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Thermally responsive ionic liquids and polymeric ionic liquids: Emerging trends and possibilities

Nupur Gupta[a], Yen Nan Liang[a], Xiao Hu*[ab]

[a]Nanyang Environmental & Water Research Institute, 1 Cleantech Loop, Singapore

*[b]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798.

E-mail: asxhu@ntu.edu.sg

Abstract

Ionic liquid (IL) including polymeric ionic liquid (PIL) is a rapidly growing and widely research area due to its unique properties such as non-volatility, high ionic conductivity, electrochemical stability, and solvation potential. This focused review covers the advancement of thermally responsive ILs/PILs for applications in which their osmotic potential and reversible interactions are exploited for water treatment and energy conversion through osmotically driven membrane processes and energy-saving smart windows. Our goal is to survey the recent key developments by highlighting the opportunities and challenges in this emerging and exciting field.

Keywords: Ionic liquids, poly (ionic liquid), thermally responsive, water treatment, heat engine, solar modulation

1. Introduction

After the first ionic liquid (IL), ethanol ammonium nitrate and first room-temperature IL, ethyl ammonium nitrate were reported individually by Gabriel in 1888 [1] and by Paul Walden in 1914 [2], the potential of the breakthrough went unnoticed for a long time. A renewed interest in ILs was triggered by the search for high-performance electrolytes in advanced electrochemical devices like batteries, capacitors [3, 4], or as solvents for catalysis and chemical extraction [5]. Another advantage of ILs over conventional solvents lies in their tunable properties such as selective solvation ability and miscibility depending upon the choice of cation and anion ILs, expanding their applications from metal ions separation to chromatography [6-8]. Recently, polymeric ionic liquid (PIL) has gained research interest as a new class of polyelectrolyte [9]. The scope and utility of PILs are ever expanding to fuel cell membranes [10], solid-state electrolytes for dye sensitised solar cells [11-13] and batteries [14],

CO_2 sorbents [15, 16], bio and gas sensors [17]. Extensive work in this direction is highlighted by many reviews on ILs and PILs [18-21]. There is recently increased attention on the development of advanced stimuli-responsive materials (SRMs) based on ILs [22].

In general, SRMs undergo change in molecular configuration under external stimuli e.g. temperature, light, pH, etc. [23], which triggers cascading microscopic and macroscopic changes, often associated with change in physical and chemical properties [24-26]. An important aspect of the response of the SRMs lies in its dynamic reversibility tunable by subtle molecular design and strength of the stimulus. Among stimuli-responsive systems, thermally-responsive phase behavior of the aqueous polymer solutions and hydrogels have been widely investigated. These polymers show a drastic change in the solubility at a certain temperature i.e. critical solution temperature. Depending upon increase or decrease of the solubility with temperature, it is termed as either upper critical solution temperature (UCST) or lower critical solution temperature (LCST) respectively. Non-ionic polymers such as poly (N-isopropyl acrylamide) (PNIPAM) [27] are well-known to display such behavior.

While numerous efforts have been devoted to study stimuli-responsive polymers, studies on SRMs based on ILs have only gained momentum very recently in past 10 years. Distinct from the previous reviews on ILs and PILs, this focused review aims to highlight some of the most significant developments in the field of thermally responsive ILs and PILs and their applications owing to their unique reversible properties e.g. water affinity, osmotic pressure, and phase transition. Advantages of them will be discussed comparing to their conventional counterparts. Three exciting applications i.e. water treatment, osmotic energy conversion, and energy saving smart window using this unique class of materials are specifically highlighted.

2. Thermally Responsive ILs

Although the thermally responsive UCST type IL was first referenced as early as 1998 for imidazolium-based IL [28], LCST type IL/water system based on tetra N-butyl phosphonium cation was only reported in 2007 [29]. Details on molecular structures and phase transition behavior of various IL/solvent systems can be found in other reviews [30, 31]. The temperature dependence of solubility of the IL/solvent mixtures was found to result from the hydrogen bonding influenced by both the nature of IL and solvent used [31]. The hydrophilicity/hydrophobicity balance of the cations and anions forming the ILs critically affects the phase transition temperature of the IL/water mixture.

