

A glance on thermo-responsive ionic liquids as draw solution in forward osmosis system

Mohd Amirul Mukmin Abdullah, Muhammad Suhaimi Man, Syamsul B. Abdullah*, Syed Mohd Saufi

Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Gambang Campus, Lebuhraya Tun Razak, 26300 Kuantan, Pahang Darul Makmur, Malaysia, email: syamsul@ump.edu.my (S.B. Abdullah)

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ABSTRACT

The promising forward osmosis (FO) membrane desalination is viewed as a potentially viable energy-efficient performance technology compared to other techniques. But, the core problem in the FO process is the absence of appropriate draw solutes that can be effectively regenerated. Thermoresponsive materials are thus attractive to draw solutes to promote in realizing this target. Among those, thermoresponsive ionic liquids stand out as prominent candidates as their ionic nature generally pledge a high osmotic pressure. The water flux achieved in the FO process indicated there indeed still a need for a better approach in identifying an ideal draw solution. Besides water flux, the attempt to clarify the factor that effect FO performance such as osmotic pressure, operating conditions and membrane selection yet vague. Due to a large number of possible ionic liquids (ILs) combination, there are several prediction methods in screening a potential ILs before synthesis instigated. Finally, the conclusions and important summaries were presented according to the data collected.

Keywords: Forward osmosis; Desalination; Draw solution; Ionic liquids

1. Introduction

Desalination by forward osmosis (FO) has recently attracted much attention owing to its advantages such as operating at low hydraulic pressure and low membrane fouling propensity [1–5]. FO is a membrane-based separation process that uses the osmotic pressure gradient between a concentrated draw solution and a feed stream to drive water flux across a semi-permeable membrane [6]. The miscibility of draw solute in water is the main challenge in the FO process because the draw solute should be prepared to considerably decrease the chemical potential of water and thus achieve high osmotic pressure. Besides that, the draw solute regeneration needs more deliberation in order to find an easily regenerate the draw solute to produce water and to reuse it [7,8].

There are two main categories of draw solution: responsive and non-responsive draw solute. Non-responsive draw solute is no response to any internal or external stimuli such as pH, light, temperature, or electromagnetic field and has no noteworthy change in their water affinity after stimulated. Conventionally, in employing mineral salts such as NaCl, $(\text{NH}_4)_2\text{SO}_4$, MgCl_2 , KHCO_3 , Na_2SO_4 , $\text{Ca}(\text{NO}_3)_2$, and other organic compounds which have been initially identified as non-responsive draw solutes [9–13]. On the other hand, responsive draw solute refers to draw solution that significantly reduces the osmotic pressure of the diluted draw solute upon contact with internal stimuli such as pH, light, temperature, or electromagnetic field [12]. This class of smart draw solute can make regeneration easily and efficiently while the drawing ability remains adequately high.

* Corresponding author.

Recently, draw solutes based on temperature-sensitive or thermo-responsive compounds have been meticulously studied due to their exceptional response to temperature, the limited chemical usage and have unlimited potential to use green energy and cost-effective such as low-grade industrial waste heat and solar thermal energy [13,14]. Many compounds have been recommended as thermally responsive draw solutes, including magnetic nanoparticles [15–17], polymers [16,18–20], hydrogels [21–24], micro-gels [25,26] and ionic liquids (ILs) [27–31]. These draw solutes also can be regenerated by various approaches, and they have certain advantages; however, they also involve significant drawbacks.

A few review papers have discussed the draw solution advancement and recovery in the FO process [32–35]. In the present paper, the current attempt is to review the application of thermoresponsive ionic liquids (TRILs) as a draw solution in enhancing water flux with other parameters that affect the FO performance and their recovery method in much more details. To the best of authors' knowledge, there is no comprehensive literature on the subject focusing TRILs. Herein the review of TRILs' development as a draw solute that consists of upper critical solution temperature (UCST) and lower critical solution temperature (LCST) needed for further deeds. Besides that, in this review, we propose a group contribution method (GCM) to calculate the Van't Hoff factor (i) value without using any experimental data. Yet, no attempts have been made to apply these methods to estimate i value of the TRILs.

2. Ionic liquid

Traditionally ILs are known as molten salts that archetypally liquid at a temperature below 100°C in atmospheric pressure. The progress of new research areas on ILs is due to their unique properties such as chemical and thermal stability, negligible vapor pressure (non-volatile), high ionic conductivity, high solubility and non-flammability [36–43]. Many unsafe volatile organic compounds as a solvent can be replaced with ILs because of negligible vapor pressure thus could be considered as “green solvent” [44–46]. In addition, by tuning the alkyl chain can accomplish up to trillion cation and anion combination possibilities, and an ionic precursor is a significant advantage that made ILs commonly used for other application including catalysis [47–49], electrochemistry [50], extraction [51,52] and many more. In the separation process using membrane especially for desalination, ILs have been used as liquid membranes [53,54], supported membrane [55–57], lithium recovery from seawater using dialysis [58], and osmotic heat engine [59].

