST-type thermo-responsive ionic liquid used as the draw solutes for the FO process. The LCST-type thermo-responsive ionic liquid used as the draw solute for FO process was first reported by Cai et al. [20]. In their work, the observed LCST was between 30°C–50°C for the tetrabutylphosphonium 2,4-dimethylbenzenesulfonate and tetrabutylphosphonium mesitylenesulfonate ionic liquids. However, the water recovery characteristics and the phase separation type were not mentioned in their work.

The liquid–liquid phase separation type can be macroscopic phase separation or microscopic phase separation. In considering the economic application of FO process, it is highly expected that the LCST-type thermo-responsive ionic liquid having macroscopic phase separation, and the phase separation time to two distinct clear phases can also be short if possible. In this study, the LCST-type thermo-responsive [P_{4444}][hydrogen maleate] ionic liquid was synthesized. Its aqueous solution behaviors and the LCST phase separation type were investigated. The water content and temperature effect on the LCST were studied to investigate the appropriate water content and temperature, where the macroscopic phase transition can be achieved. The phase separation time was also determined. Finally, the thermo-responsive [P_{4444}][hydrogen maleate] ionic liquid used as the draw solute for the FO process is demonstrated and briefly discussed.

2. Experimental

2.1. Synthesis and characterization of the [P_{4444}][hydrogen maleate]

[P_{4444}][hydrogen maleate] was obtained by mixing the tetrabutylphosphonium hydroxide[P_{4444}][OH] aqueous solution (Alfa Aesar, United States), (41.6 wt% in water) and maleic acid (Vetec Quimica, United States) with mole ratio of 1:1. The mixture was stirred for 24 h at room temperature. The crude product was extracted with dicloromethane, and then vacuum distillation was performed for removing the residual moisture or dicloromethane. The structures of the produced [P_{4444}][hydrogen maleate] was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy (Varian Unity Inova 500 MHz nuclear magnetic resonance spectroscopy, Agilent, United States). The test samples for NMR analysis were prepared by ultrasonic mixing the suitable amount of [P_{4444}][hydrogen maleate] with D_2O in NMR tube at room temperature. The ^{1}H NMR was operated with pulse 45.0° and an acquisition time of 2.048 s at 25°C, and the ^{13}C NMR was operated with pulse 30.0° and acquisition time of 1.041 s at 25°C. (12H, t, CH_2CH_3), 1.40–1.57 (16H, m, CH_2CH_3), 2.10–2.17 (8H, m, $-P^+-CH_2CH_2$), 6.33 (2H, s, CH = CH) ppm. ^{13}C NMR (500 MHz, D_2O) d = 12.72 (s, $-P^+-CH_2CH_2CH_2CH_3$), 17.44 (s, $-P^+-CH_2CH_2CH_2CH_3$), 22.90 (d, $-P^+-CH_2CH_2CH_2CH_3$), 135.61 (s, –CH(COOH)), 168.83 (s, –CH(COO)) ppm.(Fig. S1). The chemical shift of each peak in ^{1}H NMR spectrum matches with the values of the spectrum peaks reported in a study by Fukaya et al. [22]. [P_{4444}][hydrogen maleate] has been successfully synthesized. The viscosity of [P_{4444}][hydrogen maleate] aqueous solution at some different concentrations was measured by Brookfield viscometer. The measured viscosity at the concentration of 80 and 70 wt% was 44.4 and 20.2 mPas (Table S1).

2.2. LCST determination with macroscopic phase separation

Different concentrations of the [P_{4444}][hydrogen maleate] 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 LCST with macroscopic phase separation.

2.3. FO test

A FO device was assembled in our laboratory, as shown in Fig. 1. An 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-Filmtec Co., United States). Solutions were, respectively, introduced into the feed part and draw solution part by a pump, and they circulated in the feed part (deionized water) 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 (SUNTEX EC-410) at different time were logged by the computerized data acquisition system for each minute.

The FO performances including water flux and draw solute flux were evaluated. The FO water flux J_w was calculated by measuring the weight of the feed side:

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

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.