The tremendous potential offered by the dynamic nature of the thermally responsive IL/water system, demonstrated in chemical extraction [32] and as a solvent for catalysis, [31] can also be exploited for desalination using forward osmosis (FO). In a typical FO operation, the spontaneous movement of water molecules is driven by the osmotic potential gradient of feed and draw solution across a semi-permeable membrane [33, 34]. The draw solution gets diluted in the process and needs to be regenerated to sustain the driving force for FO. The conventional draw solutes e.g. inorganic salts and volatile gases, although can provide significant osmotic pressure, have drawbacks of high reverse solute diffusion and requirement of costly regeneration techniques e.g. membrane distillation (MD) or reverse osmosis (RO) [35]. Adoption of thermally responsive systems can lower the regeneration cost. Use of LCST-type thermally responsive IL/water mixture for FO was first introduced by Cai et al. [36] While the traditional PNIPAM based copolymers [37] and non-ionic polymers [37] can hardly draw water due to limited osmotic pressure, thermally responsive ILs could draw water from 1.6 M NaCl feed solution, which is 3 times the salinity of the seawater owing to high osmotic potential. Responsive ILs offer clear advantages in terms of high osmotic pressure, improved water flux and substantially lower energy consumption.The structure of ILs and the schematics of the process are shown in Figure 1.The diluted draw solution undergoes liquid-liquid phase separation on heating above its LCST i.e. 60^{o}C. The IL-rich phase can be directly reused whereas the water-rich phase simply requires low-pressure nano-filtration (NF) for water recovery. Low-cost regeneration can be envisaged by using waste heat stream as it only requires low enthalpy of phase separation (3-5 kJ/kg), making ILs more attractive than conventional draw solutes. Similarly, UCST type IL was also demonstrated as draw solute for FO [38].

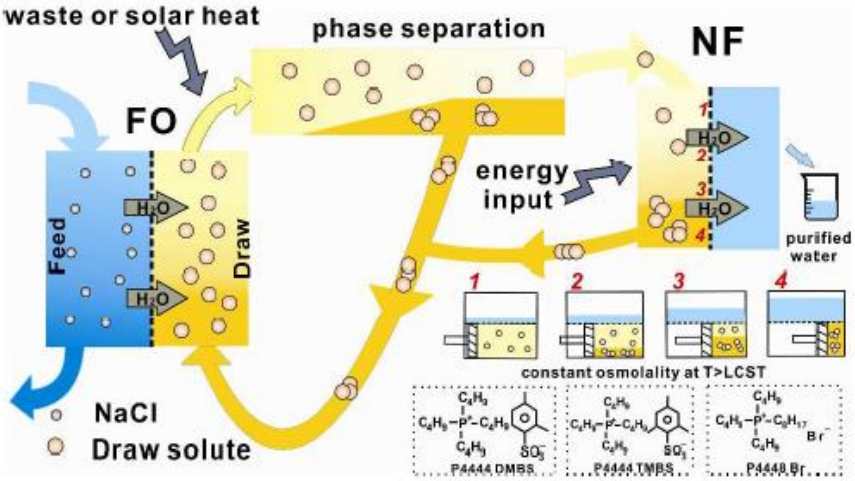


Figure 1 Graphic representation of the forward osmosis process using a LCST type IL as draw solute [36]. Published by The Royal Society of Chemistry.

