

Prospect of ionic liquids and deep eutectic solvents as new generation draw solution in forward osmosis process

Supritam Dutta^a, Kaushik Nath^{b,*}

^a Department of Chemical Engineering, L. D. College of Engineering, Ahmedabad, 380015, India

^b Department of Chemical Engineering, G. H. Patel College of Engineering & Technology, Vallabh Vidyanagar, 388120, India

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ABSTRACT

Forward osmosis (FO) can aptly contribute to increased water reuse at the expense of low energy expenditure. The distinctive feature for FO lies with the exploitation of the natural osmotic pressure gradient generated by a concentrated draw solution for water transport across a semi-permeable membrane. The selection of a suitable draw solution remains to be a grey area of commercial development of FO process. The present review summarizes the importance of ionic liquid (IL) and deep eutectic solvent (DES) with natural product components and their potential as draw solutions in FO and their industrial applications. Various factors affecting performances of ILs and DESs as draw solutions are briefly assessed and critically compared with pertinent literature. Regeneration of IL and DES as spent solution from the process, as well as pure water recovery is discussed with special reference to heat energy optimization. A future pathway for research in IL and DES as draw solute and their economic aspects are also highlighted.

1. Introduction

Forward osmosis (FO), despite being old in its concept, has spurred a renewed interest, both academically and commercially in last two decades. Being natural, clean and ecofriendly process, FO has remarkable potential in substituting or complementing many conventional separation systems. FO finds its increasing applications in the domains of desalination, irrigation, power regeneration, pharmaceutical and protein concentration, water reuse, osmotic membrane bio-reactor and enhanced oil recovery [1,2]. In this process, a semipermeable membrane is positioned in between two solutions of different concentrations (more precisely of different osmotic pressure): a concentrated solution (draw solution) and a dilute solution (feed solution). The concentration difference between the two solutions generates the required osmotic potential which provides the driving force to extract fresh water from a feed solution (such as seawater, brine, or any wastewater, dilute product solution) on the other side of the membrane. As a result the process can concentrate a solution of lower osmotic pressure with that of a higher osmotic pressure. Forward osmosis is endowed with a number of benefits to its credit. These include high salt rejection, less susceptibility to membrane fouling and above all the requirement of less hydraulic pressure compared to their pressure driven counterparts.

The selection of a safe, efficient and inexpensive draw solution plays an important role in the progress of the FO process. A good draw

solution should not only be capable of generating high osmotic potential but also be easily recoverable. However, to make FO process commercially competitive with other established separation processes, some of the key issues like low water flux rates, reverse solute flux (RSF), concentration polarization (CP) and energy efficient recovery of draw solutes also need to be addressed adequately. Interestingly, most of the issues related to CP and RSF are dependent on both membrane structure and draw solute properties. There is a strong correlation between the choice of draw solutes and progress of FO membranes research [3]. Synthetic draw solutes with tailor-made properties are being regularly developed and tested for their suitability as draw solutes however the results are met with limited success. Numerous inorganic compounds have been reported and explored in membrane literature as potential candidates for draw solutions [4,5]. Nonetheless, many of these compounds have exhibited a high reverse draw solute flux or are expensive to recycle, leave aside their toxic potency at times. Therefore, the search for a compatible and efficient draw solution assumes paramount importance in view of the wider industrial acceptance of forward osmosis.

Ionic liquids (IL) and deep eutectic solvents (DES) (also referred to as bio ionic liquids) are lately touted as green solvents to be used in a variety of separation processes. These are a few of the latest class of draw solutes which has caught researchers' attention. DES like Choline chloride – Ethylene glycol (Ch-Cl-EG) and Choline chloride – glycerol

* Corresponding author.

E-mail address: kaushiknath@gcet.ac.in (K. Nath).

Nomenclature

LLE	Liquid liquid extraction
ED	Extractive distillation
MD	Membrane distillation
UAE	Ultrasound assisted extraction
MBR	Membrane bio-Reactor
Ch-Cl	Choline chloride

EG	Ethylene glycol
MA	Malonic acid
IL	Ionic liquid
DES	Deep eutectic solvent
NADES	Natural deep eutectic solvent
LCST	Lower critical solution temperature
UCST	Upper critical solution temperature

(Ch-Cl-glycerol) has been attempted as potential draw solutes [6]. They have shown to possess high osmotic potential and can be easily recovered rendering better energy efficiency of the overall process. They are also economically competitive and environmentally benign. Although there are quite a good number of reviews on various aspects of FO in recent literature, encompassing membrane development, area specific applications, selection of draw solutions and few more, applicability of IL and DES, in particular, as draw solution have not been surveyed so far. This paper focuses on the amenability of IL and DES as draw solution and critically analyzes their applicability in forward osmosis systems with regard to concepts and key issues. Various physico-chemical parameters governing the FO performance, synthesis and recovery of draw solutes and economic aspects are adequately reviewed in the following sections. In spite of limited work reported by researchers in using IL and DES in FO process as draw solute, the impetus for the present review was stimulated firstly by the wide application potential of IL and DES as new generation eco-friendly solvents and secondly to obtain a further insight into the direction of basic and applied research in the area of FO.

2. FO membrane and draw solution

FO membranes, similar to their RO counterparts, generally contain two layers: a selective active thin layer and a porous support layer. The active layer is mainly responsible for salt rejection and the support layer provides the necessary mechanical strength to engineer the module. The two major desirable properties of a successful FO membrane are high solute rejection propensity and high water flux. It is very difficult to provide these two properties at the same time. The other desirable properties include minimal concentration polarization, long term

mechanical stability and resistance to various pH environments. Since the pioneering development of modern FO membranes by Hydration Technologies, Inc. (HTI, Albany, OR), a lot of research work on FO has been reported in literature [1]. Cellulose Triacetate (CTA) FO membranes fabricated by HTI, Inc. is credited with high water flux performance but reportedly suffers from high RSF in case of smaller solutes [7]. To mitigate the problem, a thin film composite (TFC) FO membranes, which exhibit reduced RSF without compromising the flux rates [8,9] could be used. Researchers have been working actively in developing TFC membranes for enhancing the performance of FO process further [10].

Draw solution has another dominant role to play in FO processes. A good draw solution should be capable of generating high osmotic pressure [11] and simultaneously be easily recoverable. However, these two requirements are self-conflicting as good osmotic potential needs strong affiliation between the draw solute and water molecules, e.g., via hydration or ionization, which subsequently makes recovery process difficult [5]. On the other hand, it should also have essential solvent characteristics like wide availability, high solubility, minimal toxicity, non-reactivity and above all low cost. Search for an ideal draw solution constitutes a major focus of FO research. Considering the diversity of feed streams to be treated, it may not be possible for a single universal draw solution to become a panacea to treat all type of feed streams.

Draw solutes are broadly classified into two groups; compounds that are commercially available and structurally modified synthetic compounds (Fig. 1). The commercially available compounds include inorganic salts like NaCl, MgSO_4 , NaHCO_3 , KHCO_3 , K_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 etc., organic salts like sodium acetate, sodium formate, magnesium acetate, sodium propionate, etc.; volatile compounds like NH_3 - CO_2 gas mixture, SO_2 etc.; nutrient compounds like glucose and

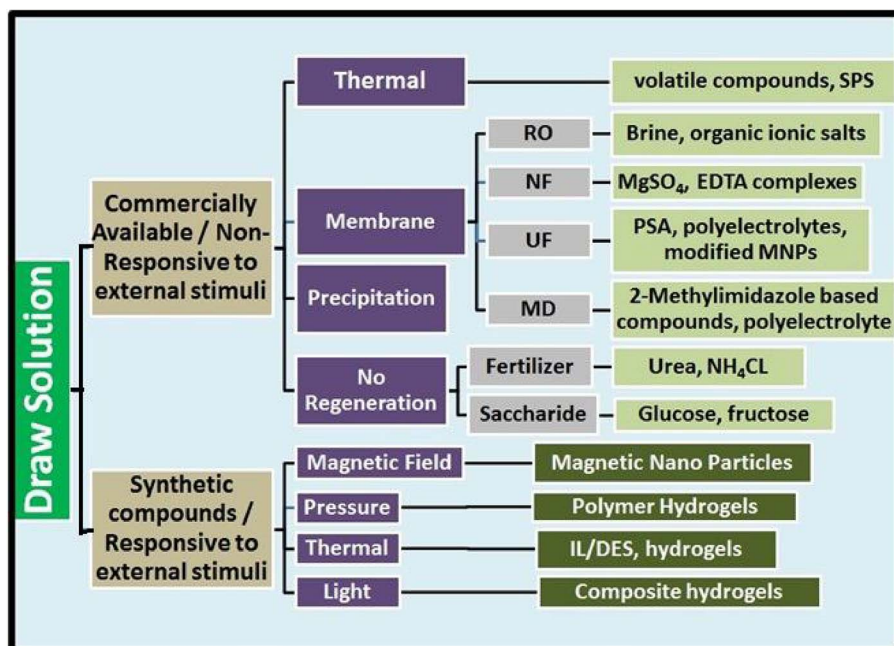


Fig. 1. Classification of draw solutes [3–5,27].

