Deep Eutectic Solvents in Separations: Methods of Preparation, Polarity, and Applications in Extractions and Capillary Electrochromatography

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Abstract

Deep eutectic solvents (DESs) have emerged as alternatives to conventional organic solvents and ionic liquids (ILs). Their tunable and designer physio-chemical properties, low cost, and ease of preparation make them attractive solvent systems for use in extractions and additives to chromatographic separations. However, due to the diverse range of hydrogen bond acceptors and donors that comprise DESs, choosing the appropriate solvent for separations can be challenging. This review discusses all methods of DES preparation and details their advantages and disadvantages. Since polarity is an important aspect in their use in separations, the classification of DESs based on the betaine dye and nile red scales as well as Kamlet-Taft parameters is also discussed. Finally, a summary of applications of DESs in various extraction processes (phenolics, fuels, metals, proteins, carbohydrates), solid-phase extraction, solid-phase microextraction, as well as capillary electrochromatography is provided.

Keywords

Deep eutectic solvents; Separation science; Preparation methods; Polarity; Extractions; Capillary electrochromatography

1. Introduction

Deep eutectic solvents (DESs) have garnered significant interest as potentially green and sustainable media over the last couple of decades. DESs are comprised of a hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) [1]. The freezing points of DESs are much lower compared to the individual HBAs and HBDs that comprise them. As eutectic mixtures, they possess lower eutectic points than that of the ideal liquid mixture. Their low cost and ease of preparation provides them a number of advantages over traditional organic solvents and ionic liquids (ILs). A particular appeal of DESs is their vast structural designability, which largely originates from the broad classes of available HBAs and HBDs. Common HBAs include choline chloride ($[Ch^+][Cl^-]$), ~~ammonium and phosphonium salts ($[N_{4444}^+][Cl^-]$, and $[P_{4444}^+][Br^-]$),~~

tetraalkylammonium halide and tetraalkylphosphonium halide salts such as tetrabutylammonium chloride ([N_{4444}^+][Cl^-]) and tetrabutylphosphonium bromide ([P_{4444}^+][Br^-]), as well as metal halides. Typical HBDs include alcohols, carboxylic acids, amides, and amino acids [2], [3]. Moreover, compounds like terpenes and fatty acids have been employed as HBDs as well as HBAs [4], [5]. In the last few years, several ternary DESs consisting of three components that are capable of hydrogen bonding have also garnered significant interest in analytical applications [6], [7], [8]. Figure 1(a) summarizes the more common HBAs and HBDs used to prepare DESs. It is important to note that HBAs can be comprised of ionic compounds (e.g., choline chloride) or neutral compounds (e.g., menthol). Figure 1(b) shows the structures of some common DESs and interactions that occur between the HBA and HBD. The convention that will be used in naming DESs in this review is shown in Figure 1(b). Namely, the HBA will be written first followed by the HBD. Additionally, different ratios of the HBA and HBD can be used, such as in the example of [Ch^+][Cl^-] : glucose and [Ch^+][Cl^-] : 2 urea, where molar ratios of 1:1 and 1:2 are represented, respectively.

DESs have been employed in various applications including catalysis [9], [10], [11], [12] solvents for organic synthesis [13], [14], [15], [16], electrochemistry [17], [18], [19], [20], extractions [21], [22], [23], [24], [25], separations [26], [27], [28], and several other fields of the chemical sciences [29], [30], [31]. A number of preparation methods have been employed to obtain DESs with low cost and high purity. Advantages and drawbacks of the different preparation methods from an analytical point of view are discussed within this review. DES purity, batch-to-batch reproducibility, and long-term stability are important factors which need to be carefully considered in their preparation. Attaining high purity of DESs is necessary for them to be employed in separations and spectroscopic studies.

A knowledge of DES polarity gives insight in understanding important solvent properties and interactions and aids in predicting their performance in a numerous chemical processes, including separations [32], [33], [34], [35]. Various solvatochromic scales including the betaine dye scale, Kamlet-Taft parameters, and nile red polarity scale have been employed to measure the solvation interactions of DESs [36], [37], [38], [39], [40]. This review will discuss these polarity scales for a variety of DESs and compare them to each other as well as conventional organic solvents and ILs. Finally, their use as solvents in extractions and additives in capillary electrochromatography is discussed.

2. Preparation of DESs

Conventionally, the chemical synthesis of any compound involves one or more chemical reactions between two or more reactants to yield a product(s). However, DESs are prepared by the simple mixing of a HBA and HBD [1], [41]. Therefore, DESs are prepared and not synthesized, as technically no chemical reaction is involved. The term "synthesis of DESs" has occasionally been used in published studies and is incorrect and should instead be referred to as "preparation of DESs" [42].

Several factors, including the purity and water content of individual HBA and HBD components as well as the storage and drying of prepared DESs, should be carefully considered before using DESs in any application. Inconsistencies in these factors can lead to variations in the physio-chemical properties of DESs and can significantly influence the reproducibility of the preparation and ultimately having detrimental effects on the desired applications [43], [44]. HBAs such as choline chloride ($[Ch^+][Cl^-]$) and tetrabutylammonium chloride ($[N_{4444}^+][Cl^-]$) and HBDs including diols and carboxylic acids are highly hygroscopic and can readily absorb moisture from the atmosphere [45]. It is important that these compounds and reagents be stored in a moisture-

113 free environment (i.e., properly sealed in storage containers and storage of reagents in a desiccator)
114 as moisture can lead to inaccurate stoichiometric calculations.

115 Several approaches have been employed for the preparation of DESs to ensure their
116 reproducibility and that their properties are constant. Starting materials can be dried under reduced
117 pressure using roto-evaporation or stored in a vacuum oven for several hours prior to use [43]. In
118 addition, activated molecular sieves have been employed to remove water from starting materials,
119 particularly those that possess high vapor pressure and can evaporate when subjected to
120 vacuum/low pressure (such as carboxylic acids and alcohols, which are extensively employed as
121 HBDs) [46]. Other approaches have dried the final product in a Schlenk line or in a desiccator
122 containing silica gel to remove water from the final DES product [37], [43]. Chemical impurities
123 in reagents can be removed by recrystallization [41].

124 Structural characterization of DESs is critical to understand hydrogen bond formation
125 between the HBA and HBD components as well as to assess their purity. Fourier-transform
126 infrared (FTIR) spectroscopy is commonly used to study the interactions of molecules and confirm
127 the presence of functional groups and bonds within molecules [47], [48]. Ren et al. have used *in*
128 *situ* IR over the entire course of DES formation to study the mechanism of their preparation [49].
129 Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy is another commonly employed
130 technique to characterize DESs and verify the molar ratio of HBA and HBD [48], [50]. Similarly,
131 traditional ^{13}C and ^{13}C-DEPT (distortionless enhancement by polarization transfer) techniques
132 have also been used to characterize DESs [51]. Two dimensional NMR techniques like ^{1}H-^{1}H
133 Correlation Spectroscopy (COSY) and ^{1}H-^{1}H Nuclear Overhauser Effect Spectroscopy (NOESY)
134 have also been used for the characterization of DESs [48], [51]. Differential scanning calorimetry
135 (DSC) analysis is commonly used to measure the melting point or glass transition temperature of

DESs while thermogravimetric analysis (TGA) is used to characterize their thermal stability [47], [50], [52]. Some studies have employed polarized optical microscopy (POM) to visually characterize the DES as no residues or crystals are observed when the DES is a uniform homogenous liquid [47], [53]. Chao et al. have employed elemental analysis to measure the carbon, hydrogen, and nitrogen content of DESs and perform comparisons to theoretical values for assessing DES purity [54].

A number of studies employing DESs for various applications have provided little or no detail on the water content of these solvents. Minor changes in the water content of DESs can translate into significant differences in physio-chemical properties such as viscosity, density or polarity [43], [55], [56]. For example, careful analysis of water content revealed that DESs such as $[Ch^+][Cl^-]$: oxalic acid can absorb as much as 20 wt% water when exposed to air for extended periods of time [43]. To obtain reproducible and reliable results from DES in various applications, it is of utmost importance to measure the water content of DESs by sensitive techniques such as Karl Fischer titration before their use in any application. Water can disrupt the HBA/HBD hydrogen bonding network since it can act as both a HBD and HBA [37], [44].

Multiple preparation methods of DESs have been employed and reported in the literature [37], [41], [43], [57], [58], [59], [60]. Each method typically has its own advantages as well as limitations and shortcomings. High purity and long-term stability of DESs is necessary for their use in separations and spectroscopic applications. Moreover, different preparation approaches are suitable for different analytical applications as some provide ease of scaling up the preparation while others allow for incorporation of biological molecules [57], [58]. A brief overview of these methods is described below.