LCST or UCST type ILs/water mixtures can also be applied in osmotic heat engine (OHE) for energy generation. The concept of recovering waste heat using a closed-loop pressure retarded osmosis (PRO), also known as osmotic heat engine was first proposed by Loeb in 1975 [39]. Basically, as water permeates from less concentrated feed to higher concentrated draw solution across the semi-permeable membrane against the hydraulic gradient, the volume increase of the diluted draw solution is manifested as mechanical energy to generate electricity using turbine [40]. The primary requirement of the OHE system is the regeneration of the salt gradient after dilution during energy harvesting step. Previously proposed OHE systems have focused on thermolytic salt systems, utilizing their dramatic change in solubility with temperature, the classic example being NH_3-CO_2 developed by Elimelech [41]. Thermolytic salts, although are of easier thermal regeneration compared to inorganics, are still limited by high reverse salt flux and operational challenges e.g. membrane stability and incomplete removal of highly soluble ammonia. Organic solvents e.g. methanol have been used for hybrid PRO-MD but suffered from high volatility [42]. The advantage of using thermally responsive IL with inherent low vapor pressure, high osmotic pressure, and low crossover due to larger size of ions was first demonstrated by Zhong et al. [43] (see Figure 2). As noticeable from figure 2(b) and 2(c) the operation of OHE requires two different working temperature i.e. T_o (<UCST) at which liquid-liquid phase separation produces IL-rich (draw) and IL-lean phase (feed) which are both separately heated to T_k (>UCST) resulting in a homogeneous diluted draw solution after PRO process. Apart from PRO, other processes e.g. reverse electrodialysis (RED) [44] and capacitive mixing (CM) [45] can also be used for OHE.

By appropriate choice of IL or IL mixtures and membranes the power density of the OHE can be further improved.

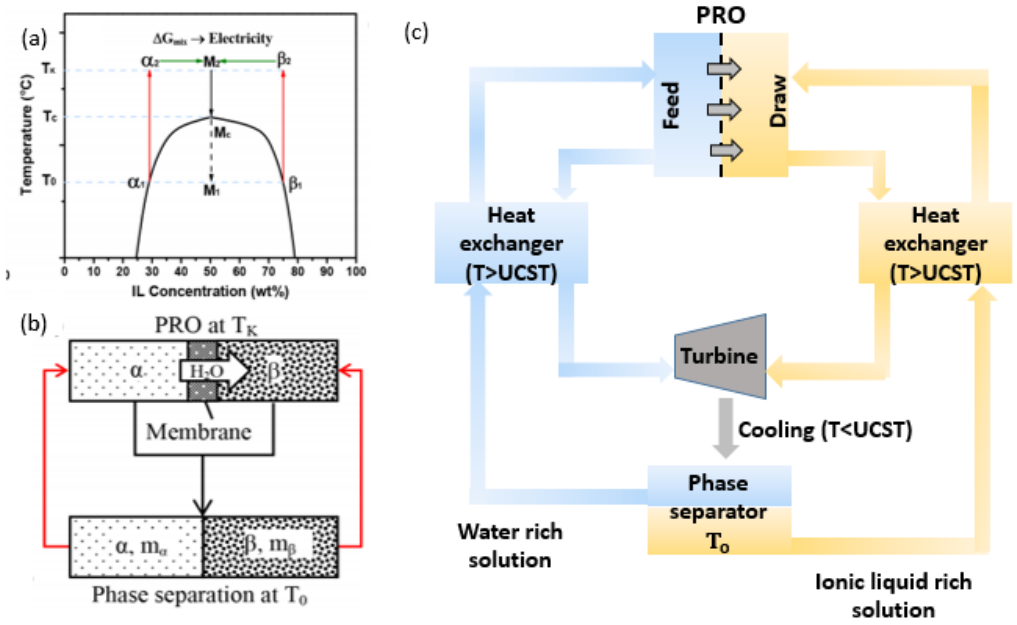


Figure 2 (a) Illustration of different phases of OHE on the binary phase diagram where α and β represents the ionic-lean and ionic rich phase respectively and T_k and T_o are the working and cooling temperature (b) and (c) Illustration of the OHE process using a closed loop PRO. Reprinted with permission from [43] Copyright (2015) American Chemical Society.