Generally, the classification of ILs consists of hydrophilic or hydrophobic at room temperature depending on miscibility in water. However, the solubility of certain ILs towards water depends on the temperature that making them ambiguous. The first LCST-type ILs as draw solute was proposed by Cai et al. [27] and followed by Zhong et al. [28] for UCST-type ILs. The TRILs can play a significant role in the development of great desalination draw solutes that have water-drawing ability up to three times of seawater concentration which equals 1.6 M NaCl of feed solution. The cation and anion of TRILs that had been studying as a

draw solution are summarized in Fig. 1. From the observation, the presence of fluoride ion (F^-) strongly tends to mold the thermo-responsiveness of ILs besides sulfate ion (SO_4^-) in anion structure.

2.1. LCST behavior

The critical solution temperature (CST) can be understood as the temperature that instantaneous change causing solubility. In the phase separation of the LCST-type, the IL/water mixture became immiscible after heating, but it became miscible again after cooling (Fig. 2). Up to now, out of millions even many more different cation–anion combinations, the phosphonium based cations, such as tributylmethyl or tetrabutylphosphonium cations ($[P_{4448}]$ or $[P_{4444}]$) and tetrabutylammonium $[N_{4444}]$ are commonly reported. On the other hand, whereas trifluoroacetate [TFA] and derivatives of benzenesulfonate $[C_6H_5O_3S]$ are typical anions have been carried out to make LCST-type ILs [29,53].

Kohno and Ohno [60] are pioneering in LCST phase changes in ILs and was introduced ILs/water phase separation originally from amino acid derivation which reported back in Fukumoto and Ohno [61]. The ion structure and water content could be repeatable to influence the phase separation temperature of ILs/water mixtures and it was found that the LCST value of these mixtures are depending on the hydrophilicity of the component ions [62]. Consequently, it showed that IL/water mixture CST value could be determined by estimating the hydrophilicity of selected cation and anion combinations. Prior to the beauty of this LCST behavior (miscible with water at the mild condition and separate it at high temperature) got researchers' skeptical whether the substance can withstand up to waters' high boiling point for tranquil regeneration undertakings.

2.2. UCST behavior

Contrary to the LCST-type IL, the UCST-type IL which is IL/water mixture became immiscible upon cooling but becoming miscible again upon heating (Fig. 3). Zhong et al. [28], was the first study UCST-type IL as a draw solution is to treat high salinity water using protonated betaine bis(trifluoromethylsulfonyl)imide $[Hbet][Ntf_2]$. Recently, Abdullah et al. [31], was reported 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM) $[BF_4]$ also can be used as a draw solution. The physicochemical properties of most ILs are heavily reliant on the species of cation and anion [63]. Compare to LCST type-ILs, the combination of imidazolium-based cation with different anion such as bis(trifluoromethylsulfonyl)imide $[Ntf_2]$, tetrafluoroborate $[BF_4]$ and hexafluorophosphate $[PF_6]$ were reported as UCST type-ILs [64]. The above-mentioned anions having fluoride ion (F^-) dominantly frame the thermo-responsiveness behavior toward water separable.

In most cases, increasing the length of the alkyl chain attached to the cation will increase the mutual miscibility in non-aqueous solutions. It has been observed that UCST type-ILs were not only delimited by the solution's boiling temperature, and the mutual miscibility of ILs with the solvent by naked eyes or visual method was almost impossible to identify. Therefore, spectroscopic understandings