2.1. Heating and stirring method

DESs were first introduced by Abbott et al., where the properties of $[Ch^+][Cl^-]$ and urea mixtures were studied [1]. However, no detailed description of their preparation was provided. In a subsequent study, the $[Ch^+][Cl^-]$ HBA was mixed with various carboxylic acid HBDs in stoichiometric ratios and the two components were heated at 100 °C with constant stirring until a homogenous mixture was obtained [41]. The heating and stirring method is the most commonly employed method for the preparation of DESs. Various studies have employed different temperatures, ranging from as low as room temperature to as high as 130 °C for a period of a few hours, depending on the melting point, boiling point, and stability of the reagents [23], [61], [62], [63]. A slightly different approach has been used by Ruggeri et al. where they used a water bath at 65 °C to uniformly heat a vessel containing the HBA and HBD components for three hours, as opposed direct heating on a hot-plate [17]. After obtaining a uniform colorless eutectic solvent by heating, the DESs were dried by either vacuum oven, roto-evaporation, or in a desiccator.

The heating and stirring method is a simple approach to prepare DESs. However, there are limitations which should be considered before employing this approach in the preparation of DESs. Gurkan et al. reported an interesting finding of crystal formation over time when the $[Ch^+][Cl^-]$ HBA was mixed with two equivalents of ethylene glycol [42]. Crystal formation is often associated with the preparation being carried out at too low temperatures and/or heating and stirring times that are too short. Figure 2 compares a homogenous DES prepared by appropriate heating and stirring and a heterogenous DES formed due to crystallization [42]. Identifying the appropriate temperature and stirring time is necessary to achieve proper homogenization of all components for successful DES preparation [42].

The use of prolonged high temperature conditions has been shown to lead to decomposition and the formation of by-products [58], [64], [65]. The thermal stability of carboxylic acid-based

DESs has been studied by Delgado-Mellado et al. and Skulcova et al. [66], [67]. Moreover, Rodriguez et al. extensively studied the rate of esterification of DESs comprised of the [Ch^+][Cl^-] HBA and carboxylic acid HBDs at different temperatures [64]. As an example, the formation of ester from mixing and heating [Ch^+][Cl^-] and oxalic acid increased from 10, 29, 34 mol % when temperatures of 60 ℃, 80 ℃, and 100 ℃, respectively, were employed. Esterification also results in the production of water as a by-product and an increased water content of the resulting mixture was observed by Karl Fischer titration. However, measurable levels of esterified products have been observed even at room temperature and increased when the same mixture was analyzed after several months [64]. This observation gives considerable insight into the possibility that certain HBAs and HBDs can undergo chemical reactions over long periods of time or when employing high temperatures. Therefore, judiciously choosing appropriate HBA and HBD combinations and extensively characterizing the product is important to ensure that the resulting DES maintains long-term stability.

Spectroscopic approaches such as UV-vis spectroscopy, Raman, infrared, and fluorescence correlation spectroscopy have been extensively employed to characterize and understand the molecular dynamics of DESs [68], [69], [70], [71], [72], [73]. It is widely recognized that DESs, like their IL counterparts, should be colorless but this is not true in all cases. In some cases, a yellowish color of DESs can be observed and in extreme cases brownish color emerge when high temperatures are employed for several hours. Abbott et. al. has reported a comparison of DESs prepared by the heating and stirring method and the mechanochemical twin screw preparation method [58]. Figure 3a shows the color difference between the conventional heating and stirring preparation method and the mechanochemical twin-screw extrusion preparation method for the [Ch^+][Cl^-] : D-fructose DES. The color of DES prepared by heating and stirring method is observed

to be brownish, while the DES prepared by twin-screw extrusion is colorless. Figure 3b shows the absorption spectra of the $[Ch^+][Cl^-]$: D-fructose DES. Preparation by heating and stirring method resulted in strong absorption (molar extinction coefficient = 3513.17 $dm^3mol^{-1}cm^{-1}$ at 283 nm) compared to the DES prepared by twin-screw extrusion method (molar extinction coefficient = 256.74 $dm^3mol^{-1}cm^{-1}$ at 280 nm) [58]. The background fluorescence and UV absorption of colored DESs can significantly impede their spectroscopic analysis [74]. Previously, activated charcoal has been used for decolorization of ILs [75]. However, no studies to date have explored in depth the decolorization of DESs. Therefore, it is important that suitable temperatures be employed to avoid discoloration while yielding uniform homogenous eutectic mixtures.

2.2. Freeze-drying method

The freeze-drying method involves the addition of stoichiometric amounts of HBA and HBD followed by dilution with distilled water to achieve approximately a 5% aqueous solution. The aqueous solution is frozen at a very low temperature (77 K or 253 K) and then freeze-dried by lyophilization to achieve a clear viscous liquid [57], [76], [77], [78]. The freeze-drying process allows for the incorporation of organic self-assemblies, such as large unilamellar vesicles of liposomes, microorganisms, as well as protein-based polymers in DESs [57], [76], [79]. The presence of water is necessary for the formation of liposomes. However, direct mixing of liposomes in aqueous solution with neat DESs can lead to a simple aqueous solution of both DES constituents. The freeze-drying method also allows for the incorporation of micelles and vesicles in DESs which can act as nanoreactors and capsules, leading to a plethora of biological and pharmaceutical applications of DESs [57].

2.3. Vacuum evaporation method

The vacuum evaporation method is an approach in which the HBA and HBD are dissolved in water and the water evaporated by rotary evaporation at a temperature of 50 °C to yield the DES [30], [37], [44], [80]. Dai et al. employed this approach for the preparation of natural deep eutectic solvents (NADESs) [37]. NADESs are DESs comprised of natural compounds, particularly primary metabolites such as organic acids, amino acids, and sugars [81]. After evaporation of water, the obtained liquid is then dried in a desiccator with silica gel until a constant weight is obtained [37]. This method uses relatively lower temperatures compared to the heating and stirring method and is suitable for the preparation of NADES, since most natural compounds used in their preparation possess high melting points [37]. To employ this method, the constituents must be soluble in water. Additionally, complete removal of water from the aqueous solution at a temperature of 50 °C can be challenging and time consuming.

2.4. Grinding method

The grinding method has been employed by Florindo et al. to prepare DESs without the use of any heat [43]. This method involves mixing the HBA and HBD components and grinding them in mortar and pestle at room temperature until a homogenous mixture is obtained [43], [82], [83], [84]. To remove moisture, the $[Ch^+][Cl^-]$ HBA is first dried for two days in a vacuum oven at 40 °C and then maintained in a Schlenk under high vacuum for 4 days, due to its hygroscopic nature. The grinding method was compared with the heating and stirring method and the purity of DESs analyzed [43]. Figure 4 shows proton nuclear magnetic resonance (^{1}H NMR) spectra of the $[Ch^+][Cl^-]$: glutaric acid DES prepared by the heating and stirring method and the same DES prepared by the grinding method. The presence of peaks at chemical shifts of 1.9, 2.4, 3.3, 3.6, and 4.5 ppm (highlighted by red circles) correspond to ester formation between the $[Ch^+][Cl^-]$ and

carboxylic acid. The heating and stirring method resulted in 5-30 wt% esterification, while no esterification was observed when the DES was prepared by the grinding method [43].

2.5. Twin screw extrusion method

A mechanochemical approach using a twin-screw extruder (TSE) has been employed by Crawford et al. for the large scale (several kilograms) preparation of DESs to overcome the potential limitations of the heating and stirring method [58]. A similar approach has also been employed to scale-up the solvent-free synthesis and preparation of several organic compounds and metal organic frameworks [85], [86]. Zdanowicz et al. have employed TSE to prepare thermoplastic starch films using DESs [87]. TSE is comprised of two co-rotating or counter rotating screws encased in a stainless-steel barrel. The screws constitute multiple conveying and kneading sections, where conveying sections move the materials forward and the kneading section applies high shear and compression forces on the material as it passes through. The HBA and HBD constituents are mixed manually or through the use of a planetary ball mill, when batch sizes are too large. The preparation of DESs is performed by preheating all sections of TSE followed by adding the HBA and HBD in stoichiometric ratios through a feed port. The colorless DES produced is collected on the other end of the TSE in a container and stored properly [58]. The TSE method has several important advantages including, a) efficient and continuous route of DES preparation, b) easily scalable allowing for high throughput production, c) no thermal degradation due to short heat exposure times, and d) easy collection of highly viscous DESs in containers, thus overcoming the challenges of transferring the product from reaction vessels to final storage containers often encountered by other preparation methods [58].

2.6. Microwave irradiation method

Gomez et al. have reported the microwave-assisted preparation of DESs [59]. This technique decreases the time and energy cost of DES preparation, making it a highly ecofriendly preparation approach [88], [89]. In its most simple operation, a mixture of HBA and HBD components is enclosed in a 20 mL vial and then microwave irradiated for 20 seconds. This method reduces the preparation time from several hours to only 20 seconds and consumes 650 times lower energy compared to that of the heating and stirring method [59]. The microwave irradiation method is generally a faster, cheaper, easier, and greener route for DESs preparation compared to conventional methods [59], [88]. However, the HBA and HBD combinations should be judiciously selected and experimental variables, such as heating time and power, should be carefully optimized to prevent side reactions.

2.7. Ultrasound-assisted preparation

DESs can be prepared through the use of ultrasonic waves [60], [88], [90], [91]. In this method, stoichiometric amounts of HBA and HBD are mixed in a glass vial. The vial is then sealed and placed in an ultrasonic bath for 1-5 hours and temperature modulated from room temperature to 60 °C, depending upon the DESs constituents. After preparation, the DESs are kept for 24 hours in the same vial under ambient conditions to ensure the formation of a homogenous mixture. DESs prepared by this method are stable over time and are not prone to crystallization even after several days [60]. Moreover, similar physio-chemical characteristics (FT-IR spectra, density, viscosity, and decomposition temperature) have been observed upon comparing DESs prepared by ultrasonic-assisted and heating and stirring methods [88].