fructose; fertilizers like urea, NH_4Cl , etc. and polymers. The synthetic compounds developed by various researchers show great potential as draw solutes. These include hydrophilic magnetic nanoparticles (MNPs); polyelectrolytes like polyacrylic acid sodium (PAA-Na) salts; hydroacid complexes, switchable polarity solvents (SPSs) like mixtures of carbon dioxide, water and tertiary amines; deep eutectic solvent (DES) like choline chloride-ethylene glycol, choline chloride-glycerol etc.; polymer hydrogels; dual responsive polymers etc. More and more synthetic compounds are being tested for application in FO as draw solutes. Yet another classification of draw solution can be made on the basis of the recovery methods of draw solute. Here the draw solutes are classified as responsive and non-responsive [5] to some external stimuli. The non-responsive draw solutes include the commercially available compounds mentioned above, while the responsive draw solutes are mostly the synthetic compounds which give response to some kind of stimuli. These can be further categorized based on type of stimuli like thermal, pressure, magnetic field and so on.

Despite the extensive research efforts devoted in the pursuit of identifying novel draw solutes, simple dissolved inorganic and thermolytic salts (e.g., NaCl [12–14], MgCl_2 [15] etc.) are the most popular and widely-used for various applications. Also, they are probably the most effective draw solutes [16] reported so far. Around 40% of research work has been reported using NaCl as draw solution because of its abundant availability, high solubility, non-toxicity and being inexpensive [2]. NaCl generate high osmotic pressures at low solution viscosities and have high diffusivities but suffer from RSF problem. Researchers are still trying to improve the performance of NaCl draw solutes [17]. Nevertheless, NaCl (2M and 3M) remains to be the benchmark for the performance of draw solutes. As none of the commercially available non-responsive draw solutes could show satisfactory performance with respect to all the above mentioned parameters and recovery method, the research focus has now been shifted to the development of synthetic draw solutes with tailored properties. Synthetic materials which are highly soluble in water and form homogeneous solutions show better performance as draw solution. However, the RSF should be maintained within the acceptable limits [3].

2.1. Recovery of draw solute

The recovery and recycle of draw solute is of prime importance as both of these require expenditure of energy. This is one of the grey areas of FO research and development. Recovery of draw solute is necessary because of two important reasons viz. loss of draw solute needs costly replenishment and in most application pure water is recovered as a product. So, high level of separation is an essential prerequisite of a commercial FO process. This can be achieved by using thermal separation process like heating; membrane process like reverse osmosis (RO) [18], nanofiltration (NF) [12,19], ultrafiltration (UF) [13], membrane distillation (MD) [14,20], electrodialysis (ED) [21]; precipitation using chemicals like $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$ [22]; external stimulus like magnetic field [23], sunlight, heat combined with hydraulic pressure. In addition synergic combination of two or more process like precipitation-magnetic field [24], precipitation-thermal, hot-ultrafiltration [25], integrated electric field NF system [26] etc. have also been explored to optimize the overall energy consumption.

Numerous methods for draw solute recovery have been attempted by the researchers [27]. The choice of recovery methods depends largely on two major factors namely the amount of energy required and the extent of separation of draw solutes from the solution. A highly efficient recovery method demands minimum energy consumption and maximum draw solute recovery which in turn ensures maximum pure water recovery. All the recovery methods reported in literature could achieve fairly high degree of separation however at the expense of high energy consumption. Certainly the conventional separation methods would not live up to the expectation in making solute recovery energy efficient. In order to make FO competitive, alternative options are being

suggested in the form of responsive draw solutes which may consume less direct energy [24] or less expensive form of energy like low grade heat or solar energy [27]. This could be possible in industry where lot of waste heat is available. The other option is to make an optimum economic balance between draw solute recovery cost, replenishment cost and cost of fresh water generated. In remote application like treatment of effluent generated on site during oil and gas drilling operation, FO has been demonstrated to be effective in osmotic dilution mode [18,28]. FO is used to recover part of water from drilling waste streams. A balance is made in generating local, reusable water source onsite thereby limiting fresh water and wastewater transport. NaCl is used as draw solute which does not need costly replenishment [29,30]. In fertigation process, fertilizers like urea, NH_4Cl , NH_4NO_3 , KCl, $\text{NH}_4\text{H}_2\text{PO}_4$ etc. are used as a drawing agent and the resulting dilute fertilizer can be used for irrigation instead of recovering (osmotic dilution mode) [31,32]. In the commercial application of FO the focus is more on making FO process economically competitive by harping on the drawbacks of other technologies (in most cases RO) rather than improving the FO process itself. Also intelligent process design and optimization have enabled hybrid FO systems commercially implementable [33]. Researchers in FO community are convinced that a breakthrough in either membrane side or draw solute side can be made in near future thereby rendering the FO process directly competitive with other separation processes. Exploration of ILs and DESs as potential draw solutes may be a step towards that direction.

2.2. Concentration polarization

Concentration polarization (CP) is one of the major reasons which contribute to decrease in the net driving force (osmotic pressure). Based on the position where CP occurs, it can be classified into two categories: external concentration polarization (ECP) and internal concentration polarization (ICP). ICP phenomenon occurs inside the porous support layer due to the opposite diffusion of water and solutes. It is the most challenging phenomenon which occurs in FO processes as it cannot be easily eradicated. The decline in water flux in FO process is predominantly caused by ICP [7] and the flux reduction can be very high, in some cases up to 80% [3]. ICP is caused by the gradual dilution of the draw solution and the gradual concentration of the feed solution inside the membrane. With solvent permeating from the feed side to the draw solution continuously and in absence of any external turbulence, the draw solute concentration at the surface of membrane gradually becomes lower than its bulk concentration, and correspondingly the feed concentration at the surface of membrane increasingly becomes higher than its bulk concentration. This leads to net reduction in concentration difference between the two sides. As the concentration difference between the draw and feed solution is the only driving force, hence any reduction in the net concentration difference tends to slow down the process. This effect is somewhat analogous to the reduction in available temperature difference (driving force) in an evaporator due to boiling point elevation of the solution. To alleviate the problems of ICP, the support layer for FO membrane should be as thin as possible, with high porosity and low tortuosity [34]. A major spotlight in FO research is development of FO membranes with high permeability and high hydrophilicity combined with low structure parameter to tackle the issue of CP [35]. Draw solutes that have high diffusivities give rise to higher water flux thereby decreasing the effect of ICP. On the contrary ECP phenomenon occurs at the outer surface of the membrane active layer. It merits mentioning that incorporating methods like increase of flow turbulence or calculated augmentation of water flux can substantially alleviate the effect of ECP on permeate flux [36].

2.3. Reverse solute flux

The occurrence of RSF adversely affects the performance of FO process and lead to other problems. It is one of the major parameters

which determine the selection of draw solutes. It not only diminishes the driving force [2] but also contaminates the feed solution (e.g. dewatering). In addition, it also causes the loss of precious draw solute. This in turn tends to increase the replenishment cost of the draw solute. For example, if FO technology is applied in dewatering of dilute proteins or pharmaceuticals using brine as draw solution, the RSF phenomenon may contaminate these products. Salt sensitiveness could even result into denaturation of products. Also, high RSF could lead to severe membrane fouling [37]. Although small molecular size draw solutes generate high water flux but these suffer from high RSF. Small size solutes like NaCl are more prone to RSF while larger solutes like polymer and nanoparticle based draw solutions, has the advantage of essentially eliminating RSF. While selecting draw solutes, the process designer generally should make a trade-off between small solute size to limit ICP and large solute size to decrease RSF [36]. The advent and expected commercialization of highly selective TFC-FO membranes may promote the use of small, highly-mobile solutes and decrease the need for exploring draw solutes with larger molecular size. A major part of research in FO process constitutes exploring draw solutes with low RSF [20,38].