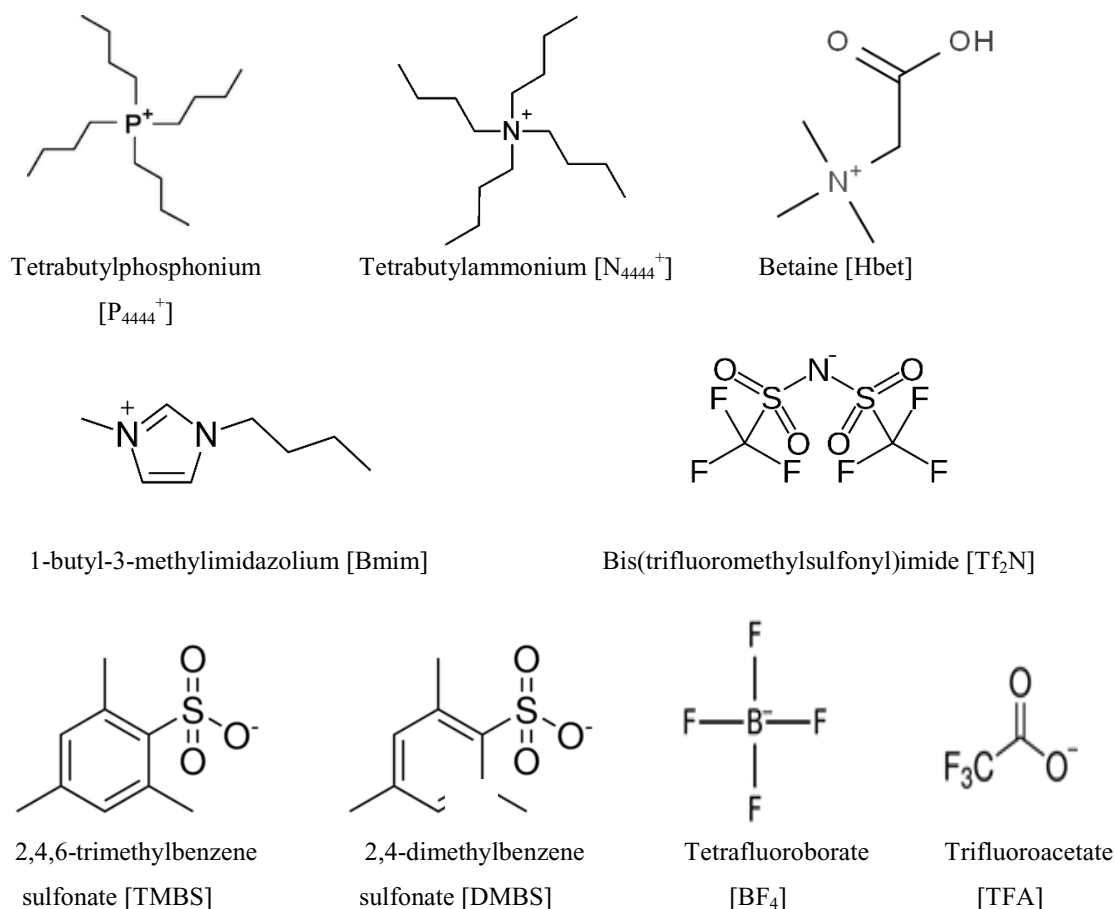


Fig. 1. Cation and anion structure of TRILs that had been used as draw solute.

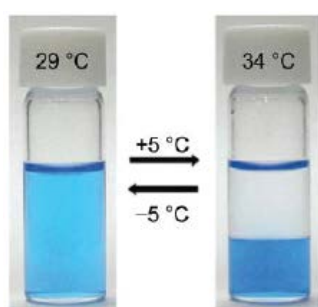


Fig. 2. LCST-type phase transition of ionic liquid [60].

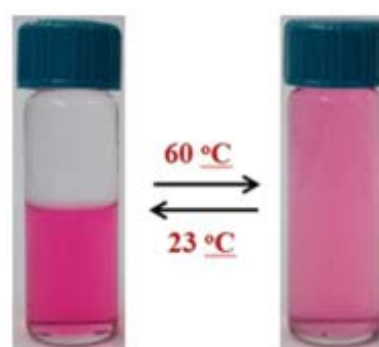


Fig. 3. UCST-type phase transition of ionic liquid [28].

by means of nuclear magnetic resonance, UV-Vis, inverse gas chromatography, Fourier-transform Raman spectroscopy, conductivity measurements, or other techniques were necessary for identifying miscibility gap and region is essential for further classified potential cation and anion before synthesizing ILs as draw solute [60,65].

Meanwhile, ILs' thermo-regulated property can be described as a temperature-dependent solubility property, where hydrogen bonding is a significant impact on miscibility (mostly identified via density functional theory calculations) or other possible intramolecular interactions between ILs and several solvents. Based on a previous study

conducted by Vreekamp et al. [66] and Nockemann et al. [67] using proton or hydrogen nuclear magnetic resonance (¹H NMR), they investigated the significant weakening of the hydrogen bond between anion and cation above CST for UCST type-ILs [66,67]. It can be understood that the homogeneous solution can be formed when the intramolecular interaction in ILs is strengthening and phase separation occurs when the intermolecular interaction between water and ILs is weakened physical intermolecular interaction mostly driven by temperature change.

3. FO performance

One key component for the successful development of FO technologies is the selection of an optimal draw solution. The first criterion is that the draw solution has a high water flux (J_w). The J_w in a pressure-driven membrane separation process is directly proportional to the applied pressure (Δp) and the osmotic pressure difference between the two solutions ($\Delta\pi$) [68].

$$J_w = A (\Delta p - \sigma \Delta \pi) \quad (1)$$

where A is the pure water permeability, and σ is the reflection coefficient which describes the fraction of the solutes reflected or rejected by the membrane. For ideal membranes with no solute transport, its value is unity. In an FO process, no pressure is applied ($\Delta p = 0$) and the water flux through the membrane is just due to the difference in the osmotic pressures of the draw and feed solutions, given by Eq. (2):

$$J_w = A (\pi_{D,b} - \pi_{F,b}) \quad (2)$$

where $\pi_{D,b}$ and $\pi_{F,b}$ is the osmotic pressures of the draw and feed solutions, respectively. Table 1 shows the water flux of TRILs that had been applied as draw solutes. Instead of achieving high water flux, other factors effect FO

performance such as osmotic potential, operating condition, draw solution concentration and type of membrane.