3. Polarity of DESs

Solvent polarity can be characterized using semi-empirical linear free energy relationships. The polarity of DESs has been assessed through the spectroscopic response of absorbance and

fluorescence solvatochromic probes. Figure 5 shows several absorbance and fluorescence-based probes that have been employed and will be discussed in more detail within this section.

Absorbance solvatochromic probes provide a measure of polarity through the shift of UV-vis absorbance spectrum when the probe molecule interacts with the solvent of interest. Polarity is measured through the fluorescence emission maxima in the case of fluorescence-based probes. Absorbance-based methods include the betaine dye scale, Kamlet-Taft parameters, and nile red polarity scale and have been extensively used to study the effect of DES structural modifications on overall solvent polarity [36], [37]. A fewer number of studies have employed fluorescence-based probes for the measurement of polarity [38], [62].

3.1. Betaine dye scale

One of the most used approaches is the $E_T(30)$ polarity scale of Dimroth and Reichardt [92]. Owing to the large shift in the lowest energy charge-transfer band upon interaction with non-polar and polar solvents, Reichardt's dye (2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate; betaine dye 30) is one of the most commonly used solvatochromic probes to measure solute-solvent interactions. The negative solvatochromism exhibited with decreasing solvent polarity results in a large bathochromic shift in the absorption band [92]. $E_T(30)$ is defined as the molar transition energy of the dye in kcal mol^{-1} at room temperature and normal pressure and is calculated from the absorption maxima (in nm) of Reichardt's dye via equation (1) [36].

$$E_T(30) = 28591/\lambda_{max} \quad \text{(eq 1)}$$

The solubility of betaine dye 30 is often very low in most DESs [84]. Additionally, the solvatochromic behavior is significantly affected by characteristics of the HBD due to the fact that hydrogen bond donating solvents stabilize the ground state more than the excited state of the probe

316 molecule [84]. Since many DESs are comprised of an acidic HBD, they significantly interfere with
317 the dye's solvatochromic behavior [32]. Therefore, a derivative of betaine dye 30 (see Figure 5)
318 called betaine dye 33 (2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate), is often
319 employed to measure the polarity of DESs [84]. Betaine dye 33 possesses a dichloro functional
320 group substituted in place of the diphenyl group, making the molecule zwitterionic and enhancing
321 its solubility in many DESs. The lowest energy absorbance transition [i.e., $E_T(33)$] of betaine dye
322 33 is calculated by equation (2) [84].

323 $$E_T(33) = 28591/\lambda_{max} \quad \text{(eq 2)}$$

324 $E_T(33)$ provides a measure of the solvent's overall polarity and averages the
325 dipolarity/polarizability and/or HBD ability of the solvent. Additionally, $E_T(33)$ can easily be
326 converted to $E_T(30)$ using equation (3) [84].

327 $$E_T(30) = 0.9953(\pm 0.0287) \times E_T(33) - 8.1132(\pm 1.6546) \quad \text{(eq 3)}$$

328 Most often, the polarity values are reported as a normalized polarity scale (E_T^N scale) that is
329 calculated from $E_T(30)$ using equation (4), where TMS stands for trimethylsilane, $E_T(30)_{water}$ =
330 63.1 kcal mol^{-1} and $E_T(30)_{TMS}$ = 30.7 kcal mol^{-1}. E_T^N is a dimensionless normalized polarity scale
331 and varies between 0 for TMS (least polar) and 1 for water (most polar) [84].

332 $$E_T^N = \frac{E_T(solvent) - E_T(TMS)}{E_T(water) - E_T(TMS)} = \frac{E_T(solvent) - 30.7}{63.1 - 30.7} \quad \text{(eq 4)}$$

333 Polarity values of a variety of DESs containing various HBA and HBD combinations as
334 measured by $E_T(30)$ or $E_T(33)$ scales are summarized in Table 1. For comparison purposes, values
335 are also provided for select water as well as select organic solvents and ILs. The first effort to
336 measure the polarity of DESs using the $E_T(30)$ polarity parameter was made by Abbott et al. where
337 they characterized DESs comprised of the [Ch$^+$][Cl$^-$] HBA combined with glycerol as HBD [36].

The measured $E_T(30)$ values were normalized to calculate the E_T^N parameters. The E_T^N values were observed to increase as the concentration of [Ch^+][Cl^-] increased. The E_T^N polarity of neat glycerol was observed to be 0.817 and increased linearly from 0.841 to 0.858 when the HBA:HBD ratio was varied from 1:3 to 1:1 (see Table 1) [36]. Reline ([Ch^+][Cl^-] : 2 urea), ethaline ([Ch^+][Cl^-] : 2(1,2-ethanediol)), and glyceline ([Ch^+][Cl^-] : 2 glycerol) are among the most commonly studied DESs [38], [93], [94], [95], [96]. Figure 6 shows the absorption spectra of betaine dye 33 in the glyceline, ethaline, reline, and maline DESs [38]. The low energy intermolecular charge-transfer band is obscured within the high-energy band of the maline DES resulting in its E_T^N polarity not being determined using betaine dye 33 [38]. The E_T^N values were measured to be 0.81, 0.82, and 0.84 for reline, ethaline, and glyceline, respectively [38]. As shown in Table 1, these polarity values are higher than short chain alcohols (ethanol (0.66) and methanol (0.76)) as well as common imidazolium-based ILs (such as, 1-butyl-3-methylimidazolium tetrafluoroborate ([$BMIM^+$][BF_4^-]) (0.69) and [$BMIM^+$] trifluoromethanesulfonate ([OTf^-]) (0.71)) [38]. The higher polarities of these DESs can be attributed to their high hydrogen bond donating ability and/or their high dipolarity/polarizability. Pandey et al. also studied the effect of temperature and water on E_T^N polarity of reline, ethaline, and glyceline using the $E_T(33)$ probe molecule. A decrease in E_T^N polarity was observed when the temperature was increased from 30 ℃ to 90 ℃, where the rate of decrease in polarity was highest for ethaline, followed by glyceline and reline. Alcohol-based HBDs, such as glycerol and 1,2-ethanediol, were more sensitive to temperature compared to that of urea. Preferential solvation of betaine dye in an aqueous solution of DESs resulted in a slight increase in E_T^N polarity values due to increased water content [93].

The solvation properties of DESs can be manipulated through the addition of a cosolvent, which can be used to manipulate properties of DESs for particular applications [95]. Since DESs

are more polar than many conventional organic solvents, dilution of DESs with cosolvents results in decreased polarity. The addition of tetraethylene glycol (TEG) in reline resulted in a decreased E_T^N polarity value from 0.83 to 0.64 when the TEG mole fraction (x_{TEG}) was increased from ~~0 1~~ 0 to 1 [94]. The addition of dimethyl sulfoxide (DMSO) also resulted in a linear decrease in E_T^N polarity value from 0.84 (ethaline) and 0.85 (glyceline) to 0.44 (DMSO), when the DMSO mole fraction (x_{DMSO}) was increased from ~~0 1~~ 0 to 1 [95]. Moreover, Aryafard et al. also observed a linear decrease in E_T^N polarity values for glyceline, ethaline, and reline upon increasing the mole fraction of polyethylene glycol (PEG 400) as cosolvent [96].

Florindo et al. measured solvatochromic parameters of various DESs comprised of $[Ch^+][Cl^-]$, $[N_{4444}^+][Cl^-]$, and DL-menthol-based HBAs mixed with acid-based HBDs [84]. First derivatives of spectra were used to measure the absorption maxima, since the absorption peaks for some DESs (e.g., $[N_{4444}^+][Cl^-]$: 2 octanoic acid) were difficult to detect [84]. Previously, Pandey et al. also encountered a similar challenge in measuring the absorption maxima of the $[Ch^+][Cl^-]$: 2 malonic acid DES [38]. The E_T^N polarity values of DESs were observed to be lower compared to their analogous ILs. For example, the normalized polarity of the $[Ch^+][Cl^-]$: 2 levulinic acid DES was found to be 0.35 compared to that of 0.61 for the $[Ch^+][Lev^-]$ IL (see Table 1) [84]. However, it is important to note that DESs are different solvent systems than ILs [84]. Moreover, the normalized polarity of $[Ch^+][Cl^-]$: 2 levulinic acid (0.35) was much lower than $[Ch^+][Cl^-]$: 2 malonic acid (0.79), corresponding to the higher polarity of DESs containing dioic acid-based HBDs [84].