There is an increase of research interest given to stimuli-responsive smart windows, which offers better energy efficiency via regulation of penetration of solar irradiation by changing its optical transmittance [46]. Although electrochromic devices have been widely adopted for electrically switchable smart windows, self-contained autonomous systems triggered by external stimuli are of particular interest contributed by lower fabrication and maintenance cost [47-49]. While the use of PNIPAM hydrogel has been demonstrated (Figure 3(a)) [50], there are concerns regarding its shrinkage during phase transition, water freezing and evaporation. Using pure ILs for smart window application poses two main challenges, i.e. its encapsulation and narrow spectrum for solar modulation. Lee et al. [51] reported stable and reversible optical switch between high and low optical transmittance at the transition temperature of ionogel, a semi-solid material with polyurethane network percolating through imidazolium based ILs. . The observation was attributed to change in interaction of the polymeric/IL system, with hydrophobic association dominating above the transition temperature resulting in microphase separation (see Figure 3(b)). This phenomenon is different

from macrophase separation observed for hydrogels, thus avoiding shrinkage issues. Not only wide-spectrum solar modulation ability can be achieved by incorporation of plasmonic nanoparticles, the tunability of transition temperature of ionogel from subzero to above 100 ^{o}C is made possible by varying the composition of ILs; making them particularly useful for smart window. Other notable developments of smart window include co-existing active and passive switchability [52] and multifunctional organic/inorganic hybrid e.g. VO_2 nanoparticles/IL-Ni-Cl hybrid film [53-55].

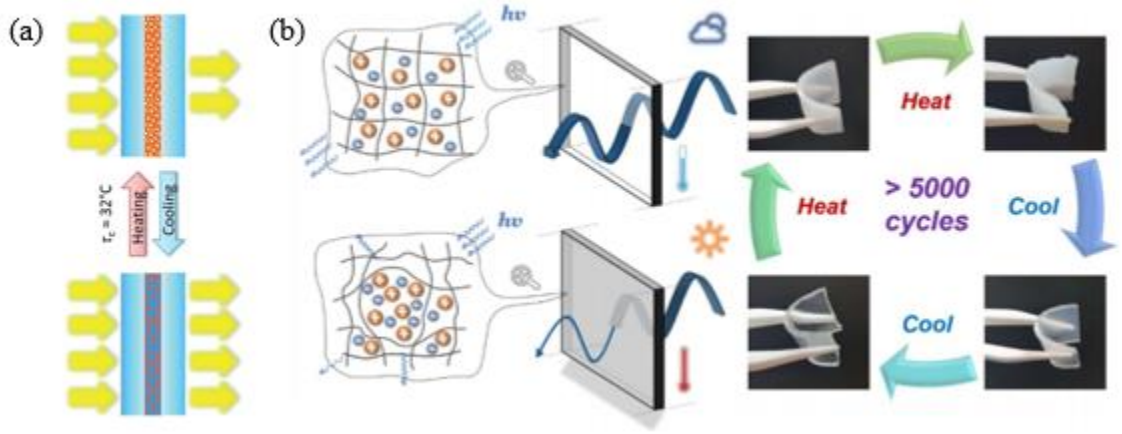


Figure 3 (a) PNIPAM hydrogel transmitting light at $T<T_c$ and partially blocking the radiation at $T>T_c$. Reproduced from [50] with permission from The Royal Society of Chemistry. (b) Illustration of solar modulation mechanism using a thin film of ionogels. Reprinted with permission from [51]. Copyright (2017) American Chemical Society.

3. Thermally Responsive PILs

Despite the research progress made in the field of ILs and PILs, thermally responsive PILs have only recently gain significant research interest. Earlier preparation of charged polymers exhibiting LCST were mainly obtained by copolymerising thermally responsive non-ionic monomer with ionic monomer. The first fully ionised polymer exhibiting LCST/UCST type phase behavior i.e. LCST type PIL of $[P_{4444}][SS]$ was reported by Ohno and Kohno [56]. PILs were found to exhibit LCST and UCST type phase transition in water by tailoring the hydrophilic/hydrophobic balance of the components ions of the IL monomers, polymer concentration, and solvent [57, 58]. The transition temperature can also be tuned by blending two or more PILs with different hydrophobicity [59] or by salt addition [60]. The sharper temperature response of PIL than that of copolymerised polymers offers advantage for practical applications and give potential for advanced smart materials.

