



## The potential of monocationic imidazolium-, phosphonium-, and ammonium-based hydrophilic ionic liquids as draw solutes for forward osmosis



Hana G. Zeweldi<sup>a,1</sup>, Lawrence A. Limjuco<sup>a,1</sup>, Anelyn P. Bendoy<sup>a</sup>, Han-Seung Kim<sup>b</sup>, Myoung Jun Park<sup>c</sup>, Ho Kyong Shon<sup>c</sup>, Eldin M. Johnson<sup>d,e</sup>, Hanki Lee<sup>d</sup>, Wook-Jin Chung<sup>a,\*</sup>, Grace M. Nisola<sup>a,\*</sup>

<sup>a</sup> Energy and Environment Fusion Technology Center (E<sup>2</sup>FTC), Department of Energy Science and Technology (DEST), Myongji University, Myongji-ro 116, Cheoin-gu, Yongin-si, Gyeonggi-do 17058, Republic of Korea

<sup>b</sup> Department of Environmental Engineering and Energy, Myongji University, Myongji-ro 116, Cheoin-gu, Yongin-si, Gyeonggi-do 17058, Republic of Korea

<sup>c</sup> Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney (UTS), P.O. Box 123, 15 Broadway, NSW 2007, Australia

<sup>d</sup> Center for Nutraceutical and Pharmaceutical Materials, Myongji University, Myongji-ro 116, Cheoin-gu, Yongin-si, Gyeonggi-do 17058, Republic of Korea

<sup>e</sup> Department of Life Science, Food Microbiology and Bioprocess Laboratory, National Institute of Technology, Rourkela, India

### ARTICLE INFO

#### Keywords:

Desalination  
Draw solution  
Forward osmosis  
Ionic liquids  
Van't Hoff factor

### ABSTRACT

The widespread implementation of forward osmosis (FO) is highly constrained by the limited availability of suitable draw solutes (DS). Herein, monocationic hydrophilic ionic liquids (ILs) were probed as FO DS. Water ( $J_w$ ), reverse solute ( $J_s$ ), and specific reverse solute ( $J_s/J_w$ ) fluxes were determined and correlated with IL properties: Van't Hoff factor ( $i$ ), ionic strength, hydrated ionic radius ( $r_H$ ), diffusivity and membrane affinity. Most of the ILs have comparable  $J_w$  with the benchmark draw solute NaCl but their  $J_s$  were significantly lower, particularly under PRO mode. Their remarkably lower  $J_s/J_w$  (i.e.  $< 0.010 \pm 7.45 \times 10^{-4} \text{ mol L}^{-1}$ ) than NaCl ( $0.021 \pm 0.003 \text{ mol L}^{-1}$ ) validates their potential use as FO DS. Tetraethylammonium bromide ([N2222]Br) is the most suitable IL DS due to its high  $\pi$ , high ionic strength, small  $r_H$ , least membrane permeability ( $B = 0.14 \text{ L m}^{-2} \text{ h}^{-1}$ ) and lowest  $J_s/J_w = 0.004 \pm 5.53 \times 10^{-4} \text{ mol L}^{-1}$ . Moreover, [N2222]Br effectively desalinated seawater (0.6 M NaCl). It is thermally stable and can be effectively regenerated through direct contact membrane distillation. The final permeated water had only trace [N2222]Br, which is safe for consumption as confirmed by *in vitro* toxicity tests. These results demonstrate that certain ILs like [N2222]Br can be identified as suitable draw solutes for FO desalination process.

### 1. Introduction

Forward osmosis (FO) has emerged as one of the most promising technologies in desalination [1,2], power generation [3], wastewater reclamation [4], and fertigation [5]. FO is an innovative membrane separation technology that relies on osmotic pressure gradient ( $\Delta\pi$ ) between two solutions separated by a semi-permeable membrane [6,7]. FO membranes selectively reject solutes from the feed while allowing water molecules to permeate through the membrane [8]. The diffusion of water molecules results in the concentration of the feed and the dilution of the draw solution (DS). In contrast to pressure-driven

processes such as reverse osmosis (RO), ultrafiltration (UF), and nanofiltration (NF), osmotically-driven membrane process like FO is less prone to fouling making it a viable alternative process to treat complex feeds [9,10].