Cai et al. have studied the polarity of DESs comprised of $[Ch^+][Cl^-]$ HBA with a broad range of HBDs including carboxylic acids, alcohols, monosaccharides, as well as metal halides. This study employed 70 wt% aqueous solution of DESs for the extraction of caffeine. The

polarities of all DESs were similar and ranged from 0.82-0.88, except for the [Ch^+][Cl^-] : zinc chloride DES, in which the E_T^N polarity value was significantly lower (0.54) [35]. Oh et al. have employed several ternary DESs as reaction media for lipase [97]. [Ch^+][Cl^-] HBAs were mixed with various combinations of one or two HBDs. The E_T^N polarity values of DESs studied in this work ranged from 0.781-0.857 and were found to be much higher compared to that of 0.670 for the [$BMIM^+$][BF_4^-] IL [97]. The E_T^N polarity values of DESs increased as the polarity of HBD increased, with the following trend observed: triethylene glycol < diethylene glycol < acetamide < formamide < ethylene glycol < urea < glycerol < thiourea [97]. For example, the highest polarity was observed for ternary DESs comprised of the most polar HBDs thiourea and glycerol ([Ch^+][Cl^-] : glycerol : thiourea ($E_T^N = 0.857$)) [97]. The E_T^N polarity values of similar ternary DESs have also been measured and used to interpret lipase activity and stability in various DESs [33].

A plethora of DESs comprised of ammonium halide-based HBAs and diol-based HBDs have been employed for desulfurization of fuels. The length of the alkyl chain substituents was increased from [N_{2222}^+][Br^-] to [N_{8888}^+][Br^-], while the HBD was varied from 1,2-ethanediol to 1,5-pentanediol. The E_T^N polarity values of DESs ranged from 0.560-0.784. The [N_{4444}^+][Cl^-] : 4 (1,3-propanediol) DES had the highest E_T^N polarity (0.784) while that of [N_{6666}^+][Cl^-] : 4 (1,4-butanediol) was lowest (0.560) [98]. These DESs were observed to be less polar than free alkyl diols, which can be attributed to the combination of non-polar ammonium salts with the diols [98].

3.2. Kamlet-Taft parameters

The multi-parameter scale of Kamlet and Taft has also been extensively employed to characterize the solvation interactions of DESs. The Kamlet and Taft multi-parameter scale is comprised of "π*" (dipolarity), "α" (hydrogen bond acidity), and "β" (hydrogen bond basicity) of

406 the solvents. The "π*" parameter provides a measure of the solvent's dipolarity/polarizability. The
407 magnitude of "π*" values depends upon the dye and the calculated value is unique to each dye
408 depending on the solvent-dye interactions. The "π*" parameter can be calculated by measuring the
409 shift of *N*,*N*-diethyl-4-nitroaniline using equation (5), where v is the experimental wavenumber
410 and ν (cm^{-1}) = 10^7 / λ_{max} (nm) [84].

411 $$\pi^* = 0.314\,(27.52 - \nu_{N,N\text{-dimethyl-4-nitroaniline}}) \quad \text{(eq 5)}$$

412 The Kamlet and Taft "α" parameter is a measure of the hydrogen bond donating ability of
413 the solvent. This can be calculated by combining $E_T(33)$ and the "π*" parameter using equation
414 (6) [84].

415 $$\alpha = 0.0649E_T(33) - 2.03 - 0.72\pi^* \quad \text{(eq 6)}$$

416 Since the "α" parameter uses the absorption of betaine dye 30 and betaine dye 33, which
417 are not suitable to characterize the polarity of DESs possessing acidic HBAs, several studies have
418 employed other methods to measure this term [84], [32]. Dwamena et al. have used the absorption
419 maxima of the nile red solvatochromic probe to measure the hydrogen bond acidity, by using
420 equation (7) [32].

421 $$\alpha = (19.9657 - 1.0241\pi^* - \nu_{NR}) / 1.6078 \quad \text{(eq 7)}$$

422 Teles et al. have employed a ^{13}C NMR based approach using the pyridine-*N*-oxide (PyO) probe
423 (see Figure 5) to measure the "α" parameter [40]. The chemical shifts, $\delta(C_i)$ (in ppm), of the
424 carbon atom in positions i=2 and 4 of PyO were determined, and the "α" parameter calculated by
425 equation (8), where $d_{24} = \delta_4 - \delta_2$ [40].

426 $$\alpha = -0.15 \times d_{24} + 2.32 \quad \text{(eq 8)}$$

Ren et al. have exploited the Hammet acidity function using the nitroaniline probe to measure the hydrogen bond acidity of DESs, shown in equation (9), where *I* represents the nitroaniline indicator and $pK(I)_{aq}$ is a constant (0.99). The $[I]_s/[IH^+]_s$ ratio is determined through the Beer-Lambert Law using the wavelength of absorption maxima (λ_{max}). The terms $[IH^+]_s$ and $[I]_s$ represent the molar concentration of the protonated and unprotonated form of *I*, respectively [39], [99].

$$H_o = pK(I)_{aq} + \log\left([I]_s/[IH^+]_s\right) \quad \text{(eq 9)}$$

The "β" parameter is attained by comparing the solvent-induced shift of the absorption bands of the 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline probes [100]. Both probes are structurally similar, as shown in Figure 5, except that 4-nitroaniline possesses hydrogen bond donating ability, which is absent in *N*,*N*-dimethyl-4-nitroaniline. Both probes exhibit good correlation when they are present in solvents incapable of acting as a hydrogen bond acceptor, but their shifts differ significantly when they are introduced to hydrogen bond accepting solvents. Owing to these characteristics, this set of probe molecules can be used to measure the hydrogen bond accepting ability (β-term) by using equation (10) [40]

$$\beta = (1.035\nu_{N,N\text{-dimethyl-4-nitroaniline}} + 2.64 - \nu_{4\text{-nitroaniline}}) / 2.80 \quad \text{(eq 10)}$$

The probes 4-nitrophenol and 4-nitroanisole have also been proposed by Kamlet and Taft to measure the "β" parameter. However, the 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline probes are most commonly used to measure the hydrogen bond accepting ability of DESs. A summary of previously reported Kamlet-Taft parameters for over 100 DESs is shown in Table 2.

In initial efforts to measure the polarity of DESs, Abbott et al. studied the Kamlet-Taft parameters for DESs comprised of the $[Ch^+][Cl^-]$ HBA and glycerol HBD, where the relative ratio

449 of HBA and HBD was varied [36]. As shown in Table 1, a linear increase in "π*" (0.970 to 1.003)
450 and "α" (0.914 to 0.923) parameters was observed when the relative ratio of HBA:HBD was
451 decreased from 1:3 to 1:1. However, the "β" parameter did not change [36]. Pandey et al. studied
452 the effect of temperature and water on Kamlet-Taft parameters for glyceline, ethaline, and reline.
453 Interestingly, no change was observed in the "π*" or the "β" parameters when the temperature was
454 varied from 30 °C-90 °C. However, the "α" parameter decreased with an increase in temperature,
455 in the same order as that of the E_T^N value (i.e., ethaline > glyceline > reline). This indicates that the
456 decreasing E_T^N value of these DESs corresponds to the hydrogen bond basicity and not
457 dipolarity/polarizability interactions [93]. Moreover, the "π*" values increased with the addition
458 of water, while the "α" term did not change; additionally, a decrease in "β" parameter was
459 observed when the mole ratio was increased from 0 to 1 [93].

460 DESs comprised of the [Ch^+][Cl^-] HBA mixed with imidazole, urea, and ammonium
461 thiocyanate in a relative ratio of 3:7, 1:2, and 1:1, respectively, have been employed for the
462 dissolution of cellulose. Solvation characteristics of these DESs were measured using the Kamlet-
463 Taft empirical polarity scale for dipolarity/polarizability (π*) as well as the hydrogen bond basicity
464 (β); the Hammet acidity function (H_o) was employed to measure the hydrogen bond acidity.
465 Properties of DESs were compared with the allylmethylimidazolium chloride ([$AMIm^+$][Cl^-] IL.
466 The "β" values were observed to be highest for the [Ch^+][Cl^-]:imidazole DES (0.864) compared to
467 that of [$AMIm^+$][Cl^-] IL (0.830) as well as other DESs including [Ch^+][Cl^-] : urea (0.821) and
468 [Ch^+][Cl^-] : ammonium thiocyanate (0.810). The "π*" values were observed to be 0.382, 0.319,
469 and 0.258 when the [Ch^+][Cl^-] HBA was mixed with imidazole, urea, and ammonium thiocyanate
470 HBDs, respectively. Moreover, the order of H_o was similar for the DESs as that of basicity, such
471 that [Ch^+][Cl^-] : imidazole (1.869) > [Ch^+][Cl^-] : urea (1.732) > [Ch^+][Cl^-] : ammonium thiocyanate

(1.575) [39]. In another similar study, Ren et al. examined the role of HBA towards cellulose dissolution by using the conventional DES comprised of [Ch^+][Cl^-] HBA and oxalic acid HBD and another customized DES comprised of allyltriethylammonium chloride ([$ATEAm^+$][Cl^-]) HBA with the oxalic acid HBD [101]. The "π*", "β", and "α" values for the [$ATEAm^+$][Cl^-] : oxalic acid DES were found be much higher than the [Ch^+][Cl^-] : oxalic acid DES [101]. The allylic group delocalizes the charge on the cation and provides a π- π conjugative effect resulting in enhanced solvation interactions [101].