3.1. Osmotic potential

There are several conditions that influence the osmotic potential, π produced by draw solutes such as solute concentration, solute molecular weight (MW) and solution temperature. It has been observed by Taylor and co-workers, that high osmotic potential could be spawned by low MW draw solute and vice versa [7]. This can be demonstrated by the Van't Hoff equation:

$$\pi = icRT \quad (3)$$

where i is the Van't Hoff factor refers to the amount of moles of species formed by dissociating solutes in the solution which is sometimes known as the degree of ions dissociation, c is the concentration of solute in molar (M), R is the universal gas constant ($R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$) and T is solution's absolute temperature. The above equation can be generalized by include MW:

$$\pi = i \frac{m}{\text{MW} \cdot V} RT \quad (4)$$

Table 1
Comparison FO performance for different type of TRILs

Type of ILs	Membrane used	Feed conc.	Draw solution conc.	Ratio draw solution to feed	Water flux, ($\text{Lm}^{-2} \text{ h}^{-1}$)	Operation cond. ($^{\circ}\text{C}$)	Separation cond. ($^{\circ}\text{C}$)	References
LCST								
[P ₄₄₄₄][DMBS]	TFC, Ind.	1.62 wt. %	70 wt. %	43	4.01	24	Heating (30–50)	[27]
		1.62 wt. %	70 wt. %	43	4.20	14		
[P ₄₄₄₄][TMBS]	CTA HF, TOYABA Co., (Japan)	DI water	0.96 M		0.69	25		[29]
		TFC, Ind.	1.62 wt. %	80 wt. %	49	2.00	24	Heating (30–50)
[N ₄₄₄₄][TMBS]	CTA HF, TOYABA Co., (Japan)	DI water	1.35 M		0.71	25		[29]
		CTA HF, TOYABA Co., (Japan)	DI water	0.75 M		6.3	25	Heating (30–50)
[N ₄₄₄₄][DMBS]	CTA HF, TOYABA Co., (Japan)	DI water	0.42 M		9.3	25	Heating (30–50)	[29]
		CTA HF, TOYABA Co., (Japan)	DI water	0.24 M		10.6	25	Heating (30–50)
[P ₄₄₄₄][TFA]	CA	0.04 M	0.087 M	2	0.44	20	Heating (30–60)	[30]
		CTA, HTI Inc., (USA)	3.5 wt. %	82 wt. %	23	3.40	35	
					4.8	50		
UCST								
[Hbet][Tf ₂ N]	TFC, Toray, (USA)	DI water	3.2 M	3.2	2.27	60	Cooling (Room temp.)	[28]
		0.17 M	3.2 M	18	0.85			
		0.6 M	3.2 M	5	0.5			
[BMIM][BF ₄]	CTA, HTI Inc., (USA)	0.04 M	0.087 M	2	0.71	Room temp.	Cooling (4–6)	[31]

where m is the solute mass and V is the solvent volume. The above equation is relevant for ILs because it is frequently used to determine large MW of solute but it is extremely limited for dilute solutions [69]. Another limitation with this equation is the i values of ILs are not available in most of the literature.

Therefore, Ou et al. [20] and Long et al. [8] have proposed a freezing point depression method using a lab-scale set-up to overcome this limitation. First, the aqueous solution of 0.5 M ILs was put with vented caps in 100 mL glass tubes. The tubes were then submerged as a refrigerant at -20°C in a chiller filled with ethanol. The sample temperatures of freezing point (T_f) were measured using the thermocouple [21,70]. The above-mentioned method sounds promising in evaluating the proper of various ILs for thermo-responsiveness ability.

3.2. Operating condition

Based on a study of TRILs as draw solution in FO have been mostly carried out using bench-scale systems as illustrated in Fig. 4 consists of a peristaltic pump, feed and draw tank, tubes, balance and membrane test cell loaded with a flat-sheet membrane but only Kamio et al. [29] using FO membrane module consisting of a bundle of 15 cellulose triacetate (CTA) hollow fiber membranes in a stainless steel casing. When dealing with TRILs, the operation temperature is very important due to the amphiphilic behavior of this type of ILs that effected the miscibility towards the water at different temperatures. To generate high osmotic pressure, the draw solution must exhibit high miscible in water to cause high water flux across the membrane. In this study, water flux was found to increase significantly by reducing the temperature of the draw solution for LCST type-IL and vice versa for UCST type-IL as shown in Table 1.

On the other hand, the properties of solution affected by temperature for instance diffusivity of solutes, density and viscosity that can influence both the hydrodynamic boundary layer and concentration. Feed and draw solution temperatures not necessarily the same for both sides in the FO process, and they may change slowly as the streams flow through the membrane element due to heat transfer across the membrane [71]. Therefore, TRILs draw solution temperature will impact significantly on the efficiency of the process at their CST. Classifying the CST region (needed for phase separation of draw solute after FO process) shall be conducted earlier in optimizing draw solution ability before applying on the FO system.