PIL hydrogels made from poly [P_{4444}][SS] was first reported by Ziółkowski and Diamond [61]. However, as compared to sharp phase transition observed for the linear polymer, significant broad transition regime was observed, This was attributed to both non-homogenous crosslinking density and restricted PIL mobility within the gel. Use of thermally responsive hydrogels for quasi-continuous FO applications was first demonstrated by Cai et al. as shown in Figure 4, which drives water permeation across membrane by its swelling pressure [62]. Water recovery is done by deswelling the swollen hydrogel above its transition temperature. Major advantages of hydrogel over other draw solutes is zero reverse solute diffusion and direct water recovery without needing any further purification. High water recovery of PNIPAM based semi-IPN hydrogel was demonstrated at 40^{o}C, despite low FO water flux [63]. The high swelling ratio of [P4444][SS] PIL hydrogel, i.e., 20 times of that of PNIPAM semi-IPN hydrogel, resulted in enhanced water flux [62]. They also envisaged the concept of integrating hydrogel within a desalination module with cyclic reversibility, as well as proposed criteria for developing even better PIL hydrogels. Thermally responsive PIL hydrogel has also been used in microfluidic actuators [64], electrochemical sensors [65-67], actuators [68], protein separation [69, 70] and as flocculants for water purification [71].

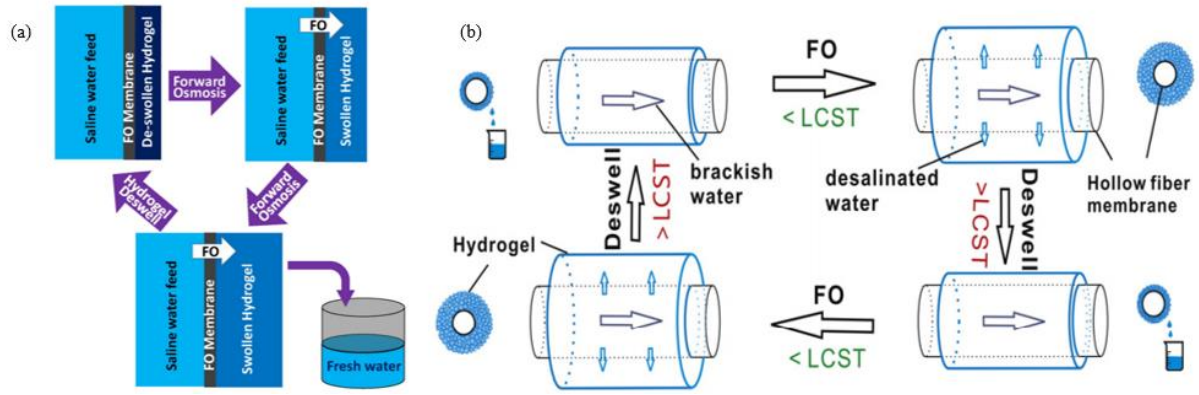


Figure 4(a) Illustration of using stimuli responsive hydrogels as draw solutes for Forward Osmosis, 4(b) [33] Reprinted with permission. Copyright 2016, Elsevier.

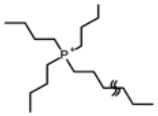
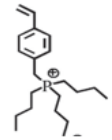
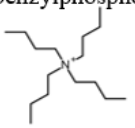
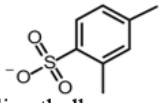
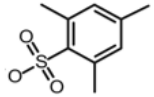
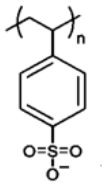
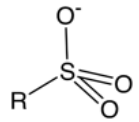
4. Challenges, prospects and opportunities

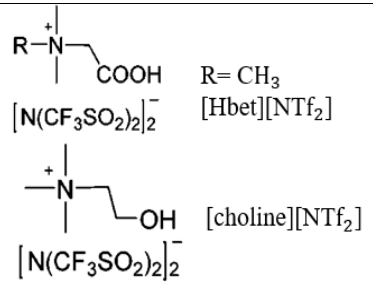
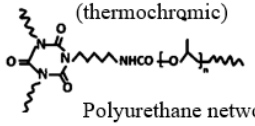
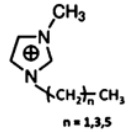
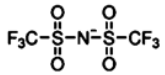
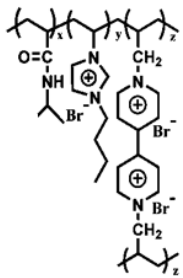
In this focused review we have specifically looked into the reversible change in physio-chemical properties e.g. osmotic pressure and solubility of ILs/PILs incurred by temperature, enabling the development of advanced stimuli responsive materials. The unique properties of ILs and PILs combined with thermal response can be further exploited. Here we have shown the potential applications of tailorable ILs/PILs in a newly emerging area of osmotically driven