2.4. Applicability of FO

FO has a remarkable potential in reclamation of complex wastewater streams generated from diverse areas of operation. FO applications encompass osmotic dilution prior to desalination, water recovery from wastewater, fertigation, emergency water supply in military, space and humanitarian aid and treatment of high salinity brines. FO is generally most viable in the scenarios of highly saline solutions where other methods of water recovery become operationally unsuitable or in situations where the draw solution can be directly used for beneficial purposes. It could also be useful in the dilution of a high salinity feed stream with a low salinity waste stream. More and more applications of osmotic dilution mode are being explored where FO is increasingly recognized as an effective technique [18]. It can be used in remote areas where availability of energy is an issue. Here FO systems using low grade energy could be highly effective. Generation of potable water in portable devices using FO in water scarce areas has been already been reported [1]. In industrial hubs the liquid effluents generated are often treated in common effluent treatment plant (CETP). These CETPs often suffer from huge loads, in some cases exceeding their capacity. These CETP effluents are a very complex combination of effluents from various industries resulting in a mixture very difficult to treat. In such cases FO could be particularly useful. It has been demonstrated that in treatment and desalination of high fouling complex industrial streams and wastewater generated by mining and oil and gas exploration activities [39], FO process is proven to be beneficial [29,39]. In addition, FO can be used to pretreat the feed to the RO system, running a closed loop draw solution re-concentrated by RO in a complementary process [40]. In such applications, FO can protect the RO system ensuing less frequent cleaning protocols thus prolonging the RO membrane life. In standalone chemical process plants, concentration and dilution of process streams may occur simultaneously at different places. FO could be suitable for doing both these operations in one step with very low energy consumption. For example, FO process could be used for dewatering of effluent streams by using a concentrated stream from the same industry (which needs dilution). Satisfactory results could be anticipated by doing proper stream networking along with some reorientation in pumping requirements. Similar to energy/mass integration, concentration integration could become the next promising area.

3. Ionic liquids (IL)

Ionic liquids (ILs) are salts that have low melting point thereby making them liquid at low temperature, typically less than 100 °C at atmospheric pressure. They have favorable properties such as negligible

vapor pressure (non-volatile), high ionic conductivity, high solubility, non-flammability, chemical and thermal stability [41] rendering them ideal candidates for numerous industrial applications. Being non-volatile they have potential to replace many harmful traditional volatile organic compounds as solvent thus earning the tag of “green solvent” [42,43]. Some of the undesirable properties of ILs like high viscosity, combustible character, poor biodegradability and high cost of production has been reported and discussed in literature [41]. However, the major advantage that made ILs popular is the numerous structural possibilities that can be achieved by tweaking the alkyl chain and the anionic precursor. In fact, by suitable selection of cations and anions they can be tailored for specific applications.

Ionic liquid and water can form homogenous solution and exhibits unique phase behavior. There are two types of IL-water mixture based on the temperature at which mixture undergoes phase separation – lower critical solution temperature (LCST) and upper critical solution temperature (UCST). In LCST type mixture the phase separation occurs at temperature above the LCST point, while in UCST type mixture the phase separation occurs at temperature below the UCST point. The phase separation generally results in an IL rich phase and water rich phase.

ILs are applied as electrolytes in battery and fuel cells [44,45]; as catalytic agent in various chemical synthesis like biodiesel production [46]; as solvents in extraction process [43,47] like separation of heavy metals [48,49], aromatics from pyrolytic sugars in bioethanol production [50]; absorbents in gas separation [51]. In membrane based separation process, ILs have been reportedly used as mobilizer in pervaporation membranes [52]; as liquid membranes [53] for various separation processes; lithium recovery from seawater using dialysis [54] and numerous other applications. ILs being a broad family, its successful development as well as use is also marred with controversies in regard to toxicity and environmental concerns [55]. Hence, developing new ILs needs careful environment impact assessment. In not doing so, their industrial utilization may be restricted due to stringent environmental regulations [56]. In the quest to develop green solvents which are also commercially viable, a new class of ILs known as deep eutectic solvents has come into limelight.

3.1. Deep eutectic solvents (DES)

Deep eutectic solvent (DES)s are a class of ILs. They cannot be strictly defined as ILs as they are mixtures whereas ILs are single salts. They are eutectic mixture of Lewis or Bronsted acids and bases that can contain a variety of anionic and/or cationic species having melting point significantly less than the individual components. For example, the melting point of pure choline chloride (Ch-Cl) and urea is 302 °C and 134 °C respectively, whereas Ch-Cl + urea mixture in 2:1 molar ratio which forms an eutectic solvent has freezing point of 12 °C (Fig. 2) which is substantially less than the individual components [57]. They are obtained by the complexation of a quaternary ammonium salt with a metal salt or hydrogen bond donor. Different categories of DES are summarized in Table 1.

The term deep eutectic solvent was coined initially to describe type 3 eutectics but has subsequently been used to describe all of the eutectic mixtures [58]. The wide array of choice of hydrogen bond donor makes it easier to develop DESs with required properties. The same characteristics and properties which make ILs attractive for industrial application are also shared by DESs. DESs exhibit negligible vapor pressure (non-volatile), high ionic conductivity, high solubility, non-flammability, bio-degradability, chemical and thermal stability making them highly acceptable as solvents, catalysts and absorbents for various applications (Table 3). Over and above, they are cheap, environmentally benign and easy to manufacture making them a viable alternative for many existing commercial application [42,58,59]. Choline chloride (Ch-Cl) is the most common quaternary ammonium organic salt used as it is cheap, non-toxic and bio-degradable. It has a

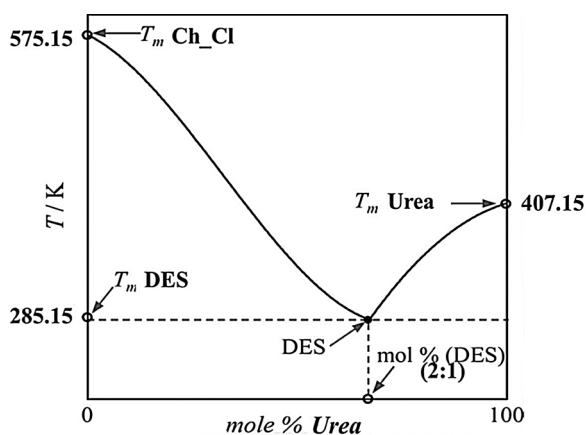


Fig. 2. Phase diagram of Choline Chloride and urea in 1:2 molar ratio [41].

choline cation with a chloride anion (IUPAC name: 2-hydroxyethyltrimethylammonium; chloride). It is regarded as a component of vitamin B-complex and can be extracted from biomass. Abbott et al. was the first to report DES based on Ch-Cl and urea (1:2 molar ratio) in 2003 [57]. Other salts, such as imidazolium-, ammonium-, and phosphonium-based ones, have also been studied, but to a lesser extent.

Table 1
Category of Deep Eutectic Solvents.

Category	Types	Examples	Reference
Type 1	Metal salt + organic salt	[AgCl, CuCl, LiCl, CdCl ₂ , CuCl ₂ , SnCl ₂ , ZnCl ₂ , LaCl ₃ , SnCl ₄] + [Choline Chloride, N-ethyl-2-hydroxy-N,N-dimethylethanaminium chloride; 2-(chlorocarbonyloxy)-N,N,N-tri dimethylethanaminium chloride; N-benzyl-2-hydroxy-N,N-dimethylethanaminium]	[58,60]
Type 2	Metal salt hydrate + organic salt	[CoCl ₂ ·6H ₂ O, CrCl ₃ ·6H ₂ O, CuCl ₂ ·2H ₂ O, NiCl ₂ ·6H ₂ O, FeCl ₃ ·6H ₂ O] + [Choline Chloride, N-ethyl-2-hydroxy-N,N-dimethylethanaminium chloride; 2-(chlorocarbonyloxy)-N,N,N-tri dimethylethanaminium chloride; N-benzyl-2-hydroxy-N,N-dimethylethanaminium]	[58,66]
Type 3	Organic salt + hydrogen bond donor	[Choline Chloride, N-ethyl-2-hydroxy-N,N-dimethylethanaminium chloride; 2-(chlorocarbonyloxy)-N,N,N-tri dimethylethanaminium chloride; N-benzyl-2-hydroxy-N,N-dimethylethanaminium] + [urea, thiourea, benzamide, glycerol, ethylene glycol, benzoic acid, malonic acid]	[41,59,60,62,86,87]
Type 4	Metal salt (hydrate) + hydrogen bond donor	[CuCl ₂ , SnCl ₂ , ZnCl ₂ , CoCl ₂ ·6H ₂ O, CrCl ₃ ·6H ₂ O, NiCl ₂ ·6H ₂ O, FeCl ₃ ·6H ₂ O] + [urea, thiourea, benzamide, glycerol, ethylene glycol, benzoic acid, malonic acid]	[60,66,88]