3.3. Feed and draw concentration

The feed and draw concentration play significant parameters in ensuring high osmotic pressure achieved during the FO process based on Eq. (2) that indicate osmotic pressure is directly proportional to concentration. The various feed and draw solution concentrations have been studied from 0.04 M up to 0.65 M NaCl (3.5 wt.%) and 0.087 M of IL up to 80 wt.% of IL respectively. Likewise, lowering the ratio interrelated between draw solutions toward feed is better in minimizing the mass of draw solution.

During the experiment, the feed side became concentrated because, owing to the bi-directional diffusion of solutes during osmosis, the permeation of feed water into the draw solution. Unlike the draw solution, the water permeation from the feed into the draw solution becomes more diluted. Therefore, the initial and final concentration of feed solution was measured using a conductivity meter and the weight change of draw solution was measured using digital mass balance connected to a computer as illustrated in Fig. 4 in order to determine water flux.

All this draw solution concentration and the concentration difference across the membrane produce a reasonable water flux in both high and low permeability FO membranes. As per Table 1 shows, most researchers had been carried out either using deionized (DI) water or brackish water as feed solution which is indeed known as low salinity water. These studies would have been more useful if a wider range of feed concentration had been explored based on seawater concentration and high salinity for a further range of applications.

3.4. Type of membrane

The selection of a tailored FO membrane as well as a suitable draw solution is critical to the desalination process [72]. The great FO membranes must have high water flux, low salt permeability, low concentration polarization, minimal membrane fouling and good chemical stability [73,74]. Until now, the ready-made membranes such as CTA, cellulose triacetate hollow fiber (CTA HF), thin-film composite (TFC) polyamide and cellulose acetate (CA), have been commercially available and tested for FO processes using TRILs as draw solution.

From the experiment data tabulated in Table 1, we can see that the CTA HF membrane achieved the highest water flux which is 10.6 LMH compare to other flat sheet membranes.

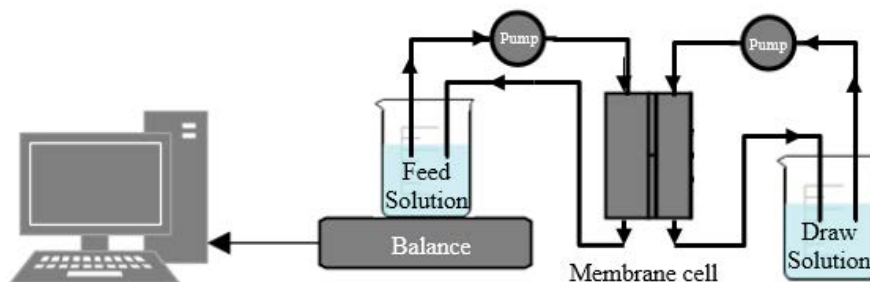


Fig. 4. Bench-scale FO setup.

The finding from this study show reasonably high fluxes but very limited progress and data have been made to overcome the salt leakage, internal concentration polarization (ICP), and FO performance against seawater. Even though the FO process exhibits less membrane fouling tendency compared to reverse osmosis (RO), further research could also be conducted to determine the corrosiveness of the membrane, especially when dealing with cellulose type membrane because there is a strong possibility that some of the ILs species can dissolve cellulose based on a previous study [75–78]. In order to overcome the above-mentioned drawback, a pre-screened procedure shall be conducted to identify only non-vulnerable ILs species towards cellulose that can proceed for FO system performance study.

3.5. Membrane orientation

The actual flux in a FO process is much less than the theoretical flux derived from Eq. (2) showing reduced driving force. On the feed side, where the solvent permeates through the membrane, the membrane retains the solutes which increase their concentration on the surface of the membrane referred to as concentrative external concentration polarization (ECP) [79]. The permeate entering the draw side dilutes the draw solution known as dilutive ECP at the membrane surface. Figs. 5a and b represent concentrative and dilutive ECP and ICP occurring in processes of FO and pressure retarded osmosis (PRO). All of these processes lead to a reduction of the net osmotic pushing force through the membrane, and hence decreasing the flux.

The ECP can be mitigated by inducing turbulence which enhances the mixing and consequently levels the concentration difference between the bulk and adjacent solution to the membrane surface [80]. However, the polarization of concentration in FO is not simply limited to ECP. FO membrane structure is typically asymmetric, that is, a thin active layer that governs the rate of molecular transport is coated on porous support that provides mechanical strength [81]. In the FO mode (when the active layer and support are facing the feed and draw solutions, respectively), a more severe concentration polarization

takes place inside the porous support layer of the membrane, known as ICP [70]. The enhanced dilution of the draw solution inside the porous support contributes to a massive decline in the osmotic pressure difference, thereby decreasing the flux more severely [82]. It shows that the feed solution and the degree of concentration are the determinant parameters on the efficiency of these two orientations agreed that water flux in PRO mode is higher than in FO.