A great deal of research has been directed at the fabrication of FO membranes and development of draw solutes. These efforts have led to the development of advanced membranes that are on route to commercialization [11–14]. However, the availability of a suitable draw solute is also crucial for the future of FO desalination technology. An ideal draw solute should produce sufficient osmotic pressure ( $\pi$ ) to induce water permeation. Apart from that, it must be impermeable to

\* Corresponding authors at: Energy and Environment Fusion Technology Center (E<sup>2</sup>FTC), Department of Energy Science and Technology (DEST), Room 8807, Engineering Building 2, Myongji University, Myongji-ro 116, Cheoin-gu, Yongin-si, Gyeonggi-do 17058, Republic of Korea.

E-mail addresses: [wjc0828@gmail.com](mailto:wjc0828@gmail.com) (W.-J. Chung), [grace.nisola@gmail.com](mailto:grace.nisola@gmail.com) (G.M. Nisola).

<sup>1</sup> Co-first authors.

the FO membrane to alleviate gradient loss, which could be detrimental to the process efficiency, and to minimize its leakage, which would add cost for its replenishment. Furthermore, desirable draw solutes are expected to have low volatility, be strongly compatible with existing FO membranes, and easy to recycle or separate from the permeated water [15–17].

Conventional mineral salts (NaCl, MgCl<sub>2</sub>, NaHCO<sub>3</sub>, KBr, K<sub>2</sub>SO<sub>4</sub>) [18], thermolytic inorganic salts (NH<sub>3</sub>-CO<sub>2</sub>, switchable polarity solvents) [19–21], and organic-based compounds (Zwitterions, hydroacid complexes, EDTA-metal complexes, EDTP sodium salts, 2-methylimidazolium based compounds) [22–27], and thermo-responsive materials [28–32] have been tested and used as draw solutes. But despite the recent progress, investigations on the development or identification of ideal draw solutes are still very limited. Particularly, studies which relate draw solute properties (i.e. colligative, solution, volume, structural and other physico-chemical attributes) with their behaviors during FO operation are still needed to achieve better understanding on draw solute selection for maximum FO process efficiency.

One particular group of organic salts which have high potential as draw solutes are the ionic liquids (ILs). These compounds usually consist of large asymmetric organic cations and organic or inorganic anion [33]. Hydrophilic ILs can be easily dissolved in water to constitute a DS. ILs are environmentally benign due to their high thermal stability and negligible vapor pressure [34]. Their high ionic conductivity suggests their ability to induce water permeation in FO system. In addition, ILs have moderate to large molecular size, hence their loss through reverse solute flux could be minimized. The use of monomeric ILs as drawing agents is largely unexplored in literature; one closest study focused on 2-methylimidazole-based compounds including neutral imidazoles as well as mono- and di-imidazolium salts paired with iodide anions [27]. The unique property of ILs is that their physicochemical properties can be changed by varying and selecting the appropriate anion and cation pairs to meet a specific application [35]. This tunable property of ILs indicates their untapped potential and the need for investigation as draw solutes.

Moreover, ILs can be regenerated by implementing a recovery step [28]. An effective technique to re-concentrate IL solutions and simultaneously produce clean water is direct contact membrane distillation (DCMD). It involves a hydrophobic membrane that separates two aqueous solutions with different temperatures. The spent IL DS can be fed at an elevated temperature in a DCMD unit and the vapor pressure difference could facilitate the selective water transport across the membrane as it is condensed by a cooled permeate stream [27,28]. DCMD can be operated simultaneously or after an FO process to ensure long-term use of ILs as DS.

Herein, five hydrophilic ILs were selected and investigated as draw solutes for FO process. The ILs were thoroughly characterized and their

FO performances were correlated with their properties. Meanwhile, DCMD was performed to evaluate the feasibility of IL recovery for continuous application. From the DCMD permeate, the quality of de-salinated water was examined and the safety of IL use was determined through *in vitro* cytotoxicity tests.

## 2. Materials and methods

### 2.1. FO and DCMD membranes

Cellulose triacetate (CTA) FO membrane, which was formerly produced by Hydration Technology Innovations (HTI, Albany, OR), was used in all FO runs. While the production of this membrane has been discontinued, it still remains a suitable choice for testing DS performances. Its use would provide straightforward comparison with other reported DS in literature, which were tested using the same FO membrane. The FO membrane is ~90 μm thick, comprised of a salt rejecting active layer and a support embedded in a polyester (PET) mesh. Its active layer has a contact angle of 55.1 ± 5.5° while its support has 79.1 ± 4.2°. Membrane samples were stored at 4 °C in deionized (DI) water and were allowed to equilibrate for 30 min at room temperature before use.