The solute flux J_s was calculated by measuring the conductivity of the feed side:

$$J_s = \frac{m_{\text{feed},t} / \rho_{\text{feed}} \times C_t - m_{\text{feed},0} / \rho_{\text{feed}} \times C_0}{A_{\text{eff}} \times \Delta t} \tag{2}$$

where $m_{\text{feed},t}$ and $m_{\text{feed},0}$ are the weight of the feed side at certain and beginning time; and C_t and C_0 are the concentrations of the solute in the feed side at certain and beginning time. The J_s/J_w index is referred to the specific reverse salt flux, which is the solute flux normalized by water flux.

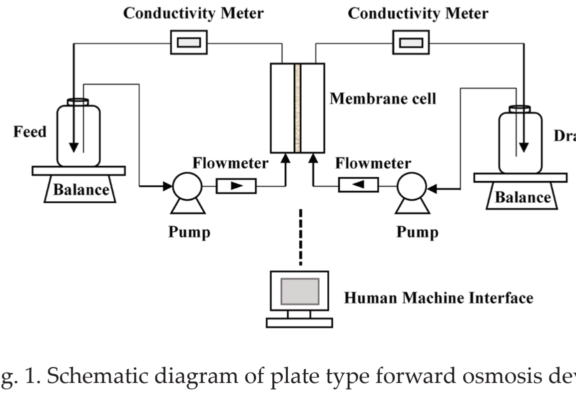


Fig. 1. Schematic diagram of plate type forward osmosis device.

3. Results and discussion

3.1. The conductivity and the osmotic strength of the [P$_{4444}$] [hydrogen maleate] aqueous solution

In bulk state, most of the thermo-responsive hydrophilic ionic liquid molecules are existed as aggregates. The aggregates have a tendency to form large agglomerates due to the hydrophobic interaction between the alkyl chains of the cations. Hence, the conductivity of the bulk ionic liquid system is low [21]. As described above, when the water is added, the anion of ionic liquid can interact with water molecule through the hydrogen bonding. The ionic liquid can dissociate to produce two ionic species and the conductivity of the aqueous solution increases. The conductivity of the [P$_{4444}$][hydrogen maleate] aqueous solution at different water concentrations is shown in Fig. 2. As shown in Fig. 2, the solution conductivity is only about 3 mS/cm at the water content of 10%. However, the solution conductivity increases with increasing the amount of the added water and up to a maximum. It shows a typical conductivity behavior of the conventional hydrophilic ionic liquid aqueous solution [23]. Osmotic strength is a function of the dissolved ion concentration in aqueous solution (can be expressed as conductivity). Hence, the initial osmotic strength with increasing initial water concentration ranges can be expected in the [P$_{4444}$][hydrogen maleate] ionic liquid aqueous solution. These properties make [P$_{4444}$][hydrogen maleate] be considered to use as the draw solute for the FO process.

3.2. The general picture of the LCST phase separation for the thermo-responsive ionic liquid aqueous solution

Before discussing the LCST phase separation type of the [P$_{4444}$][hydrogen maleate] ionic liquid aqueous solution, let us first describe the general picture of the LCST phase separation physical chemistry of the thermo-responsive ionic liquid aqueous solution. The LCST phase transition is kinetically driven aggregation process. The first step of the LCST phase separation is the dehydration of hydrated ionic liquid induced by heat, and then aggregation of the dehydrated ionic liquid is triggered. Different aggregate morphology and characteristics can be achieved for different thermo-responsive ionic liquids. The type of LCST phase separation of the thermo-responsive ionic liquid aqueous solution can undergo macroscopic or microscopic phase separation. Whether the LCST phase