4. Prediction method

ILs is also called “designer solvents” due to a large number of possible formulations, through the combination of different cations and anions can be synthesis especially for draw solution and many other application. Based on a previous study, it is not feasible to select potential ILs using the experimental method because the cost to purchase ILs is high [83,84]. In order to screen potential ILs as draw solute, the predictive tool or method should be used to tune ILs by predicting the water miscibility, hydrogen bonding, activity coefficient, CST and other important parameters before synthesis and test in the FO system.

To date, the most efficient and accurate technique for ILs screening has been disclosed by a number of studies using the conductor like screening model for real solvents (COSMO-RS) [85–88] and the other computational method that studies the theoretical of ILs is molecular dynamics simulations (MD) [89–91]. Meanwhile, the critical properties of the IL/water mixture can be envisaged using solution theory even over the entire composition range [64]. Besides that, as a colligative property, Eq. (3) implies the π is depending on ILs concentration and van't Hoff factor (i). As stated above, the so-called GCMs have been commonly used to estimate the critical properties of many substances for which these properties are not available.

4.1. Conductor like screening model for real solvents

The COSMO-RS theory is based on the quantum chemical continuum solvation model COSMO, which is an extension

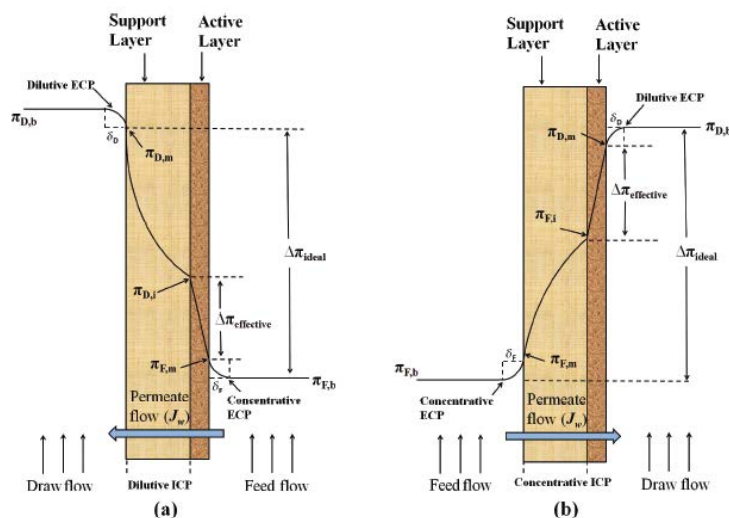


Fig. 5. The direction of water flux and the concentration profile developed across the membrane in (a) FO mode and (b) PRO mode [79].

of the basic quantum chemical method to the liquid phases and to supply a virtual conductor environment for the quantum chemical calculations [92]. This software has the ability to predict the thermodynamic properties like solubility and calculate the chemical potential of an arbitrary solute in any pure or mixed solvent at a variable temperature [52]. Hence, the sigma (σ) profile and potential, charge density, activity coefficient and other thermodynamic properties could easily predict and calculated using COSMO-RS by only provide the structure of molecules without any experiment data and functional group parameter. For this purpose, it can deal with virtually all ILs and mixtures, including the complex combinations of cation and anion and uncommon species of ILs [41,86]. However, the prediction using COSMO-RS so far is not rendered with experimental findings that mislead toward the determination of LCST and UCST behavior.

4.2. MD simulations

MD simulations generate information at the microscopic level, including atomic positions and velocities. This approach is valuable in visualizing and interpreting the interactions that exist between both the ions of an ionic liquid and any dissolved solutes and between the ions themselves [93,94]. The LCST phase separation mechanism of mixed ionic liquids in the water had been studied by Zhao et al. [95] using this computational approach. The ternary mixtures containing two different ILs and water at different temperatures and the radial distribution functions (RDFs) and various interaction energies were analyzed for these mixed systems. In the case of amino acid derivative ILs, one anion group of amine ($-\text{NH}_2$) or carboxylic ($-\text{COOH}$) may have a hydrogen bonding interaction with another carboxylic anion ($-\text{COO}^-$) [92]. The hydrogen-bonding interactions between anions have been demonstrated by an increase in temperature, and the anion- H_2O electrostatic interactions have been weakened, leading to LCST-type phase separation of the ILs/water mixture.

4.3. Solution theory

Alternatively, excess Gibbs energy models for the correlation of the phases of equilibrium or excess molar enthalpy from the combination of binary-ternary mixtures can be used in the prediction of CSTs which is the universal quasi-chemical (UNIQUAC), non-random two-liquid (NRTL) and electrolyte-NRTL (eNRTL) model [96,97]. These methods are widely used due to the low percentage error between the calculated results and experimental results that can be obtained using these models [98–100]. Among these conventional thermodynamic-based model approaches, the NRTL model is the most appropriate model for equilibrium data correlation with ILs. In this model, the ILs is expected to be completely associated, that is, anion and cation are paired and well-thought-out to be a single molecular species in the solution. Unlike NRTL, which consists only of enthalpy terms. The coefficient activity for the UNIQUAC model used in the portrayal of phase equilibria involves the term enthalpy and entropy [64].