Kim et al. as well as Oh et al. have characterized the polarity of a variety of DESs and used this information to study the effects of DESs on activity and stability of lipases. Ten different ternary DESs using [Ch^+][Cl^-] as the HBA with different combinations of formamide, thiourea, ethylene glycol, urea and glycerol HBDs were studied. They also characterized glyceline, ethaline, and reline as benchmarks. As shown in Table 2, the "π*" values were similar for most of the DESs and ranged from 1.112-1.245. The highest "π*" was observed for [Ch^+][Cl^-] : urea : thiourea, which can be related to the relatively higher dipolarity/polarizability of thiourea and urea compared to other HBDs. The "α" term ranged from 0.840-0.903. An increase in "α" parameter was dependent upon the hydrogen bond acidity of HBD which was observed to be in the following order: thiourea < formamide < urea < ethylene glycol < glycerol. Similarly, the "β" parameter ranged from 0.549-0.647 for the most hydrogen bond basic HBD compared to 0.486-0.601 from DESs comprised of thiourea (the least hydrogen bond basic) [33], [97].

Shukla et al. have prepared DESs comprised of IL-based HBAs with several amine-based HBDs. They have studied the effect of HBA and HBD on the solvation properties and correlated these parameters to explain the extent of CO_2 capture. The "β" term was observed to increase as the basicity of HBD was enhanced; similarly, the "β" term also increased when the molar ratio of

HBD was increased. However, an opposite trend was observed in the case of "α" parameters for DESs employed in this study. The "α" values of DESs comprised of [N_{4444}^+][Cl^-] HBA were found to be much lower compared to DESs in which 1-hexyl-3-methylimidazolium chloride ([$HMIM^+$][Cl^-]) and the monoethanolammonium chloride HBA were employed. The "π*" values of all DESs were observed to range from 0.83-1.18, where most of the "π*" values were close to 1 [102].

Teles et al. have characterized several DESs comprised of tetraalkylammonium halide HBAs and carboxylic acid HBDs. As shown in Table 2, the "β" term increased as the length of cation alkyl substituents in the HBA and/or length of carboxylic acid alkyl chain in HBD were increased, such as the "β" term for [N_{2222}^+][Cl^-] : 2 butanoic acid DES was 0.76, while that of [N_{4444}^+][Cl^-] : 2 decanoic acid DES was 1.28. Moreover, DESs possessing the chloride anion exhibited higher "β" values compared to those possessing bromide anion in the HBA. Relatively smaller variations in the "α" term were observed upon systematically modulating the chemical structure of DESs. However, the hydrogen bond acidy of DESs containing bromide anion were higher than analogous DESs possessing chloride anion. The dipolarity/polarizability values ranged from 0.69 ([N_{4444}^+][Cl^-] : 2 decanoic acid) to 0.95 ([N_{4444}^+][Br^-] : 2 butanoic acid). The "π*" values were observed to decrease with an increase in carboxylic acid alkyl chain length of HBD [40]. Florindo et al. have studied the Kamlet-Taft parameters of DESs with HBAs including [Ch^+][Cl^-], [N_{4444}^+][Cl^-], and DL-menthol and carboxylic acid-based HBDs [84]. They also characterized glyceline, ethaline, and reline DESs and used them as benchmarks. Figure 7 shows the Kamlet-Taft parameters including "α", "β", and "π*" values for all DESs analyzed in this study [84]. It can be observed that the highest "α" values were observed for DL-menthol-based DESs, while [N_{4444}^+][Cl^-]-based DESs possessed relatively higher "β" terms and "π*" values were highest for

518 [Ch^+][Cl^-]-based DESs. The "α" term for [Ch^+][Cl^-] : 2 malonic acid (1.39) was found to be much
519 higher compared to [Ch^+][Cl^-] : 2 levulinic acid (0.51). The "β" term for DESs possessing the
520 [N_{4444}^+][Cl^-] HBA (0.82-1.04) were higher than those comprised of [Ch^+][Cl^-] (0.42-0.57) or DL-
521 menthol HBAs (0.50-0.60). The "π*" values were highest for DESs comprised of [Ch^+][Cl^-] HBA
522 owing to the presence of charged moieties with polar functional groups in its chemical structure
523 [84].

524 Martins et al. have extensively studied hydrophobic DESs prepared from terpenes and
525 carboxylic acids [103]. Thymol and L(-)-menthol were employed as HBAs while the HBDs were
526 comprised of carboxylic acids. The "π*" and "β" parameters were measured through the absorption
527 maxima of *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline probes while the "α" terms were
528 calculated using a ^{13}C NMR approach using the pyridine-*N*-oxide probe [103]. The "π*" values of
529 thymol-based DESs were observed to be higher than L(-)-menthol-based DESs due to the aromatic
530 structure of thymol. Moreover, a linear increase was observed as the HBD alkyl chain length was
531 increased along with the mole fraction of thymol, while no change in "π*" was observed for the
532 same trend in L(-)-menthol DESs [103]. The "β" values of thymol-based DESs were observed to
533 be nearly zero and did not change with increasing in the alkyl chain length of HBD and mole
534 fraction of thymol [103]. This can be correlated to the aromatic structure of thymol which makes
535 it a weak hydrogen bond acceptor. The basicity of L(-)-menthol-based DESs was higher and
536 increased linearly upon increasing the mole fraction of L(-)-menthol as well as carboxylic acid
537 alkyl chain length of the HBD [103]. Furthermore, the "α" parameters were observed to be higher
538 for thymol-based DESs compared to L(-)-menthol-based DESs [103]. The acidity decreased as the
539 mole fraction of menthol was increased and became more closer to neat L(-)-menthol. It is
540 important to separately measure the solvatochromic interactions of neat HBAs and HBDs to

541 understand their contribution towards overall solvation properties of the DES [103]. In another
542 study, Silva et al. observed an increase in both "π*" and "β" parameters upon addition of water in
543 NADESs [104]. For example, the "π*" and "β" increased from (1.13 to 1.18) and (0.23 to 0.39),
544 respectively, on addition of 9% water in the [Ch^+][Cl] : xylose DES [104].

545 Kamlet-Taft parameters of DESs comprised of the [Ch^+][Cl^-] HBA and carboxylic acid
546 HBD have been reported by Dwamena et al. [32]. As shown in Table 2, the "π*" values of DESs
547 decreased as the alkyl chain length and/or relative ratio of carboxylic acid HBD was increased.
548 For example, the "π*" of [Ch^+][Cl^-] : 2 butanoic acid was 0.945 compared to 0.327 for the [Ch^+][Cl^-]
549] : 3 octanoic acid DES. A decrease in "α" term was also observed upon increasing the carboxylic
550 acid alkyl chain length. However, the "β" term exhibited an opposite trend to that of "π*" and "α"
551 values. An increase in alkyl chain length and/or relative ratio of carboxylic acid HBD resulted in
552 an increase in the "β" term. For example, the "β" term of the [Ch^+][Cl^-] : 2 butanoic acid was 0.514
553 compared to 0.955 for the [Ch^+][Cl^-] : 3 octanoic acid DES [32]. Figure 8 illustrates a comparison
554 of DESs with other commonly used ILs and organic solvents by a ternary plot of Kamlet-Taft
555 parameters [32]. It can be observed that the Kamlet-Taft parameters of ethanol, propanol, and
556 butanol are similar to those of [Ch^+][Cl^-] : octanoic acid DESs [32].

557 **3.3. Nile red polarity scale**

558 Nile red (see Figure 5) is another probe that has been extensively employed to measure the
559 polarity of DESs. The shift in absorption maxima is measured and E_{NR} is calculated by equation
560 (11) [32]

561 $$E_{NR} = 28591/ \lambda_{max} \quad \text{(eq 11)}$$

562 Nile red exhibits a bathochromic shift in polar solvents and a hypsochromic shift in non-polar
563 solvents, opposite to that of betaine dye 30 [105]. High E_{NR} values (measured by the nile red probe)
564 correspond to lower polarity of the compounds and low E_{NR} values depict the higher polarity of
565 compounds in the nile red polarity scale. Betaine dye 30 is a zwitterionic molecule and is
566 protonated in acidic media, rendering it unable to measure solute solvent interactions in such cases.
567 Physico-chemical properties such as photochemical stability, high solubility in a diverse range of
568 solvents, and low basicity make nile red a suitable probe to measure the polarity of DESs. Table 3
569 provides a summary of all DESs that have been characterized by the E_{NR} polarity scale.

570 Dai et al. have extensively studied the preparation and properties of more than a hundred
571 NADESs. Understanding polarity of NADESs is essential to modulate their solubilizing
572 capabilities and their interactions with biomolecules. Nile red was employed to measure the
573 polarity of these NADESs, where those compounds possessing organic acid HBDs were found to
574 be most polar. For example, the E_{NR} value for malic acid : $[Ch^+][Cl^-]$: water (1:1:2) was 44.81
575 kcal mol^{-1}. The polarity of amino acids and pure sugar-based NADESs (48.05–48.3 kcal mol^{-1})
576 was similar to that of water (48.21 kcal mol^{-1}). Sugar and polyalcohol-based NADESs were found
577 to be less polar, with polarities similar to that of methanol (51.89 kcal mol^{-1}) [37].