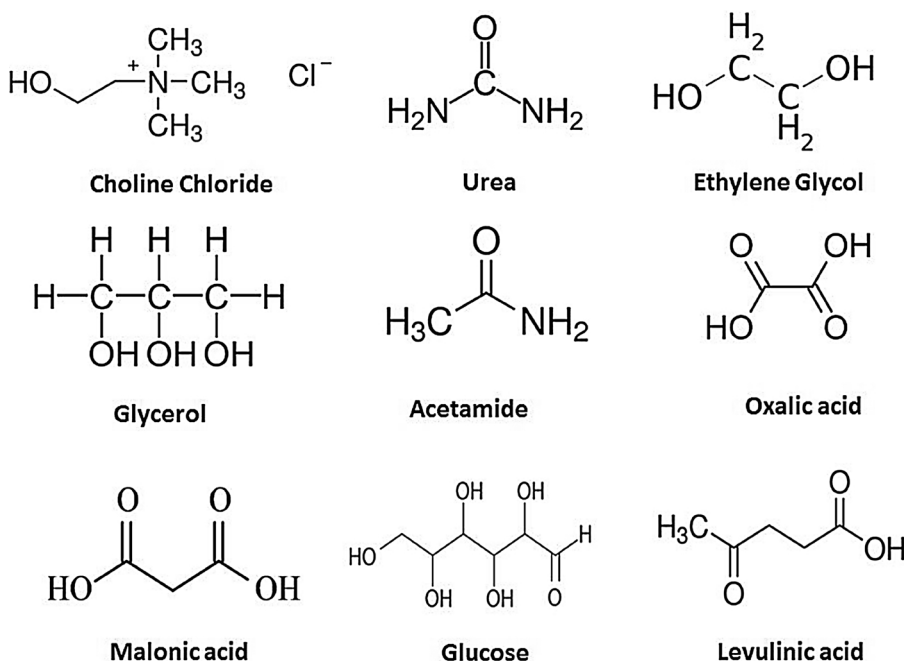


Fig. 3. Chemical structure of some compounds that can be used to form DES [58,60].

Similarly, a variety of hydrogen bond donors like ethylene glycol, acetic acid, glycerol, oxalic acid, malonic acid etc. other than urea has been studied and reported in literature. Fig. 3 presents chemical structure of some compounds that can be commonly used to form DES. It is to be noted that not all ratios of the individual components can form a DES. Some of the commercially available DESs are shown in Table 2. A lot of DESs is still being developed and reported in search of favorable properties which can be applied in suitable area [60–66].

DESs are used as solvents [67–76], entrainers [77,78], catalysts [79–82], in electrochemistry [83,84], as absorbents [85] and in numerous other ways to a wide variety of industries. Widespread application of DESs is continuously being explored and reported in literature. A short overview of the potential of DES in various fields is presented in Table 3.

3.2. Natural deep eutectic solvents (NADES)

When the compounds that constitute the DES are primary metabolites, namely, amino acids, organic acids, sugars, or choline derivatives, the DES are termed as natural deep eutectic solvents (NADES) [59]. Dai et al. [86] has demonstrated over 100 combinations of NADES which has useful properties especially in terms of solubility. They also demonstrated the possibility of the formation of ternary deep eutectic solvents (TDES) which can be explored and tweaked to improve their

Table 2
Some commonly used DES [41,60,65].

Trade Name	Complexing agent (H-bond donor) (a)	Quaternary Ammonium salt (b)	Molar Ratio (a:b)
Reline	Urea	Choline Chloride	2:1
Maline	Malonic acid	Choline Chloride	1:1
Oxaline	Oxalic acid	Choline Chloride	1:1
Glyceline	Glycerol	Choline Chloride	2:1
Ethaline	Ethylene Glycol	Choline Chloride	2:1
Acetaline	Acetic acid	Choline Chloride	2:1

properties towards their targeted applications. Also, addition of water in small quantity to some NADESs exhibit favorable property change. e.g. Glycerol:Ch-Cl at 2:1 ratio has viscosity 222 cP at 25 °C whereas Glycerol:Ch-Cl:water at 2:1:1 ratio has viscosity of 51.3 cP at 40 °C [6,58,86]. This shows that addition of small amounts of water to Glyceline reduced viscosity still preserving its essential characteristics. Moreover, the toxicity profile of NADESs in general seems to be relatively less acute than their DESs parents [87]. Henceforth, in this paper DES will include NADES for discussion purpose, unless otherwise mentioned.

3.3. Preparation of IL/DES/NADES

The synthesis of ionic liquids is generally a two-step process. The first step constitutes the formation of the desired cation which is synthesized either by the protonation of the amine by an acid or through quaternization reactions of amine with a haloalkane followed by heating. In the second step anion exchange reactions are carried out by treatment of halide salts with Lewis acids to form Lewis acid-based ionic liquids or by anion metathesis [88]. The most extensively studied and used Lewis acid based ionic liquids are $AlCl_3$ based salts. Such salts involve simple mixing of the Lewis acid and the halide salt which results in the formation of more than one anionic species. $AlEtCl_2$, BCl_3 , $CuCl$, $InCl_3$ etc. are other Lewis acids used apart from $AlCl_3$. Anion metathesis is popular choice [89] for the preparation of water and air stable ionic liquids based upon 1,3-dialkylimidazolium cations. This method involves the treatment of the halide salt with the Ag/Na/K salts of NO_2^- , NO_3^- , BF_4^- , SO_4^{2-} etc. with the free acid of the appropriate anion. Advanced techniques like microwave irradiation and ultrasound

waves are used nowadays to enhance yield and shorten reaction time. Recent introduction of one pot synthetic protocols reduce the cost and improve efficiency [88].

The preparation method of each IL is different and more complicated than DES. The presence of heavy metal precursors creates toxicity concerns and environmental issues. In addition they may aggravate the RSF issue by contamination feed solution in dewatering applications. In this aspect DES has advantage. Synthesis of DESs is almost 100% atom economic [41], easy to handle and no purification is required, thus making their large-scale use feasible [58]. The preparation of DES does not involve any complicated process and can be easily manufactured in laboratory.

DESs can be obtained by proper mixing of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) at a suitable temperature. A large number of different compounds have been attempted as HBA and HBD for the synthetic preparation of DES. The most common HBA is Ch-Cl while urea, glycerol, citric acid and ethylene glycol are common HBDs. From 2003, since Abbott discovered the first DES [57], the heating method is the most simple and popular method of preparation of DES. This method is not only cheaper but also safer considering that the components are usually thermally unstable, similar to the case of sugars or amino acids. In this method, a mixture of HBA and HBD is mixed with moderate heating and continuous stirring for a couple of hours till a homogenous and colorless DES is formed in liquid form. For example, Ch-Cl and EG in 1:2 molar ratio is mixed and heated at 80 °C with continuous stirring for around 2 h to form Ethaline. In case of NADES similar procedure can be followed at even lower temperature of 50 °C with addition of small amount of water [86].

An alternative and easy procedure for DES preparation from aqueous solutions by freeze drying method was proposed by Gutiérrez et al. [90]. In this method, urea and Ch-Cl at a 2:1 molar ratio with 5% solute content (on weight basis) was prepared by mixing separate aqueous solutions of urea and Ch-Cl. The mixed solutions were then frozen (at -196°C and -20°C) followed by freeze drying to produce a clear viscous DES. Other methods of preparation of DES are also reported in literature. The grinding method, which has been largely explored in the preparation of DESs for pharmaceutical purposes, consists in mixing the two components and then grinding them in a mortar with a pestle at room temperature until a homogeneous liquid is formed [91]. In vacuum evaporation method, the components are dissolved in water and evaporated at 50 °C with a rotary evaporator. The liquid obtained was

Table 3
Overview of application of DES in various chemical processes.

Application mode	DES used	Areas of application	Reference
Solvent	Ch-Cl + EG	Metal extraction via leaching	[67]
	Ch-Cl + glycerol	Alcohol-ester mixtures via LLE	[68]
	Ch-Cl + oxalic acid	Grape skin phenolics via UAE	[69]
	Ch-Cl + urea	Nanofibrillation of wood cellulose	[70]
	Ch-Cl + thiourea	Manufacture α -chitin nanofibers	[71]
	Ch-Cl + (ethanediol, urea, glycerol)	Enzymecatalyzed hydrolysis of chiral (1,2)- <i>trans</i> -2-methylstyrene oxide	[72]
	Ch-Cl + (Urea, MA)	Solubilizing poorly soluble compounds for enhanced bioavailability	[73]
	Ch-Cl + glycerol	SO ₂ absorption	[74]
	Ch-Cl + (urea, glycerol)	Production of agar films	[75]
	Ch-Cl + urea	Pretreatment of Oil Palm Empty Fruit Bunch to increase yield in sugar production	[76]
Entrainer	Ch-Cl + (EG, glycerol, levulinic acid)	Azeotropic separation via LLE	[78]
	Ch-Cl + (lactic acid, glycolic acid)	Azeotropic separation via ED	[77]
Catalyst	Ch-Cl + p-toluenesulfonic acid monohydrate	Bio-diesel production	[79]
	Ch-Cl + $SnCl_2$	Synthesis of quinoline derivatives via reactive chromatography	[82]
	Ch-Cl + (urea, MA)	Synthesis of N-aryl phthalimide derivatives	[81]
	Ch-Cl – Oxalic acid	Furfural production from xylose and xylan	[80]
Electrochemistry	Ch-Cl + urea	Analytical method for determination of Cd^{2+} .	[83]
	Ch-Cl + EG	Electrodeposition of Ni-Co-Sn alloy	[84]
Absorbent	Ch-Cl + (glycerol, EG, diethylene glycol, triethylene glycol, urea, MA)	Pb removal from water by functionalized carbon nanotubes	[85]