membrane processes and solar (light) modulation relevant for water and energy-related technologies. Responsive ILs/PILs have great potential for FO and OHE applications. Further development hinges on several fundamental issues, e.g. the effect of viscosity, membrane stability, and the molecular level interactions of the cations and anions of ILs or PILs with water molecules. Moreover, scale-up study is urgently needed to take the advantage of their low reverse solute diffusion and to investigate the internal concentration polarization of this new class of draw solutes for FO application. Tackling these issues requires a multidisciplinary effort. For instance, internal concentration polarization needs to be tackled by designing appropriate IL/PIL but also with proper engineering integration with membrane processes. However, their application for FO/OHE has been slowed down by concerns regarding their cost, purification and regeneration. For solar modulation, the new class of robust ionogels, in which the stimuli responsive properties were endowed by specific interaction between ILs and the polymer chains, have shown great advantages over the incumbent hydrogel counterparts. New functional ionogels combining active luminescence transmittance with autonomous solar modulation could be of interest for future study. Though several other parameters like color tunability, active switching, and material performance including durability, reproducibility, and cost should be considered for practical application.

ILs and PILs have great potential from both fundamental and application point of view both in industry and academia. In this review we have highlighted the emerging trends in the development of thermally responsive ILs and PILs for three promising applications i.e. water treatment, osmotic energy conversion and solar modulation. We believe that this summary will arouse greater research interest and accelerate development of ILs for applications within and beyond those mentioned.

Table 1 Summary of representative thermally responsive IL/PILs used for highlighted applications and their challenges/opportunities for future development

Application	Representative thermally responsive ILs/PILs	Major Challenges/Opportunities	Ref
Draw solute in Forward Osmosis	**Cations**  Alkyltributylphosphonium $[P_{444n}]^+$, n: alkyl chain length  Tributyl-4-vinylbenzylphosphonium  tetrabutylammonium $[N_{4444}]^+$ **Anions**  2,4-dimethylbenzenesulfonate $[DMBS]^-$  2,4,6-trimethylbenzenesulfonate $[TMBS]^-$  Styrene Sulfonate $[SS]^-$  Alkyl sulfonate Br^- Bromide $[Br]^-$	• Developing ILs/PILs based on molecular design of cation and anion o Offering characteristics of ideal DS e.g. high osmotic pressure (high charge density) and low to zero reverse solute diffusion (suitable viscosity). o With optimal phase change characteristic, e.g. sharp LCST near to room temperature, for facile regeneration. • Multi-functional ILs/PILs e.g. photo-, thermal, and redox-responsive • Integration of IL/PILs in FO in suitable form factor e.g. hydrogel	[36, 38, 62, 72-74]

Osmotic Heat Engine	 betainium bis(trifluoromethyl sulfonyl) imide ILs	• Development of ILs/PILs chemically benign to the membrane, on top of high osmotic pressure, low volatility, and facile regeneration • Extending ILs-based OHE to other systems e.g. RED, CM • Improve power density by appropriate choice of ILs/PILs mixtures and membrane	[43]
Smart Windows	Polymeric-IL system (thermochromic)  Polyurethane network  1-alkyl-3-methylimidazolium [$C_n$mim] cation  bis-(trifluoromethylsulfonyl)imide [NTf_2] anion Thermo- and electro- chromic P(NIPAM-BVIm-DAV) gels  3-butyl-1-vinyl-imidazolium bromide [BVIM][Br]. Diallyl viologen (DAV)	• Understanding and optimization of ILs/PILs-matrix interactions, for o Improved encapsulation and dispersion of IL/PILs o Autonomous, energy-efficient, rapid, and reversible micro-phase separation • Develop IL/PILs with wide solar modulation ability, multi-functionality, durability, and robustness	[51-53]

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