578 Mulia et al. have employed three different NADESs prepared by mixing $[Ch^+][Cl^-]$ HBA
579 with 1,2-propanediol, glycerol, and malic acid [34]. Nile red was used to measure the polarity, and
580 the following order was observed: malic acid HBD > glycerol > 1,2-propanediol [34]. Huang et
581 al. employed several DESs to study the extraction of rutin from tartary buckwheat hull [106]. All
582 NADESs characterized by nile red were observed to possess similar polarities (49.81-50.91) and
583 close to that of methanol (51.80) [106]. Trusheva et al. have employed NADESs for the extraction
584 of propolis and the polarities ranged from 49.25-49.34 [107].

The E_{NR} polarity of DESs comprised of amphiphilic *N*-oxide-based HBAs and phenylacetic acid HBD has also been reported using nile red. Higher polarity was observed when the *N*-methylmorpholine-*N*-oxide HBA was combined with phenylacetic acid HBD (50.93) compared to the case when *N*-dodecylmorpholine-*N*-oxide HBA was mixed with phenylacetic acid HBD (52.01), where incorporation of the longer chain length resulted in decreased polarity [108]. Craveiro et al. have employed nile red to measure the polarity of several NADESs. As shown in Table 3, E_{NR} values of all NADESs were found to be lower than the [$BMIM^+$][BF_4^-] IL (51.42). The [Ch^+][Cl^-] HBA, along with organic acid-based HBDs, possessed higher polarities (47.73-48.30) compared to the combination of [Ch^+][Cl^-] HBA with sugar-based HBDs (49.72-50.69). The combination of glucose HBA with tartaric acid and citric acid HBDs resulted in a polarity of 47.73 and 47.81, respectively. The slightly higher polarity (lower E_{NR} value) can be attributed to the lower pKa (2.98) of tartaric acid compared to citric acid (3.14) [109]. It is important to control the water content while characterizing DESs to avoid the results being skewed. The E_{NR} of 2[Ch^+][Cl^-] : xylose DES decreased (increase in polarity) from 50.78 to 49.72 when the water content was increased from 2.2 wt% to 7.74 wt% [109]. A variation in the water content by 4% in the 2[Ch^+][Cl^-] : xylose DES resulted in a 0.9 kcal mol^{-1} in E_{NR} value [109]. Gabriele et al. measured the polarity of several DESs by mixing [Ch^+][Cl^-] HBA with glycol-based HBDs [56]. The E_{NR} polarity of DESs containing diethylene glycol HBD with [Ch^+][Cl^-] HBA was observed to be higher (50.80) compared to that of DES comprised of polyethylene glycol 200 HBD mixed with [Ch^+][Cl^-] HBA (51.17) [56].

3.4. Fluorescence-based probes

Molecular fluorescence from an optimum fluorophore can be used as a tool to measure the polarity of complex solvents like DESs, owing to the higher sensitivity of fluorescence techniques

[110]. Fluorescence-based probes can be used to attain additional insight towards the solvation properties of DESs since every probe interacts with the solvent in a unique way [38], [62], [93].

Pandey et al. used several fluorescence-based probes, shown in Figure 5, to characterize the polarity of ethaline, glyceline, reline, and maline. The pyrene solvent polarity scale (Py I_1/I_3) revealed that these DESs are more dipolar than conventional ILs as well as common organic solvents. The Py I_1/I_3 was found to be highest for reline (2.51) corresponding to a significant contribution from the carboxyl functional group of urea, while the remaining DESs exhibited the following order: glyceline (2.21) > maline (2.18) > ethaline (2.14). The difference in trends for Py I_1/I_3 compared to that of E_T^N polarity can be justified by considering the significant contribution of hydrogen bond donating capability of DESs towards interaction with betaine dye 33, while the response of the pyrene probe is solely dependent upon static dielectric constant (ε) and refractive index (n^2) of the solvent. Another interesting observation was the difference in Py I_1/I_3 ratio for the DES and the neat HBD. The Py I_1/I_3 for glyceline was found to be 2.21 compared to that of neat glycerol HBD (1.70). The significant difference between the Py I_1/I_3 ratio of DES and the neat HBD indicates the major contribution of HBA towards overall dipolar interactions of DESs [38].

Besides the pyrene Py I_1/I_3 polarity scale, the fluorescence emission maxima (λ_{max}^{em}) of several other fluorescence probes has been used to compare the polarity of several solvents. Pyrene-1-carboxaldehyde (PyCHO, a pyrene probe with aldehyde functionality) has been employed and the λ_{max}^{em} (nm) of PyCHO were in the order of maline (460) > reline (453) > ethaline = glyceline (452). The highest shift for maline can be attributed to stronger interaction of carboxylic acid groups with the aldehyde functionality of probe molecules [38], [93].

Another very important aspect to consider is that the polarity values of DESs do not follow the same trends when the probe is changed. This is due to the fact that each probe interacts in a

particular way with the solvent and solute-solvent interactions vary when different type of probes are employed, even if the probe is used to measure the same type of solvatochromic interaction (i.e., dipolarity for pyrene and pyrene-1-carboxyldehyde). Photoinduced charge transfer probes such as 1-anilino-8-napthalene sulfonate (ANS) and *p*-toluidinyl-6-napthalene sulfonate (TNS) have been used to characterize DESs and undergo a bathochromic shift upon a change in polarity of the solvent. The trend of $\lambda_{max}^{em}$was the same for both ANS and TNS with dipolarity increasing from maline < reline < glyceline < ethaline. Furthermore, the response of neutral fluorescence probes including 6-propionyl-2-(dimethylaminonaphthalene) (PRODAN) and Coumarin-153 were higher for ethaline and glyceline DESs (corresponding to their higher dipolarity) compared to reline and maline [38],[93].

Vandenelzen et al. employed DESs comprised of chiral HBDs (i.e., D-(+)-α-glucose) as solvents in circularly polarized light-emitting materials [62]. Chiral HBDs have been employed to develop polarized light emitting materials in quantum computing and light emitting diodes. The polarity of DESs comprised of [N_{4444}^{+}][Cl^{-}] HBA mixed with D-(+)-α-glucose and D-(-)-fructose-based chiral HBDs was measured by the Coumarin-153 fluorescent probe [62]. The energy of maximum emission transition of Coumarin-153 was used to calculate the normalized polarity. The normalized polarity values ranged from 0.471-0.690, compared to that of 0.422 for chloroform, 0.719 for acetonitrile, and 0.825 for methanol [62]. Despite the normalization of polarity values measured by the Coumarin-153 dye, a comparison to organic solvent polarity shows the E_T^N values to be different than those measured through the absorption maxima of betaine dye. The normalized polarities for chloroform, acetonitrile, and methanol were reported to be 0.26, 0.49, and 0.76, respectively [92]. Therefore, the nature of probe and its interactions with the solvent need to be considered carefully before comparing the polarity of different solvents.

4. DESs in extraction systems

DESs are increasingly used in extraction studies in a number of fields ranging from food science, metal extraction, medicinal chemistry, and capture of gases. In most of these studies, the underlying advantage of using DESs as an alternative to established conventional solvents is largely due to their advantageous physical properties such as negligible vapor pressure, tunable viscosities and a broad polarity range that can be tuned by varying the type and ratios of HBA and HBD. In cases where conventional extraction methods have been developed using room-temperature ionic liquids (RTILs), substitution with DESs overcomes issues of complex synthetic routes, high toxicity, and sustainability in terms of biodegradability that have previously limited the scope of RTILs [111], [112], [113]. Therefore, when used as solvents in extractions, DESs are often perceived to be more eco-friendly and greener than RTILs [44], [114], [115].

Previously, several review papers have been published that summarize applications of DESs in various extraction processes. Cunha et al. have critically evaluated various microextraction techniques, including liquid phase microextraction (LPME), microwave-assisted extraction (MAE), and ultrasound assisted extraction (UAE), that have used DESs [116]. Dwamena et al. and Makos et. al. have focused on the applications of hydrophobic DESs in microextractions [117], [118]. Tang et al. as well as Li et al. have summarized the application of DESs in various separation processes as well as the extraction of aromatics and bioactive compounds [119], [120]. Li et al. have also extensively reviewed the application of DESs in dispersive liquid-liquid microextraction (DLLME) [121]. Shishov et al. have summarized the extraction of liquid and solid samples by DESs in various fields of analytical chemistry [122]. Extraction techniques using DESs for the extraction of bioactive carbohydrates was reviewed by Mena-Garcia et al. [123]. A recent review by van Osch et al. summarized the physio-chemical

properties of hydrophobic DESs and their applications in extraction processes [124] and Ruegas-Ramon et al. reviewed phenolic extractions using DESs [125]. The role of water in the extraction processes using DES has been reviewed by Vilkova et al. [126] while Fernandez et al. have summarized NADES-based extraction methodologies [127]. A summary of ionic DESs in the extraction of natural products was provided by Huang et al. [128]. In sections 4.1 through 4.5 of this review, we highlight the use of DESs as extraction solvents in the analysis of phenolics and natural compounds, metals, desulfurization of fuels, proteins, and carbohydrates. Finally, the use of DESs in solid-phase extraction and solid-phase microextraction is reviewed in section 4.6.