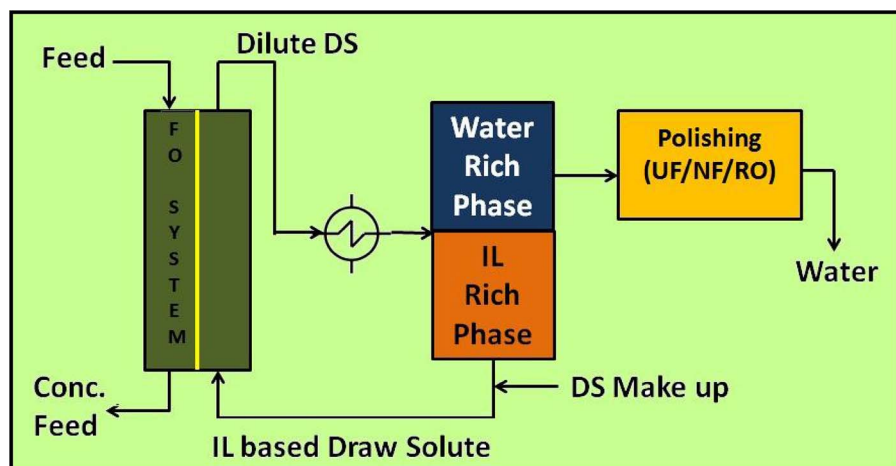


Fig. 4. A conceptual schematic diagram of ionic liquid/deep eutectic solvent based forward osmosis process. [6,95,100].

put in a desiccator with silica gel till they reached a constant weight. All the methods by and large show the same chemical profile for the obtained DES [86].

4. IL, DES and NADES as draw solute: performance check

Performance of various draw solutions in FO process is well documented in membrane literature [3–5]. A potential draw solute should primarily be able to generate high osmotic potential and should be easily recovered. Of late ILs and DESs are explored as draw solute in FO process and the results are encouraging. IL and DES as a category fall under responsive draw solutes using heat as a stimulus for regeneration and recycle of draw solutes. Both LCST and UCST type ILs are used as draw solute. Depending on whether the solution is LCST or UCST the solution is either heated or cooled beyond its critical point to form a draw solute rich and a water rich phases. Gravity separation techniques can be used to carry out bulk of the phase separation [11]. The draw solute rich phase is recycled back to the FO system while the water rich phase is further polished by RO or NF process to generate pure water as shown in Fig. 4. Retained osmolality of the dilute draw solution and the number of recycles that can be undertaken are the two important considerations in the DS rich phase. In the water rich phase the ease of separation of draw solute from water determines the additional energy consumption and in turn cost of separation.

It is worth mentioning that conventional thermal recovery of draw solutes is well reported and unanimously agreed to be uneconomical. Thermal recovery can be only viable when it is carried out at moderate temperatures using low grade heat/solar heat. Heat as a stimulus for responsive draw solutes has been discussed for other types of draw solutes such as volatile solutes [92], dual responsive polymer hydrogel [93,94] and water soluble polyelectrolytes [25]. Properties of LCST type have been exploited for regeneration and recycle in case of some polymer hydrogels [93]. Use of IL as draw agent is briefly mentioned recently in review literature [3,5]. Cai et al. reported the energy-efficient desalination by forward osmosis using responsive ionic liquid draw solute [95].

Preliminary work on LCST type draw solutes has been carried out by Mok et al., 2013 [96,97]. They studied tri(*n*-butyrylated) tris (2-aminoethyl)amine (nBu-TAEA) (MW = 356) and *n*-butyrylatedpolyethylenimine (nBu-PEI) (MW = 1238) solutions as possible LCST type draw solute. These draw solutes could display very stable phase separation behavior above LCST due to their uniform MW. The nBu-TAEA draw solutes reported osmotic flux less than $1 \text{ L m}^{-2} \text{ h}^{-1}$ up to 2 M concentration to draw water from 0.6 M NaCl and the nBu-PEI draw solute showed osmotic flux less than $1 \text{ L m}^{-2} \text{ h}^{-1}$ at 0.49 M concentration against 0.15 M NaCl. Both the draw solutes suffer from low osmotic flux which is hardly enough to draw water from artificial

sea water solution. However, the residual solute concentrations in the water-rich phase were low at 0.22 and 0.052 mol L^{-1} for nBu-TAEA and nBu-PEI respectively. The rejection efficiency was 98% and 99.6% for nBu-TAEA and nBu-PEI respectively owing to high MW of the draw solutes. The phase transition temperature was reported to be 31–32 °C and was found suitable. A similar type of work was reported by Nakayama et al. (2014) [98] using various glycol ethers as LCST type draw solute. A 12 M Di (ethylene glycol) *n*-hexyl ether (DEH) draw solution reported osmotic flux $0.62 \text{ L m}^{-2} \text{ h}^{-1}$ to draw water from 0.6 M NaCl solution which was considerably low. Water rich phase contained 0.081 M DEH. The phase transition temperature was 20 °C and the whole FO process could be operated in between 10 °C to 30 °C. CTA membranes provided by HTI Inc were used in both the cases.

Cai et al. reported use of three ILs namely Tetrabutylphosphonium 2,4-dimethylbenzenesulfonate ($\text{P}_{4444}\text{DMBS}$), Tetrabutylphosphonium mesitylenesulfonate ($\text{P}_{4444}\text{TMBS}$) and tributyl-octyl-phosphonium bromide (P_{4448}Br) as draw solution to draw water from sea water and brackish water [95]. The osmolality of the ILs was reported to be very high. The osmolality of 70 wt% solution was $5.4 \text{ osmol kg}^{-1}$ for $\text{P}_{4444}\text{DMBS}$ and $3.6 \text{ osmol kg}^{-1}$ for $\text{P}_{4444}\text{TMBS}$, which was 4.5 and 3 times of seawater's osmolality, respectively. Even after dilution they could retain much of their osmolality. $\text{P}_{4444}\text{DMBS}$ and $\text{P}_{4444}\text{TMBS}$ osmolality values of their 30 wt% ($\sim 0.95 \text{ mol kg}^{-1}$) solutions were reported at $1.34 \text{ osmol kg}^{-1}$ and $1.08 \text{ osmol kg}^{-1}$, respectively. P_{4448}Br demonstrated lower osmolality and hence could draw water only from low salinity feed solutions. The 70 wt% $\text{P}_{4444}\text{DMBS}$ draw solution could generate a water flux of $1.5 \text{ L m}^{-2} \text{ h}^{-1}$ against a feed of 1.2 M NaCl at 14 ± 1 °C. The draw ability has been found to increase with decreasing temperature. Additionally, these DS demonstrated low RSF below 30 mg L^{-1} . After FO process, the diluted 50 wt% draw solution underwent liquid–liquid phase separation at a temperature above its LCST (30–50 °C). A very mild temperature stimulus of about 35 and 40 °C could result in stable phase separation for $\text{P}_{4444}\text{TMBS}$ and $\text{P}_{4444}\text{DMBS}$, respectively. In a wide range of IL concentration between 10 and 60%, at 55 °C stable phase separation occurred containing 70% IL rich phase and 7.5% IL lean phase. The lean phase contained less than 10% draw solute concentration and high quality water was obtained by nanofiltration process. The retentate in NF along with the DS rich phase were recycled back without any further treatment. A prepared TFC membrane was used in the process. A patent application has been filed [99].

Zhong et al. [100] used 3.2 M solution of protonated betaine bis (trifluoromethylsulfonfyl)imide [Hbet][TF_2N] which was a UCST type ionic liquid to extract water from a feed up to 3.0 M NaCl solution. A BWRO type polyamide membrane YM70ACSP18 from Toray Inc. was used for the FO process. The FO process was carried out at 60 °C but subsequently cooled down to room temperature for phase separation.

At room temperature of 23 °C, the saturation concentration of [Hbet][Tf₂N] was approximately 3.2 mol L⁻¹ (88.3 wt%) in the IL rich phase and 0.36 mol L⁻¹ (13.7 wt%) in water rich phase. The water flux was very low (< 1 L m⁻² h⁻¹) which further decreased with increase in feed concentration. A very low RSF (< 1 mmol L⁻¹) was reported in the process. Increase of temperature was observed to have a positive effect on water flux. The relatively high saturation concentration of [Hbet][Tf₂N] in water rich phase needed RO process for further purification.