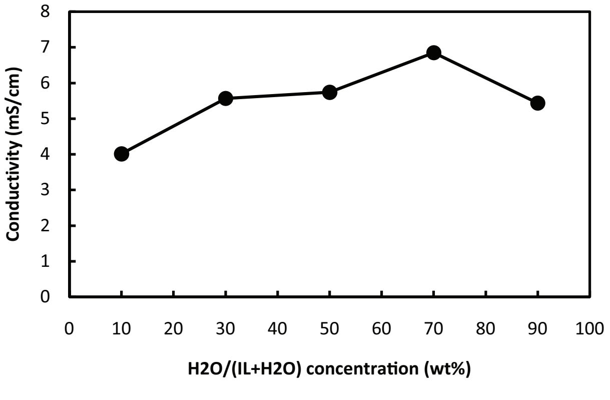


Fig. 2. The conductivity of the [P$_{4444}$][hydrogen maleate] ionic liquid aqueous solution at different water contents.

separation can undergo macroscopic or microscopic phase separation is dependent upon the characteristics of the aggregates. The main question is that the initial formed aggregates being small and stable with time or apt to form larger hydrophobic aggregates. For example, the thermo-responsive $[P_{4444}][CF_3COO]$ ionic liquid, the $[P_{4444}][CF_3COO]$ molecules can form long-living microemulsion-like aggregates in aqueous solution above LCST [26]. The number of water molecules around the $[P_{4444}][CF_3COO]$ ionic liquids are still high [27]. In such case, microscopic phase separation can be occurred. The phase separation time to two distinct phases is very long. On the contrary, the association of larger hydrophobic aggregates can result in macroscopic phase separation at a definite time. In FO process, for getting economic water recovery from the diluted draw solute solution, it is preferred that macroscopic phase separation to two distinct phases can be completed in a short time.

3.3. The LCST phase separation type and the water recovery characteristics of diluted [P4444][hydrogen maleate] aqueous solution: the formation of intramolecular hydrogen bond

Let us first talk about the LCST macroscopic phase separation of thermo-responsive poly(*n*-isopropylacrylamide (pNIPAAm) aqueous solution. Its LCST is about 32°C at the water concentration of 0.5% (w/v) [28]. The specific characteristics of this polymer are the presence of hydrophobic isopropyl group. Above LCST, the polymer chains can be collapsed. It is noted that the formation of an intramolecular C=O···H–N hydrogen bond in *N*-isopropylamide leads to the collapse of the polymer chain. Higher hydrophobic association of the collapsed polymer chain can also strengthen the water–water hydrogen bond of dehydrated water around the polymer chain and finally macroscopic phase separation will be observed [29].

The LCST phase separation of the thermo-responsive ionic liquid aqueous solution is the functional combination of the hydrophobic cation and the suitable hydrophilic anion [24]. Similar to the pNIPAAm, for a specific hydrophobic cation, the LCST macroscopic phase separation of the thermo-responsive ionic liquid aqueous solutions can be occurred if the anion of this thermo-responsive ionic liquid has ability of forming intramolecular hydrogen bond. Because the lower compatibility of such dehydrated ionic liquid with water and the greater degree of water–water hydrogen bonding interactions, macroscopic phase separation for some water concentration can be expected.