4.4. Group contribution methods

Among the several proposals presented in the literature, the approach developed by Lydersen [101], is perhaps

the most widely used GCM to estimate critical properties. Similar proposals were presented by Ambrose [102] and Klincewicz and Reid [103]. Later, Joback and Reid [104] developed a method that is frequently mentioned in the literature. Valderrama and Alvarez combined the best results of Lydersen's method with the best results of the Joback–Reid method to propose a “modified Lydersen–Joback–Reid” method that proved to give good results for molecules of high MW [105]. The method considers the equations of Lydersen for the critical pressure and critical volume and the equations of Joback–Reid for the normal boiling temperature and the critical temperature of ILs.

To date, a number of studies have been conducted using this method in several applications to predict ILs properties such as critical properties [106–108], densities prediction [109–111], estimation of surface tension [111,112] and thermal properties [113]. In all these methods, the property of a compound is calculated by summing up the contributions of certain defined groups of atoms, considering at the same time the number frequency of each group occurring in the molecule. The advantage of this method is quick estimates without requiring sophisticated computational calculations.

The i value predictions are obtained using available simple equations and the concentration of each ILs was 0.5 M. The extended Lydersen–Joback–Reid GCM proposed by Valderrama and Robles was used to determining boiling point elevation (ΔT_b) by using Eq. (5):

$$\Delta T_b = \sum n \Delta T_b \quad (5)$$

With known ΔT_b , the i values were calculated using Eq. (3) where m is the molality of the sample and K_b is the boiling point elevation constants of water ($0.514 \text{ K kg mol}^{-1}$).

$$i = \frac{\Delta T_b}{m K_b} \quad (6)$$

The van't Hoff factor is the degree by which the colligative properties including osmotic pressure, relative lowering in vapor pressure, boiling-point elevation and freezing-point depression is affected by the solute [114]. It is the ratio between the actual concentration of particles produced when the substance is dissolved and the theoretical concentration of the substance based on its mass. Hence, the van't Hoff factor is a measure of deviation from the ideal or theoretical behavior. Under complete charge

Table 2
Predicted i value and T_b based on GCM calculation

TRILs	MW	$T_{b\text{pred}}$ (K)	i_{pred}
[P ₄₄₄₄][TMBS]	458.68	825.05	4.65
[P ₄₄₄₄][DMBS]	444.65	794.53	4.52
[N ₄₄₄₄][TMBS]	441.72	803.97	4.58
[N ₄₄₄₄][DMBS]	427.69	773.44	4.44
[Hbet][Tf ₂ N]	397.25	585.00	3.43
[P ₄₄₄₄][TFA]	372.45	538.66	3.20
[N ₄₄₄₄][TFA]	355.49	517.57	3.11
[BMIM][BF ₄]	226.03	337.89	2.19

dissociation of ILs candidates in water, $i = 2$. But in real systems, i values are usually lower or higher due to ion pairing, this has been observed even for NaCl experimental value $i = 1.89$ [115].

The predicted i and T_b value of TRILs that had been used as a draw solution were listed in Table 3. The TRILs combinations were organized according to the increasing value of the van't Hoff factor. The values of the calculated van't Hoff factor indicate different degrees of IL association in water. Based on the result shown in Table 2, those ILs containing long alkyl chains have relatively higher degrees of an association primarily. It is possible that these results are due to the lower water interaction of their cations bearing hydrophobic alkyl chains [52,116].

On the other hand, anions display the larger molecule exhibits the highest degree of association but a larger amount of ILs needs to be achieved high osmotic pressure according to Eq. (4) MW is inversely proportional to the concentration. Besides that, a large molecule of draw solute has low ion mobility [108]. Therefore, a combination of properly paired ions will lead to the formation of ILs with a desirable degree of association. So, only those ILs that manifest i value greater than 2, and have hydrophilic properties can be considered useful as draw solution (DS) that can be run at room temperature condition.

5. Recovery method

In the case of TRILs, recovery of draw solute is generally achieved by phase separation through thermal stimulation depending on CST. The draw solute rich phase is recycled back and the water-rich phase is further treated for high-quality water recovery as shown in Fig. 6. In all the

FO experiments using ILs as draw solutes, the draw solute rich phase could have approximately 70%–80% concentration which helps them retain enough osmotic potential to be recycled back. In almost all cases could retain the osmotic potential even after significant dilution leading to more number of recycling. Up to three recycles can be achieved in batch systems, beyond which the draw solute needs to be replenished [69].

Membrane separation processes have been widely used in FO for diluted DSs recovery. Most of these membrane processes, RO, ultrafiltration (UF), nanofiltration (NF), are pressure-driven processes, except electrodialysis, which uses electricity, and membrane distillation, which requires heat. Each process uses a specific membrane [117]. The selection of the membrane separation process mostly depends on nature, the molecular size of the solutes that need to be rejected as shown in Table 3.