4.1. DESs in the extraction of phenolics and other natural compounds

DESs have been widely used in the extraction of phenolics from a number of different matrices. Traditionally, the extraction of phenolics was performed in alkaline aqueous solutions followed by acidification using mineral acids [21], [129]. However, this resulted in large quantities of wastewater containing phenols, which pose environmental concerns [129]. Substitution of DESs in microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), and conventional stirring extraction methods have resulted in higher extraction efficiencies and have resolved the issue of phenol polluted wastewater [129], [130], [131]. Phenolic compounds have been shown to dissolve better in DESs than in lipids or water [130]. The enhanced solubility of these compounds is attributed to the multiple types of interactions, such as hydrogen bonding, dispersion forces, and electrostatic interactions [21], [130], [132]. Hydrogen bonding is among the most dominant and significant interaction. Moreover, DESs can potentially provide a stabilizing effect for analytes that are less stable in aqueous-based extraction systems through a chelation-type mechanism with strong hydrogen bonding between solvent and solute molecules [132].

DESs continue to gain more attention in food applications. Garcia et al. reported the extraction of polyphenols from virgin olive oil using DESs and compared their results to the commonly used mixture of 80% (v/v) methanol/water [133]. While most compounds were extracted with similar yields compared to the conventional method, oleacein and oleocanthal were extracted with much higher yields using the $[Ch^+][Cl^-]$: xylitol and $[Ch^+][Cl^-]$: 1,2-propanediol DESs [133]. Wang et al. reported the DES-based extraction of free and bound phenolic compounds in tea seed oil [115]. Extraction yields of up to 93 wt% for free phenolic compounds and 51 wt% for bound phenolic compounds were obtained using a glycerol-based DES[115]. Extraction of xanthohumol from spent hops was reported using the $[Ch^+][Cl^-]$: 2 propylene glycol DES with a highest extraction yield of 2.30 mg/g [134]. Choline-based DESs provided a much higher extraction yield for polyphenolic compounds in orange peels using solid-liquid extraction (SLE) compared to the established extraction solvent system of ethanol/water (30 wt.% water), while maintaining the high antioxidant properties of the target analyte [135]. Vieira et al. reported the extraction of phenolic compounds from walnut leaves (Juglans regia L.) using the $[Ch^+][Cl^-]$: 2 butyric acid and $[Ch^+][Cl^-]$: 2 phenylpropionic acid DESs with 20% of water (w/w). The three most abundant compounds, as identified by HPLC, were neochlorogenic acid, quercetin 3-O-glucoside, and quercetin O-pentoside [136].

Apart from food products, DESs have been applied in other matrices. Park et al reported the extraction of two phenolic acids, namely chlorogenic acid and caffeic acid, from Herba Artemisiae Scopariae using the $[N_{1111}^+][Cl^-]$: 4 urea DES mixed with methanol/water (60:40, v/v) [137]. The percent recovery ranged from 97.3% to 100.4% with 9.35 mg/g and 0.31 mg/g of chlorogenic acid and caffeic acid, respectively, being extracted [137]. Peng et al. investigated the extraction of five phenolic acids from Lonicerae japonicae Flos using the $[Ch^+][Cl^-]$: 6 (1,3-

butanediol) DES with 10% water content coupled with MAE [138]. Recoveries of chlorogenic acid, caffeic acid, 3,4-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid, and 4,5-dicaffeoylquinic acid were 79.25%, 80.03%, 85.96%, 86.01% and 85.52%, respectively [138]. Barbieri et al. reported the extraction and stabilization of rosemary (Rosmarinus officinalis L.) phenolic compounds using choline-based DESs [139]. The highest extraction as a function of total phenolic content (TPC) was 62.21 ± 3.85 mg/g obtained using $[Ch^+][Cl^-]$: 1,2-propanediol DES. Compared to the conventional ethanol-based extraction, all DESs preserved a higher antioxidant capacity of target analytes regardless of the extraction efficiency of each DES [139]. The extraction of phenolic acids, namely rosmarinic acid and salviaflaside, from Prunella vulgaris has been reported [114]. Extraction yields of 3.658 mg/g and 1.049 mg/g for rosmarinic acid and salviaflaside, respectively, were obtained using the $[Ch^+][Cl^-]$: ethylene glycol (1:4) DES with water/DES ratios of between 30% and 36% (v/v) [114]. Mahmood et al. reported the extraction of polyphenolic antioxidants from chlorella vulgaris using polyol-based DESs [112]. All DESs preserved a higher antioxidant capacity of target analytes as compared to ethyl acetate and water as benchmark solvents, while the $[Ch^+][Cl^-]$: glycerol (1:2) and $[Ch^+][Cl^-]$: 1,4-butanediol (1:4) DESs were more specific towards extracting gallic acid [112].

Preservation of analyte antioxidant properties from biological matrices may be explained by the enhanced stabilizing effect that DESs have on polyphenols [132]. Evidence from NMR-based metabolomic studies suggest the formation of viscous liquid in living cells that is neither soluble in lipids or water [132], [140]. This liquid is referred to as NADES and its properties are similar to ILs [140]. The laccase enzyme was observed to be completely soluble but inactive in neat $[Ch^+][Cl^-]$: malic acid DES. However, the addition of 50 wt% water in the DES resulted in the activation of enzyme [140]. Since NADES are found in cells and involved in cell regulation,

their ability to stabilize analytes while extracting them from biological matrices is due to them being native to these analytes in such matrices [140].

Extraction of phenolics using DESs is not only limited to biological matrices. Phenol extraction from model oil was reported [129]. The procedure involved in-situ generation of DESs by introducing different ammonium salts in model oils consisting of toluene, hexane, and p-xylene. The ammonium salts formed DESs with phenol, resulting in phase separation. While no DES was found in the oil phase, toluene did partition slightly into the DES layer [129]. A subsequent study investigated the effect of substituent chain length as well as the effect of symmetry for ammonium salts, with reported extraction efficiencies of up to 99.9% [141]. Gu et al. optimized the extraction of phenolic compounds from hexane model oil using ultrasonic wave-assisted liquid-phase microextraction (LPME) with pre-synthesized DESs [142]. High enrichment factors were obtained for polar compounds including phenols, benzoic acid, and anilines, while enrichment factors for non-polar compounds such as toluene and biphenyl were negligible because of their low distribution coefficients between model oil and DESs [142]. Jiao et al. reported the separation of pyridine and phenol from coal tar using the $[Ch^+][Cl^-]$: 3 trifluoroacetic acid DES with extraction efficiencies and distribution coefficients of 90.97% and 30.23, 93.47% and 42.97 for pyridine and phenol, respectively [143]. Carbon disulfide (CS_2) was used as the back-extraction agent to regenerate DESs which could be reused over 4 cycles while maintaining more than 90% extraction efficiency [143]. Yi et al. reported the separation of phenolic compounds from coal-based liquid oil using $[Ch^+][Cl^-]$: glycerol-based DESs [113]. Strong DES-phenol aggregates were formed and disrupted existing oil-phenol aggregates. The driving force behind extraction was hydrogen bonding between the DES and phenolic compounds. The $[Ch^+][Cl^-]$: glycerol DES extracted 98.3% of the phenolic compounds [113]. Yao et al. reported the separation of phenol from model

768 oils by forming in situ DESs of phenol with quaternary ammonium-based zwitterions, betaine, and
769 L-carnitine [144]. Phenol was extracted with extraction efficiencies of up to 94.6% with the L-
770 carnitine : phenol DES using a mole ratio of 0.4 at 298.2 K and diethyl ether as the antisolvent
771 [144]. A greener method was reported to extract phenols from oils using in situ generation of
772 phenol-based DESs with halogen-free zwitterions [111]. Extraction efficiencies of up to 98.6%
773 were achieved using DESs formed between 1-(butyl-4-sulfonate)-tripropylaminium (TPA-BS) and
774 phenol, with phenol content of oil decreasing down to 4.8 g/dm^3. Eliminating halogens from DESs
775 can lead to less corrosion of refining equipment [111]. These findings show great potential in
776 replacing environmentally harmful aqueous extractions involving alkaline solutions and mineral
777 acids with DESs in industrial scale refining processes of phenols from oil products [113], [129],
778 [141], [142], [143], [144].