A group of scientists from CSIR-CSMCRI, Bhavnagar, India (Mondal et al., 2015) reported the use of DES as draw solute for dewatering process to enrich low abundant DNA and proteins [6]. The FO process reported by the group used Ch-Cl-EG (1:2) and Ch-Cl-Glycerol (1:2) as draw solution and brackish water as feed solution. An indigenously developed TFC polyamide membrane was used. A nominal flow rate of 1.8 LPM and feed inlet pressure of 1 atm was maintained on both sides. Ch-Cl-EG and Ch-Cl-Glycerol could generate very high osmotic pressure of 365 atm and 317 atm respectively. The osmotic potential could be retained ($\pi > 150$ atm) after 50% dilution and ($\pi > 60$ atm) after 80% dilution. Due to retention of osmotic potential, the draw solution could be recycled for a longer time. Both the draw solute showed high flux values of 7.85 and 3.71 L m⁻² h⁻¹ atm⁻¹ respectively. Draw solute was recovered by chilling at -5 °C. Presence of choline (2000–5000 mg L⁻¹) was reported in the recovered water. However, no further polishing was carried out.

In another experiment the same group used the same FO system for concentration of proteins and DNA. They could achieve more than 6 fold protein concentration and more than 3 fold DNA concentration. In both cases Ch-Cl-EG (1:2) was used as draw agent. An average flux of 3.10 L m⁻² h⁻¹ and 4.67 L m⁻² h⁻¹ was reported for DNA concentration and protein enrichment respectively. No loss of DNA or protein was reported. Even there was no denaturation of DNA signifying the absence of RSF. The diluted Ethaline draw solution was chilled at -5 °C to recover good quality product water and draw solution which could be reused. The recovered dilute Ethaline (~20%) was reused for three times without significant reduction of flux [101].

4.1. Osmotic potential and water flux

An overview of all the FO processes using IL and DES as draw solution is presented in Table 4. Till now limited work has been reported in literature. From the studies mentioned above, it is found that DES has melting point much below than the individual component, in some of the cases even at room temperature (e.g., Reline, T_m = 12 °C) which enable them to be used as an ambient temperature draw solute. DES such as Ethaline ($\pi \sim 365$ atm) and Glyceline ($\pi \sim 317$ atm) and IL such as P₄₄₄₄DMBS ($\pi \sim 5.4$ osmol kg⁻¹) and P₄₄₄₄TMBS ($\pi \sim 3.6$ osmol kg⁻¹) reported high osmotic potential [6,95], a primary requirement of FO process. It is worth mentioning that osmotic potential of sea water (approx. 0.6 M NaCl) is around 50 atm. (osmolality 1.2 osmol kg⁻¹). If compared to 2 M NaCl solution ($\pi \sim 104$ atm) which is often considered as a benchmark of draw solution, DES exhibits significantly higher osmotic potential. The density is comparable while the viscosity is significantly high. Table 5 shows the properties of some common DES which has potential to be applied as draw solutes.

The osmotic potential generated by the draw solutes is dependent on number of factors like solute concentration, molecular weight (MW) of the solute and the solution temperature. The number of species formed by dissociation in the solution affects the osmotic potential but it is not dependent on the types of species formed. It has been observed that draw solutes having low MW generate more osmotic potential [4]. This can be verified by Van't Hoff equation Eq. (1) [4,102]

$$\pi = icRT \quad (1)$$

Where i is the Van't Hoff factor (the number of moles of species formed by the dissociation of solutes in the solution), c is the solute concentration in mol L⁻¹ of solution, R is the universal gas constant

($R = 0.082$ L atm/mol K) and T is the absolute temperature of the solution. This equation is restricted to extremely dilute solutions and is generally used for the determination of large MW [103]. For more general solutions, the Virial equation [4,104] can be used as shown in Eq. (2)

$$\frac{\pi}{cRT} = 1 + Bc + Cc^2 + Dc^3 + \dots \quad (2)$$

where B , C and D are the osmotic Virial coefficients. The Virial coefficients can be determined empirically by fitting experimental osmotic pressure data. In general, the determination of B and C is enough to reproduce observed data [103]. Thus, a low MW solute with high water solubility will be able to generate higher osmotic pressure (on equal mass basis) resulting in high water fluxes [105,106]. The reported values of water flux in some thermally responsive ionic liquids like nBu-TAEA (MW-356), nBu-PEI (MW-1238), glycol ethers (MW ~ 200) and [Hbet][Tf₂N] (MW-398) were found to be very low (< 1 L m⁻² h⁻¹). Some of the IL like P₄₄₄₄DMBS could generate high osmotic potential (5.4 osmol kg⁻¹) and moderate water flux of ~4 L m⁻² h⁻¹ with 1.6 M NaCl feed solution. This can be attributed to the ionic nature of these classes of responsive draw solutes [95]. DES like Ethaline (MW-88) and Glyceline (MW-108) show good water flux rates (4–8 L m⁻² h⁻¹) with brackish feed water. In dewatering applications water flux of 3–4.5 L m⁻² h⁻¹ could be achieved with Ethaline as DES. Water fluxes obtained using ionic liquids are low compared to inorganic draw solutes. The MW of the DESs as mentioned in Table 5 ranges from 80 to 125 g mol⁻¹, which can be considered as low MW. They are highly soluble in water in almost any ratio. Hence it is possible for these DESs to generate high osmotic potential and consequently higher water flux rates. Even after dilution it is possible to retain the osmotic potential resulting in more number of recycle [6].

4.2. ICP effects

The MW of the DESs as mentioned in Table 5 ranges from 80 to 125 g mol⁻¹. Low MW draw solutes have higher diffusion coefficient compared to those with larger MW. Draw solutes with high diffusion coefficient encounter lower resistance and can smoothly diffuse through the membrane support layer. So, these DESs tend to have lower ICP effects [4]. This can be validated by Eq. (3) which is conveniently used to determine solute resistivity K within the porous support layer [1,36,105]:

$$K = \frac{\tau t}{\varepsilon D_s} \quad (3)$$

where t is thickness, τ is tortuosity and ε is porosity of the support layer. D_s is the diffusion coefficient of the draw solution. Minimizing the K value is one of the primary objectives of membrane manufacturers to improve the performance of forward osmosis processes. The term (τ/ε) is known as the membrane structural parameter (S). High viscosity of solutions reduces the diffusion coefficient [3]. All the DES show high viscosity at 25 °C. However, it has been demonstrated that addition of small quantities of water exhibit drastic reduction in viscosity in some DESs [58]. Also, small increase in temperature could considerably reduce the viscosity. For example, Glycerol:Ch-Cl (2:1) has viscosity 222 cP at 25 °C whereas Glycerol:Ch-Cl:water at 2:1:1 ratio has viscosity of 51.3 cP at 40 °C [6,58,86,87]. Dai et al. (2015) reported a decrease in viscosity from 397 to 7.2 cP, following the addition of 25% of water in the case of Glucose:Ch-Cl (2:5). The viscosity decreased by 1/3 when diluted with 5% water, and decreased to one-tenth of the original value with the addition of 10% water. The viscosity of Glucose-Ch-Cl(2:5) decreased by two-third when the temperature increased from 20 to 40 °C [86]. The viscosity change is achieved without changing other essential characteristics of the DES. Therefore, usage of DES as draw solutes can give the dual benefit of small MW and low viscosity which is extremely favorable as far as ICP problem is concerned. Moreover,

Table 4
An overview of IL's and DES's based Forward Osmosis process.