RO is used to concentrate DSs with low MW compounds. As described in the following section, RO has shown high water recovery rates, and high salt rejections (<99%) [118]. FO-RO hybrid process has also demonstrated the potential of energy costs saving for high salinity streams treatment comparing to standalone RO. On the other hand, the RO recovery process requires high hydraulic pressure, typically 35–100 bar [119], and thus, operating costs are still high [120].

NF process has been successfully applied to recover diluted DSs based on solutes with MWs ranging from 100 to 1,000 Da. NF regeneration has shown high recovery rates and high salt rejection due to the charge effects (especially for multivalent ions). Since NF has properties between RO and UF, it requires lower operating pressures, investment cost and maintenance costs than RO [121].

Table 3
Characteristics of RO, NF and UF

Membrane process	Particle size (μm)	Molecular weight (Da)	Particle characteristics
RO	0.0001	100	Ionic
NF	0.0001–0.001	100–1,000	Ionic to molecular
UF	0.001–0.1	1,000– 10^5	Macromolecular to cellular

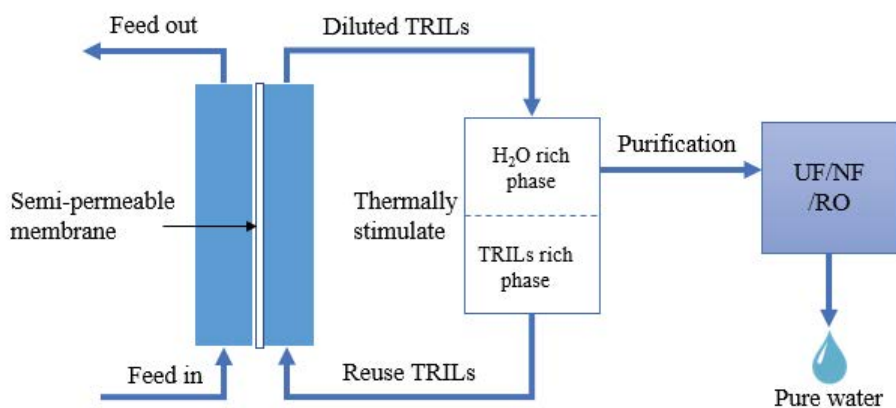


Fig. 6. Conceptual schematic diagram of TRILs recovery.

Chung et al. [74] have been proposed to integrate FO for desalination and RO for draw solute recovery is technically feasible but economically and industrially unpractical. The use of FO with the aid of membrane distillation (MD) appears to be a better idea. However, MD is not a commercially available technology even after 30 y of study. The required low quality or low-cost heat for MD is essential but cannot be easily found in a practical sense. In addition, the current MD process also suffers from several limitations as follows: low permeate flux due to membrane structure and properties; gradual deterioration of the membrane performance caused by temperature polarization after long-term operation; membrane scaling and wetting problem; and high heat lost by conduction [74].

For the case of TRILs, as can be seen from Table 1, the FO performance test was conducted at room temperatures and the phase separation was performed at mild condition around 30°C–50°C for LCST type ILs which requires low energy. On the other hand, the operating condition for [Hbet][Tf₂N] (UCST type ILs) was carried at 60°C and phase separation was achieved at room temperature. However, another UCST type ILs which is [BMIM][BF₄] were carried out at room temperature and phase separation occur at 6°C but the cooling process needed high in energy compared to the heating process.

After phase separation procedures, further purification of water rich phase much depending on application of water produced. It becomes a necessity for recovery process to purify the water produced phase; otherwise the toxicity of the draw solutes is high and unsafe for certain end-usage [122]. Depending on the MW of the draw solutes, the conventional purification method such as UF, NF, or low pressure RO (<5 bar) can be used. The existing conventional purification method is enough in getting rid of TRILs traceable draw solute in water produced phase before further applications.

6. Conclusion

The TRILs have countless potential to be utilized to draw solutions in the FO process due to unique characteristics and can be considered as a green solvent. These draw solutes have the capability to draw out water whose go up to high salinity but, the highest water flux rates were reported can only be achieved of 10.6 L m⁻² h⁻¹ thus, certain weaknesses that hinder its draw ability should be overcome for further study. The operating condition could undergo at room temperature and draw solute recovery could be conducted at the mild condition to reduce energy and cost. The TRILs-rich phase can be recycled directly without further treatment as a draw solution after phase separation. Since it could preserve its osmotic potential, even after a substantial dilution leading to a higher recycling number. While low-pressure RO, UF or NF can be used to treat the water-rich phase and the purification of water-rich is not required depending on end-uses.

Even though the TRILs can be considered as a green solvent, but they still have a traceable amount in the water-rich phase after phase separation. More research is needed on the toxicity of TRILs to estimate the amount of the safe concentrations of ILs towards humans and the environment

for a wide range of applications. Therefore, searching for the structures of ILs with lower toxicity, as well as creating a database of chemical structures of environmentally friendly ILs based on their toxicity, is necessary to obtain guidance and define legislation before production and use of ILs on an industrial scale.

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