Hydrophobic polyvinylidene fluoride (PVDF) from Merck-Millipore® (GVHP) was used for the DCMD experiments. The PVDF membrane is 125 μm thick, with pore size 0.22 μm, porosity of 75% and contact angle of 115.1 ± 3.6°. The membrane samples were stored dry at room temperature when not in use.

### 2.2. Feed and draw solutions

Deionized (DI) water with 18.2 MΩ-cm at 25 °C (Millipore Smart Synergy UV Water System, Molsheim, France) was used as feed and solvent for the preparation of DS. Sodium chloride (> 99% NaCl) was purchased from Daejung Chemicals and Metals Co., Ltd. (South Korea). Ionic liquids 1-butyl-3-methylimidazolium chloride (> 98% [BMIM]Cl) and tetrabutylammonium bromide (> 98% [N4444]Br) were procured from Acros Organics (United Kingdom), tetrabutylphosphonium bromide (98% [P4444]Br) from Sigma-Aldrich (MO, USA), 1-butyl-3-methylimidazolium bromide ([BMIM]Br, 99%) from Alfa Aesar (USA), and tetraethylammonium bromide (98% [N2222]Br) from Junsei Chemical (Japan). All chemicals were used as received without further purification. The physico-chemical properties of the ILs are summarized in (Table 1) [36,37].

### 2.3. IL properties

Each of the five IL candidates is composed of either Cl<sup>-</sup> or Br<sup>-</sup>

**Table 1**  
Characteristics of the ionic liquids and NaCl used as FO draw solutes at 25 °C.

Compound	Molecular formula	MW <sup>a</sup> (g mol <sup>-1</sup> )	MP <sup>b</sup> (°C)	ρ <sup>c</sup> (g cm <sup>-3</sup> )	V <sub>m</sub> <sup>d</sup> (cm <sup>3</sup> mol <sup>-1</sup> )	V <sub>c</sub> <sup>e</sup> (cm <sup>3</sup> mol <sup>-1</sup> )	V <sub>b</sub> <sup>f</sup> (cm <sup>3</sup> mol <sup>-1</sup> )	D <sub>aq</sub> <sup>g</sup> (× 10 <sup>-10</sup> m <sup>2</sup> s <sup>-1</sup> )
Sodium chloride	NaCl	58.440	800	2.165	26.99	n.a.	27.00	8.04 <sup>h</sup>
[BMIM]Cl	C <sub>8</sub> H <sub>15</sub> ClN <sub>2</sub>	174.671	70	1.120	155.95	585.73	226.67	6.55
[BMIM]Br	C <sub>8</sub> H <sub>15</sub> BrN <sub>2</sub>	219.120	65–75	1.300	168.55	600.25	232.56	6.45
[N2222]Br	C <sub>6</sub> H <sub>20</sub> BrN	210.159	187	1.397	150.44	605.73	234.79	6.41
[N4444]Br	C <sub>16</sub> H <sub>36</sub> BrN	322.368	104	1.039	310.27	1062.61	423.14	4.50
[P4444]Br	C <sub>16</sub> H <sub>36</sub> BrP	339.330	100–103	1.008	336.64	1169.73	467.95	4.24

<sup>a</sup> MW – molecular weight.

<sup>b</sup> MP – melting point.

<sup>c</sup> ρ – density.

<sup>d</sup> V<sub>m</sub> – molar volume of solute at room temperature estimated from MW/ρ.

<sup>e</sup> V<sub>c</sub> – critical volume of solute.

<sup>f</sup> V<sub>b</sub> – molar volume (cm<sup>3</sup> mol<sup>-1</sup>) of solute at its normal boiling temperature calculated using Tyn and Calus correlation.

<sup>g</sup> D<sub>aq</sub> – bulk diffusion coefficient calculated using Wilke-Chang method.

<sup>h</sup> NaCl D<sub>aq</sub> – bulk diffusion coefficient calculated using Nernst-Haskell equation.

Download English Version:

<https://daneshyari.com/en/article/7007643>

Download Persian Version:

<https://daneshyari.com/article/7007643>

[Daneshyari.com](https://daneshyari.com)