The phase separation behavior of the $[P_{4444}]$[hydrogen maleate] aqueous solution was studied by Fukaya et al. [22] and the LCST behavior was observed. However, the LCST phase separation type is not mentioned in their works [22]. In bulk $[P_{4444}]$[hydrogen maleate] ionic liquid, in addition to the electrostatic interactions between the $[P_{4444}]$ cation and the [hydrogen maleate] anion, there also exists an intrahydrogen bond in hydrogen maleate anion. It is the O–H…O⁻ intramolecular hydrogen bonding between the hydrogen of carboxylic acid group and the carboxylate anion [30]. When the water is added, the $[P_{4444}]$[hydrogen maleate] ionic liquids are hydrated. In hydrated $[P_{4444}]$[hydrogen maleate], the water molecules are interhydrogen bonded to $[P_{4444}]$[hydrogen maleate] mainly through the O–H or O=C of the maleate anion [31]. In $[P_{4444}]$[hydrogen maleate] ionic liquid aqueous solution, it is thought that the carboxylate group of hydrogen maleate anion is one of important factors affecting the aggregation characteristics and the LCST phase transition behaviors. Below LCST, the –COO⁻ or –COOH group of the hydrogen maleate anion could form intermolecular hydrogen bond with the water molecules. However, above LCST, the interhydrogen bond can be ruptured and the water molecules around anion are released. The –COOH group of dehydrated anion could form intrahydrogen bond with its –COO⁻ group and then aggregate with $[P_{4444}]^+$ cation. Most of the water molecules around $[P_{4444}]$ cation domain then release into the bulk. When the amount of these dehydrated $[P_{4444}]$[hydrogen maleate] aggregates increase, the hydrophobic association among dehydrated $[P_{4444}]$[hydrogen maleate] aggregates can be triggered.. Finally, LCST-type macroscopic phase transition with two distinct phases was observed. The LCST of $[P_{4444}]$[hydrogen maleate] aqueous solution varies with the water content. When the water concentration increases, the tendency of macroscopic phase separation is enhanced. As shown in Fig. 3 and Table 1, it can be seen that the lower LCST was observed at water concentration of 40–70 wt%. The tendency of macroscopic phase separation can be also enhanced when temperature and water content increase. The time for forming two stable and distinct phases becomes to be shorter, as shown in Tables 2 and 3. At water content of 30 wt%, the LCST is above 25°C, two types of $[P_{4444}]$[hydrogen maleate], that is, the hydrated and naked $[P_{4444}]$[hydrogen maleate], exist simultaneously at 25°C. The difference in refractive indices for these two types of $[P_{4444}]$[hydrogen maleate] causes light to scatter and the solution to appear cloudy. Moreover, when the concentration of $[P_{4444}]$[hydrogen maleate] is less than 30 wt% of ionic liquid, the ionic liquid phase becomes to be dispersed phase. The system shows evident clear state again.

3.4. FO test

FO test for the $[P_{4444}]$[hydrogen maleate] ionic liquid draw solute with the concentration of 70 wt% was conducted at 25°C. As shown in Fig. 4. The average water flux was 3.43 LMH. It can be seen that an acceptable J_s/J_w of 2.23 g/L can be observed. When the system is operated, the water molecule in feed solution side continuously flows into the draw solution side. The solution conductivity and the water flux

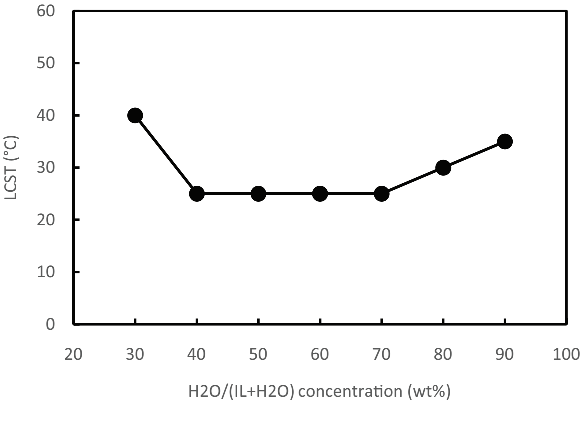


Fig. 3. The LCST phase transition temperature of the $[P_{4444}]$[hydrogen maleate] ionic liquid aqueous solution at different water contents.

Table 1
Phase transition photos of the [P_{4444}][hydrogen maleate] ionic liquid solution at different water concentrations and 25°C (each photo was taken after standing 10 min)

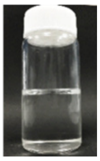
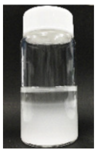
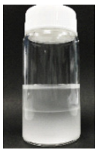
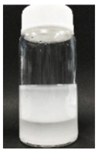
Water content (wt%)	20	30	40	50	60	70	80
Photo							
Phase separation	No	No	Yes	Yes	Yes	Yes	No

Table 2
The time forming two distinct phases at different temperature

Temperature (°C)	Time forming two distinct phases (*s*)
25	733
30	623
35	471
40	318

Note: 50 wt% [P_{4444}][hydrogen maleate] (40 mL).