Process objectives & FO process Op. temp.	Membranes used	Draw solute used & type of IL/DES	DS Recovery method	Water flux rates ($\text{L m}^{-2} \text{h}^{-1}$)	Remarks	Ref.
Desalination of brackish water (25 °C)	TFC Polyamide, Indigenous	Ch-Cl-EG (1:2) [#] Ch-Cl-Glycerol (1:2) [*] UCST type DES	Chilling (−5 °C)	[#] 7.85 [*] 3.71	High osmotic potential ([#] 565 & [*] 317 atm for 70%wt. sol.) Retention of osmotic potential after dilution (> 150 atm after 50% dilution) Further polishing of water rich phase necessary (2–5 g L^{-1} choline detected)	[6,101]
Dewatering of DNA [#] & Conc. of protein (25 °C)	TFC Polyamide, Indigenous	Ch-Cl-EG (1:2) UCST type DES	Chilling (−5 °C)	[#] 3.10 [*] 4.67	Negligible RSF (no denaturation of feed molecules detected). No DNA & protein loss. > 6 time concentration of protein and > 3 time DNA concentration achieved Retention of osmotic potential of DS after dilution (reused 3 times)	[6,101]
Desalination (0.17–3 M NaCl) (60 °C)	BWRO type TFC, polyamide, Toray Inc.	[Hbet][Tf ₂ N] UCST type IL	Cooling (23 °C)	0.85–0.14	Very low RSF (< 1 mmol L^{-1}) High concentration of IL in water rich phase (used RO for polishing) Low salt rejection (~90%) Retention of osmotic potential of DS after dilution	[100]
Desalination (0.6 M NaCl) (10 °C)	CTA, HTI Inc	Glycolithers LCST type IL	Heating (20 °C)	0.62	Very low RSF Low concentration of IL in water rich phase High salt rejection	[98]
Desalination (0.6–1.6 M NaCl) (14–24 °C)	TFC, Polyamide indigenous	P ₄₄₄₄ DMBS [#] (70%wt) P ₄₄₄₄ TMB [*] (80%wt) LCST type IL	Heating (30–50 °C)	[#] 4.0–0.5 [*] 2 for 0.6 M NaCl feed	High osmotic potential ([#] 5.4 & [*] 3.6 osmol kg^{-1} for 70%wt. sol.) Retention of osmotic potential after dilution ([#] 1.34 & [*] 1.08 osmol kg^{-1} for 30%wt. sol.) Low RSF. Further polishing of water rich phase necessary (using NF/RO)	[95]
Desalination (0.6 M NaCl) (0.15 M NaCl) (18–21 °C)	CTA, HTI Inc	nBu-TAEA, nBu-PEI LCST type IL	Heating (55 °C)	< 1	Stable phase separation behavior. High rejection efficiency (98–99.6%)	[96,97]

Osmolality of sea water ~ 1.2 osmol kg^{-1} .

Table 5
Properties of some selected DES & 2 M NaCl for comparison

DES	MW (g/mol)	ρ (g/cc)	μ (cP)	Θ (mS/cm)	T_f (°C)	A_w	Π (atm)	Ref.
NaCl (2M)	58.5	1.08	2	130	−7	0.92	104	[19,102]
Ch-Cl-EG (1:2)	87.9	1.12	36	7.61	−66	0.12	365	[6,58,60]
Ch-Cl-Glycerol (1:2)	107.9	1.18	376 (20 °C) 259	1.05	−40	0.10	317	[6,58,60]
Ch-Cl-Urea (1:2)	86.6	1.25	750 169 (40 °C)	0.75	12	–	–	[41,58,60]
Ch-Cl-MA (1:1)	121.8	1.19	400	0.55	10	–	–	[58,60]
Ch-Cl-Glycerol (1:3)	103.9	1.20	450 (20 °C)	–	1.7	–	–	[58]
Ch-Cl-EG (1:3)	81.4	1.12	19 (20 °C)	–	−22	–	–	[58]
EtNH ₃ Cl-Urea (1:1.5)	68.6	1.14	128 (40 °C)	0.348 (40 °C)	–	–	–	[58]
Ch-Cl-Phenol (1:3)	105.5	1.09	44	3.14	−19	–	–	[120]

ρ : density, μ : viscosity, Θ : conductance, T_m : melting point, T_f : freezing point, A_w : water activity, Π : osmotic potential.
All properties at NTP.

Properties may be considered approximate in nature.

recycling of the dilute DES can add to reduction of viscosity. Ambient conditions of hot countries may be beneficial in further reduction of viscosity. It was demonstrated that the DES draw solutes could be recycled up to 3 times without much change in the water flux rates [6].

4.3. Reverse solute flux effects

All the IL and DES based draw solutes reported to have low RSF. Cai et al. reported RSF of about 30 mg L^{−1} for P₄₄₄₄DMBS and P₄₄₄₄TMBS [95]. High RSF leads to loss of precious draw solute and also contaminates the feed solution. In general high RSF is attributed to low MW draw solutes (e.g. NaCl (0.75 g L^{−1}) and NH₄HCO₃ (> 2 g L^{−1})). ILs like P₄₄₄₄DMBS, P₄₄₄₄TMBS and [Hbet][Tf₂N] has high MW (nearby 0.4 g mol^{−1} approx.) which contribute to low RSF. However, low RSF in DESs having MWs ranging between 0.08–0.125 g mol^{−1} may be attributed to high reverse solute flux selectivity (RSFS). RSFS is defined as the ratio of water flux (J_w) to reverse salt flux (J_s) in the FO process. A higher RSFS indicates the increase in membrane selectivity which in turn increases the efficiency of the FO process. This parameter is determined by the selectivity of the membrane active layer. RSFS is independent of the membrane support layer properties [87] and can quantitatively describe the FO membrane performance as shown in Eq. (4) [107–109].

$$RSFS = \frac{J_w}{J_s} = n \frac{A}{B} RT \quad (4)$$

where, n is the number of dissolved species created by the draw solute, T is the draw solution temperature, and R is the universal gas constant. A and B are water and solute permeability coefficient respectively. To maximize RSFS, the A/B ratio must be maximized. Slightly higher temperatures could lead to an increase in RSFS by reducing the CP resistances of FO membrane (both active layer and support layer) and also by increasing the wettability within the effective porosity of the SL [109]. It is to be noted that high RSFS is associated with decreased water permeability.

4.4. Recovery of IL/DES/NADES draw solute and pure water recovery

In case of IL/DES/NADES, recovery of draw solute is generally achieved by phase separation through thermal stimulation depending on whether the eutectic point is a LCST or UCST. The draw solute rich phase is recycled back and water rich phase is further treated for high quality water recovery. In all the FO experiments using IL/DES/NADES 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 the cases IL and DES (except PEI derivatives and glycol ethers) could retain the osmotic potential even after significant

dilution leading to more number of recycle. Up to three recycles can be achieved in batch systems, beyond which the draw solute needs to be replenished. In most cases the FO process are carried out at ambient temperatures. In case of UCST type draw solutes the temperature rise necessary for phase separation is moderate (up to 60 °C) which requires low energy. This can be provided by alternate energy ideas. LCST type draw solutes using DES [6] operated at ambient temperature and phase separation was carried out at −5 °C and using IL [100] operated at 55 °C and phase separation was carried out at around 30 °C. The low freezing point behavior of Glyceline and Ethaline (−40 °C and −66 °C respectively) can be exploited to generate industrial grade ice. The energy required for separating the water as ice is significantly less than that required to separate it by evaporation [110]. This can generate pure water but it is worth highlighting that energy cost of chilling is high. The system can be optimized by doing necessary energy calculations.

In all the above mentioned methods, further polishing of water rich phase becomes a necessity for pure water recovery. The factors which determine the type of polishing requirement include the end-use, toxicity of the draw solutes and energy cost. In most of the cases this can be possible by UF, NF or low pressure RO (< 5 bar) [111–114] depending on the MW of the draw solutes. All these processes are low energy intensive process where alternative energy sources can be useful. In these cases, less expensive form of energy like low grade heat or solar energy can be utilized. This is possible in industry where lot of waste heat is available. Usage of low grade heat is being explored extensively for economical thermal recovery of draw solutes. MD involves low capital cost if it utilizes low grade heat [27,105]. Solar energy should be utilized effectively for the regeneration of both conventional and temperature sensitive draw solutes [27]. Studies have shown that the enthalpy of phase separation of these responsive ionic liquid draw solutes is in the range of 3–5 kJ/kg which is substantially low making them very attractive [5].

5. Economic aspects

FO process does not need any external driving force to occur. The major operating cost involves energy costs for draw solute separation with recycle along with pumping costs. The operating cost also involves periodic maintenance cost incurred in fouling control, replenishment of draw solute etc. Most of the DES constituents can be derived from bio-based resources and are generally available in abundance. They are available in the market as well at very reasonable bulk rates, Ch-Cl (~1 \$/Kg), EG (~1 \$/Kg), Glycerol (~3 \$/Kg), urea (~0.25 \$/kg), malonic acid (~10 \$/kg). The major advantage of DES over IL is that they are easier to prepare with high purity at a relatively low cost.