Table 3
The time forming two distinct phases at different ionic liquid concentrations

Concentration (wt%)	Time forming two distinct phases (*s*)
40	590
50	733
60	820

Note: 25°C, 40 mL [P4444][hydrogen maleate].

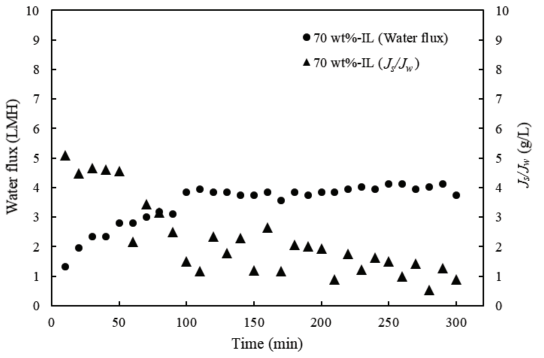


Fig. 4. The water flux and J_s/J_w for FO process utilizing 70 wt% [P_{4444}][hydrogen maleate] aqueous solution as draw solution and feed part was deiomized water at 25°C.

increased with increasing time, shown in Fig. 5. As described above, the initial increasing conductivity and osmotic strength of [P_{4444}][hydrogen maleate] ionic liquid aqueous solution can compensate the water dilution effect of the draw solute solution. Hence, we can achieve a stable flux at our experimental condition. FO performance for other weight percentages (50%, 60%, and 80%) can be seen in Fig. S2.

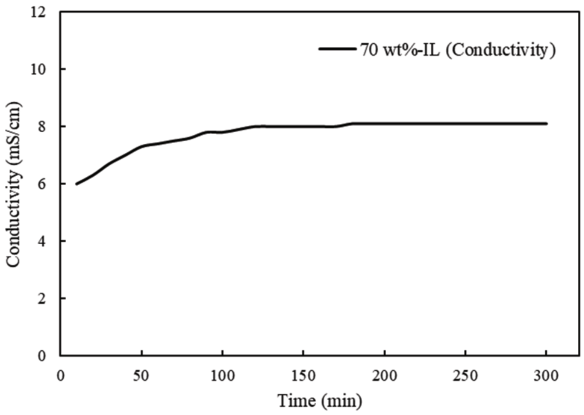


Fig. 5. Conductivity change in draw solution side for the FO process utilizing 70 wt% [P_{4444}][hydrogen maleate] aqueous solution as initial draw solute solution.

Fig. 6. Two clear distinct phases were observed after standing for some time.

In FO test, the LCST macroscopic phase separation and two distinct phases were observed after standing for some time, as shown in Fig. 6. Apparently, the technical advantage of [P_{4444}][hydrogen maleate] ionic liquid draw solute is that most of the ionic liquids can be removed easily after LCST macroscopic phase separation. The ionic liquid-rich sediment after LCST phase separation can be directly reused. In addition, the recovery of water is conducted from water-rich supernatants instead of whole diluted draw solution.

4. Conclusion

In this study, the water recovery characteristics and the LCST phase separation of thermo-responsive [P_{4444}][hydrogen maleate] ionic liquid draw solute were investigated. Above LCST, the dehydrated hydrogen maleate anion can form the intramolecular hydrogen bond before the occurrence of macroscopic phase separation. It was found that macroscopic phase separation and two distinct phases can be completed in a definite time. The macroscopic phase separation time to two distinct phases depends on water content and temperature. In FO test with the initial concentration of 70 wt%, a stable water flux of 3.43 LMH can be maintained and an acceptable J_s/J_w of 2.23 g/L can be observed. The technical advantage of LCST type of thermo-responsive ionic liquid is that ionic liquid layer can be directly reused and the recovery of water is conducted from water-rich supernatants.