As mentioned above, being low temperature operation, energy requirement of FO process along with recovery of draw solute can be

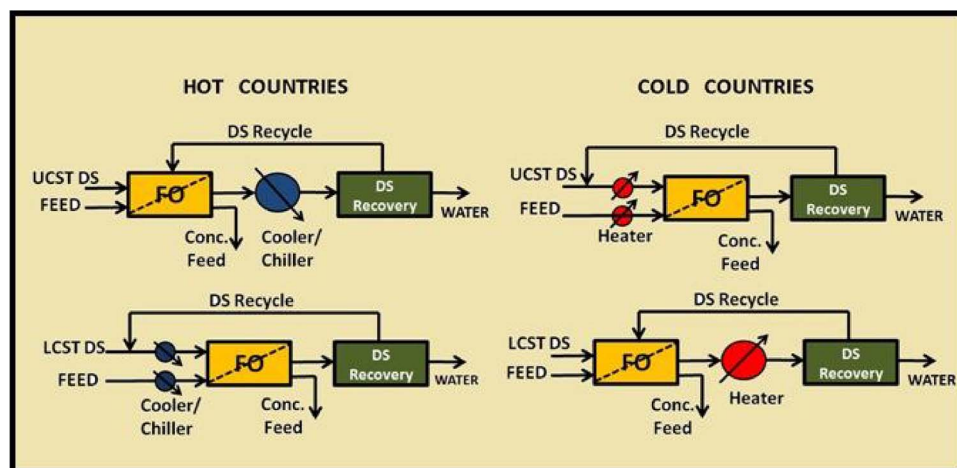


Fig. 5. Arrangement of forward osmosis system using DES as draw solute for different atmospheric conditions.

provided by low grade heat or solar energy, thus replacing costly electrical energy. Low cost sedimentation techniques can be used to carry out majority of the phase separation in the regeneration process. Expensive electrical energy is only required for polishing of the water rich phase. Cai et al. showed that the electrical energy required in FO seawater desalination using P_{4444} DMBS draw solute is only 0.17 kWhm^{-3} . If separation cost of 50% dilute P_{4444} DMBS draw solution by nanofiltration is included then total electrical energy required comes around 1.8 kWhm^{-3} [95]. The theoretical thermodynamic minimum energy of desalination for seawater at 35,000 ppm salt concentration and at a typical recovery of 50% is 1.09 kWhm^{-3} [115]. Thus, if it is assumed that low grade energy is utilized, the net electrical energy requirement is 63% more than theoretical minimum. In case of RO, actual theoretical minimum is 1.56 kWhm^{-3} and a state of the art sea water RO plants operate at around 2 kWhm^{-3} . The actual energy requirement in RO can be as high as $3\text{--}4 \text{ kWhm}^{-3}$ [116]. Similarly, Zhong et al. showed that upto 70% reduction in electricity consumption can be achieved by using a FO + (RO/NF) combination if renewable energy is used [100]. So, if low grade heat can be utilized, FO could be commercially competitive. In addition to this, other benefits of FO process need to be utilized to its full potential. FO process has low fouling propensity. The fouling films are loose in case of FO and normal backwashing is sufficient to reverse the fouling phenomenon [28]. Even biofouling of the membrane in seawater desalination is less severe in case of FO compared to RO [117]. Low fouling tendency may lessen or eradicate the need for pretreatment of feed and chemical cleaning protocol of membrane, which can reduce costs. In this area FO has a technical edge making it competitive with RO technology [118]. However, more long term pilot plant studies need to be undertaken to get the true picture [18].

If we consider all the cases the overall temperature band of FO process and draw solute regeneration range between -5°C and 60°C , the ambient temperature being almost in between. Keeping this in mind, the prevailing local environment conditions can be also exploited for making the overall process economically competitive. In hot countries, the natural high temperature can be utilized to perform FO operation using UCST type ILs which can be cooled or chilled using energy to get separation. Similarly, in cold countries, the FO system can be operated at elevated temperatures using UCST type ILs which can be naturally cooled to get phase separation. Similar reverse approach can be undertaken for LCST type ILs as shown in Fig. 5. A detailed energy calculation will be helpful in selecting the proper draw solute.

6. Potential application of IL/DES in FO

Thermally responsive ILs and DESs have good potentials to be exploited as draw solutes for FO desalination. These draw solutes can

extract water from brine with high salinity of 1.6 M NaCl . However, the water flux rates were reported to be less than $10 \text{ Lm}^{-2}\text{h}^{-1}$ thus providing a scope for improvement. At the same time the reported RSF were also low. The diluted draw solutions could undergo liquid–liquid phase separation at near ambient temperatures. The IL-rich sediment phase can be directly recycled as draw solution without further treatment, while the low concentration water-rich supernatant can be treated by low pressure membrane operations like UF or NF. In most of the cases IL and DES (except PEI derivatives and glycol ethers) could retain the osmotic potential even after significant dilution which leads to more number of recycle. Both the FO operating temperature and draw solute generation have been demonstrated to be operable between -5 to 60°C , which are near ambient and low temperature operation. The selection of draw solutes (LCST or UCST) must be judicious depending on the prevailing ambient conditions (Fig. 5). In gulf countries the prevailing hot conditions can be utilized for FO process using UCST type draw solutes which can be then cooled/chilled for phase separation.

DESs are combination of an organic salt and a hydrogen bond donor. Ch-Cl is the most common halide salt of quaternary ammonium used as it is cheap, non-toxic and bio-degradable. It is extracted from biomass and is used as additives in bird and animal feed to boost productivity [119]. The hydrogen bond donors which are studied and considered include ethylene glycol, acetic acid, glycerol, oxalic acid, malonic acid and so on (Table 2). These DESs are mostly non-toxic even making them suitable as food and pharmaceutical ingredients. This can be observed from their usage profile like EG is an anti-freezing agent, glycerol a food additive, malonic acid is used as a pharmaceutical ingredient to control acidity and also as natural preservative additive for foods, urea apart from being a fertilizer is used as animal feed, dermatological products and as additive in many products. DESs are considered as non-volatile organic solvents and not flammable, hence they can be handled and stored easily. These type of DESs can be used as draw solutions for dewatering process [6]. They offer significant technological benefits and can be applied to product sensitive industries such as biomedical, food processing, and pharmaceutical.

7. Concluding remarks

One of the significant dimensions in FO research is the selection of a draw solute which can generate high osmotic potential with minimum RSF and can be easily regenerated using minimum energy. Though very little work has been reported on IL and DES as draw solutes, the results indicate that this new class of thermally responsive draw solutes can generate high osmotic potential resulting in appreciable water fluxes which can be retained even after dilution. FO along with regeneration can be carried out at near-ambient temperatures thereby making the process less energy extensive. Even inexpensive forms of energy such as

low grade heat or solar energy can also be used to make the whole process economical. Thus, FO with IL/DES as draw solutes has immense potential to be utilized for desalination. Being low temperature operations, they can be used for dewatering of thermal sensitive products as well. However, more work is needed in pilot plant scale to fine tune the operational parameters. Successful outcomes can be further extended for treatment of difficult-to-treat streams such as RO brine and other produced water including industrial waste streams or product streams from mining and oil exploration activities. Having lower fouling propensity and higher fouling reversibility compared to RO, FO does not require extensive pretreatment of feed and frequent chemical cleaning of membrane. Nevertheless, a more detailed and long term parametric study on the difference in mechanism and extent of fouling in FO compared to RO needs to be undertaken. The economic benefits of prolonged membrane life also need to be investigated rigorously.

It is important to note that the first generation FO membrane i.e. the CTA membrane by HTI Inc. was only used initially by Mok et al. and Nakayama et al. for IL based draw solutions. All the other reported works thereafter find the use of second generation polyamide TFC membranes provided by HTI Inc. or indigenously developed with better performance. To reduce the viscosity of draw solutes and particularly in case of UCST draw solutes it may be necessary to operate FO at slightly higher temperatures. The long term membrane stability operating at higher temperature conditions for prolonged period needs to be analyzed. There is still scope of fine-tuning the issue of RSF by increasing the selectivity of membrane active layer. TFC membrane with modest water permeability, high active layer selectivity, inert surface chemistry and very low structural parameter may be the need of future. Recent development of inorganic membranes based on zeolite, aquaporins and graphene can also be checked for potential application in FO process. Custom designed membranes for specific application may be also the solution especially for difficult feed solutions.

In case of draw solutions, DESs have shown distinct advantages over ILs in the form of (i) ease of synthesis, (ii) low price, and (iii) low toxicity, especially DESs derived from Ch-Cl and renewable chemicals. DESs are also environment friendly with no serious disposal problems. DES may be especially suitable for dewatering of sensitive products such as pharmaceutical and food products as they are non-toxic. DES like Reline, Maline and Acetaline can be immediately taken up to check their potential as draw solutes. Reline has very good and favorable solvent properties. Reline and Maline has freezing point of 12 °C and 10 °C which makes them suitable for ambient temperature operation. For UCST type DES, chilling process can be used to recover the draw solute or water based on the freezing point temperature. Hence, it can be concluded that although research in FO still has a long way to go nevertheless green shoots are already visible. Most of the work reported so far are preliminary laboratory scale studies showing encouraging results which needs to be carried forward. In case of pilot plant studies and commercial applications prolonged operational data need to be collected and studied to check long term stability of FO process. A proper combination of imagination along with intelligent economics can make this technology successful in near future.

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