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Supplementary information

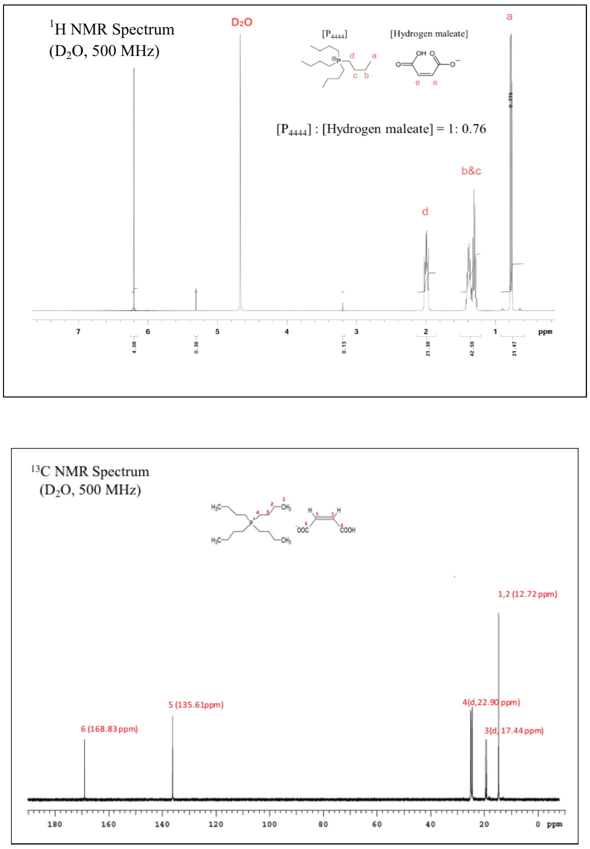

Fig. S1. (a) ^{1}H NMR (D$_2$O, 500 MHz) and (b) ^{13}C NMR (D$_2$O, 500 MHz) spectra of [P$_{4444}$][hydrogen maleate].

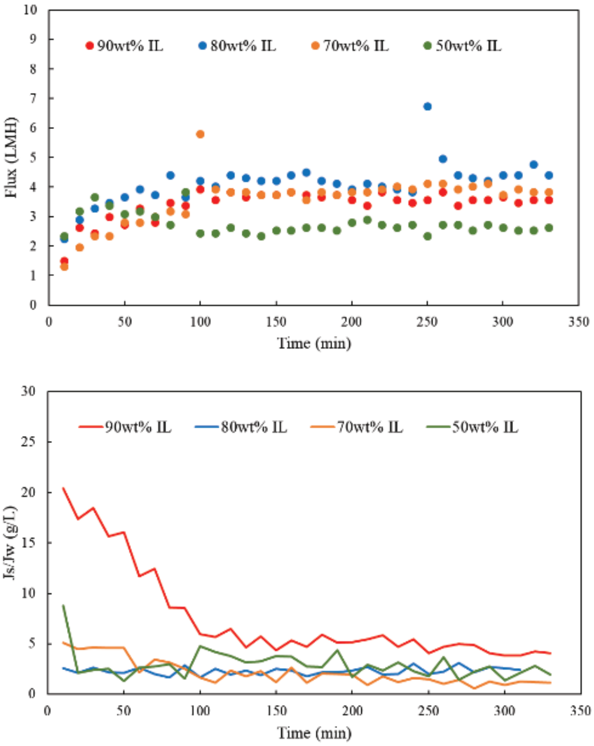

Fig. S2. The FO performance of different IL weight percentages: IL concentration of 80 wt% has higher flux of 4.2 LMH and an acceptable J_s/J_w of 2.30 g/L.

Table S1
The measured viscosity of [P$_{4444}$][hydrogen maleate]aqueous solution at different concentrations

Concentration (wt%)	10%	30%	50%	70%	80%	90%	100%
P$_1$Mal	8.3	9.3	13.2	20.2	44.4	57.3	123

Note: The measured viscosity of [P4444][hydrogen maleate] aqueous solution is 20.2 mPas (at 70 wt%) (measured by Lamy Rheology – RM100 viscometer). Lower viscosity can be found at the concentration below 70 wt%, which is a range we apply.