779 While establishing the efficacy of DESs in extractions, it is important to identify the
780 optimum extraction method [130]. One method may be optimal for one set of analytes and class
781 of DESs while another may give better results for another system. Most studies have tested
782 multiple extraction methods for their system and have reported the optimized parameters for the
783 method that provided the highest extraction efficiencies. Bubalo et al. reported that UAE
784 outperformed microwave-assisted extraction (MAE) and the conventional stirring method in the
785 extraction of phenolic compounds from grape skin, where extraction yields of over 25 mg/g were
786 obtained for some analytes [130]. In contrast, phenolic compounds from the herbaceous plant
787 Pyrola incarnata Fisch. were extracted with better efficiency via MAE using polyol-based DESs,
788 where hyperin, chimaphilin, quercitin, quercitin-O-rhamnoside, and 2'-O-galloylhyperin were
789 extracted with extraction yields of over 1.5 mg/g, 0.3 mg/g, 0.2 mg/g, 0.5 mg/g and 4.8 mg/g,
790 respectively [145]. Variables including extraction temperature, extraction time, and water content

were optimized to yield the optimum extraction method [21], [130], [132], [145]. While MAE utilizes microwaves to heat the sample and solvent to accelerate extraction kinetics, temperatures beyond a certain threshold can be damaging if the thermal stability of the analyte is exceeded, which is especially important for phenolic compounds [130], [116]. Higher temperatures often lower viscosity and surface tension of the DES leading to an increase in its solvation power [130]. However, prolonged and excessive heating is generally not recommended, especially for DESs comprised of [Ch^+][Cl^-] HBA and carboxylic acid-based HBDs where slight ester formation is known to alter the properties of the DESs [43]. On the other hand, UAE allows higher dispersion of DESs without the need of a dispersive solvent and enhances mass transfer of the analytes using ultrasonic frequencies [142], [116]. The greater penetration ability of the extractant with UAE is particularly useful in solid samples. Nevertheless, ultrasonic frequencies may lead to degradation of the chemical structure and minimizing extraction times in both MAE and UAE can help overcome stability issues [130], [142]. Conventional extraction methods performed on a shaker, however, offer a cheaper and less complicated setup compared to UAE or MAE and may or may not be coupled with a water bath to raise the extraction temperature.

Extractions with mixtures of DESs and water have been widely reported. While DESs are considered as designer solvents where structural modifications can be made to produce physical properties best-suited for an application, the tunability of physical properties is also accomplished by purposefully varying the water content [130]. Dilution assists in lowering the viscosity leading to greater dispersion and intercalation of the extractant within matrix layers and ultimately enhancing extraction efficiency [130]. The addition of water lowers the cost of extractions and enhances the polarity of the extractant to favor the extraction of polar over weakly polar analytes [132]. However, there is a limit to the percentage of water that can be added without disrupting

814 the hydrogen bonding between the components of the DES that results in their segregation [130].
815 Most studies have examined a range of water content and its effect on extraction yields and
816 optimize within that range [44]. Nevertheless, the addition of water does not always yield higher
817 extraction efficiencies. In systems where the target analyte is less stable in aqueous solutions, poor
818 extraction yields can be obtained. Dai et al. reported the decreased stability of carthamin, the bulk
819 of the red pigment in safflower, with the increase in DES water content [132]. Carthamin was best
820 extracted with highly viscous and non-acid containing DESs [132].

821 The regeneration and reuse of DESs is an important aspect in extraction applications [129],
822 [141]. The sustainability of their use becomes limited in scope if DESs are not recycled. Many
823 studies predominantly focus on extraction efficiencies while making comparisons to industrial
824 scale refining processes such that they often undermine the need for DES regeneration by citing
825 that DESs are cheap and easy to prepare [129], [141], [142], [143]. Nevertheless, some studies
826 have incorporated means of DES regeneration within their scope and have shown the effectiveness
827 with which DESs can be reused [129], [141]. Macroporous resins have been demonstrated to be
828 useful in recovering analytes from DESs. Garcia et al. reported analyte recovery from the DES
829 phase by passing it through a column filled with pre-treated hydrated Amberlite XAD-16 resin
830 [133]. The DES was first eluted from the column using distilled water while phenolic analytes
831 were eluted with methanol [133]. Similarly, bioactive flavonoids extracted from the herbal
832 medicine Equisetum palustre L. were recovered from the DES layer using a HPD-826
833 macroporous resin column [146]. The column was first rinsed with deionized water followed by
834 95% aqueous ethanol (v/v). The resin treatment facilitated analyte enrichment. Studies reporting
835 the in-situ generation of DESs by introducing different ammonium salts in model oils consisting
836 of toluene, hexane, and p-xylene were able to regenerate the ammonium salts using either diethyl

ether or dibutyl ether [129], [141]. Ether functioned as an antisolvent and assisted the crystallization of ammonium salts with the phenolic moiety (HBD) dissolving in ether. Choline-based ammonium salts were not found to dissolve in diethyl ether and were completely crystallized [129]. In the case of the tetramethylammonium chloride (TMAC) salt, dibutyl ether could remove phenol with a removal efficiency of above 95% [141]. The recovery of ammonium salt starting materials works best if the two components of the DES have drastically different solubilities in the antisolvent. The addition of an infinite volume of antisolvent results in disruption of hydrogen bonding between the two components of the DES and leads to structural disintegration [44]. Upon component segregation, the HBA and HBD either dissolve in the antisolvent or are crystallized/precipitated based on their individual polarities [129], [141]. This versatility offered by DESs greatly improves their feasibility of purification and generally does not exist with RTILs.

4.2. DESs in the extraction of metals

DESs have been employed as solvents for the dissolution of several metals and their oxides [24], [41], [147], [148]. Abbott et al. employed DESs comprised of $[Ch^+][Cl^-]$ HBA and carboxylic acid HBDs for the solubilization of three different transition metal oxides. Each metal oxide was observed to possess significantly different solubility in the different DESs. For example, CuO was most soluble in the $[Ch^+][Cl^-]$: 2 phenylpropionic acid DES, Fe_3O_4 exhibited the highest solubility in the $[Ch^+][Cl^-]$: 2 oxalic acid DES, while the solubility of ZnO was observed to be highest in the $[Ch^+][Cl^-]$: 2 malonic acid DES. In another study, Abbott et al. used an electrocatalytic approach to solubilize metals in ethaline DES [147]. Rodriguez et al. have employed p-toluenesulfonic acid (p-TSA)-based DESs for solubilizing metal oxides [24]. A number of metal oxides including MnO, MnO_2, Fe_2O_3, Fe_3O_4, Co_3O_4, CuO, Cu_2O, ZnO, In_2O_3, PbO, and PbO_2 were studied and varying solubilities were observed. For example, the solubility of Cu_2O and In_2O_3 in the 2 $[Ch^+][Cl^-]$: p-

860 TSA DES was more than 100 g/L while that of PbO was negligible in the same DES [24].
861 Moreover, solubilities also varied upon changing the molar ratio of HBA and HBD. The solubility
862 of In_2O_3 decreased from 183.7 g/L to 1.8 g/L when the ratio of $[Ch^+][Cl^-]$: p-TSA was changed
863 from 2:1 to 1:1 [24]. Recently, Damilano et al. have reported that the solubility of metal oxides in
864 DESs can be further enhanced by using thiol-based HBDs instead of alcohol-based HBDs. The
865 solubility of FeO was observed to be much higher in the $[Ch^+][Cl^-]$: 2 thioglycolic acid DES (29.91
866 g/L) compared to that of the $[Ch^+][Cl^-]$: 2 glycolic acid DES (2.99 g/L) [148].

867 A number of studies have utilized DESs for the extraction of metals from aqueous solutions
868 [149], [150], [151], [152]. Hydrophobic DESs comprised of varying ratios of lidocaine and
869 decanoic acid in the removal of alkali and transition metal ions from water have been employed
870 by van Osch and co-workers. Distribution coefficients of all studied transition metals were found
871 to be >0.99 while those of alkali metals ranged from 0.20-0.27 when a lidocaine : 2 decanoic acid
872 DES was used for extraction [149]. The same DES was employed in another study to extract Fe(III)
873 and Mn(II) from water. Complete separation of Fe(III) was achieved at a DES concentration of 25
874 g/L while Mn(II) required 300 g/L [150]. Recently, Shi et al. have prepared DESs by mixing
875 trioctylmethylammonium chloride $[N_{8881}^+][Cl^-]$ and hydroxy benzoates of varying alkyl chain
876 length for the extraction of Cr(VI). The maximum extraction capacity of Cr(VI) was determined
877 to be 66.7 mg/g [151]. Schaeffer et al. have utilized novel phosphine oxide-based DESs for the
878 separation of Pt^{4+} and Pd^{2+} from transition metals in aqueous solutions. The order of metal
879 extraction was observed to be $Pt^{4+} > Pd^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+}$ [152].

880 Several studies have employed DES-based digestions or microextractions for the
881 determination of hazardous metals by atomic absorption spectroscopy in food samples [153],
882 [154], [155], [156], [157], [158], [159]. A digestion method using the $[Ch^+][Cl^-]$: oxalic acid DES

was developed by Habibi et al. for determination of Fe, Zn and Cu in fish samples. Limits of detection (LODs) were determined to be 0.053, 0.012, and 0.006 μg/mL for Fe, Zn, and Cu, respectively. The extraction recovery of all metals was greater than 95.3% [153]. Similarly, Ghanemi et al. employed a microwave-assisted digestion of the $[Ch^+][Cl^-]$: oxalic acid DES for determination of Cu, Fe, Ni, and Zn in marine biological samples using inductively coupled plasma-optical emission spectroscopy (ICP-OES). In this study, recovery of all elements of interest was observed to be greater than 96.1% [154]. An ultrasonic energy assisted preconcentration method for the extraction of Pb and Cd from cosmetics was developed by Kazi et al., and LODs of 0.86 and 0.66 μg/L, respectively, were found. The Pb and Cd content in lipstick samples were found to be in the range of 15.3-21.8 μg/g and 16.3-22.6 μg/g, respectively [155]. Other studies have determined the content of transition and heavy metals in honey, rice, mushroom, non-alcoholic beverages, and milk by atomic absorption spectroscopy [156], [157], [158], [159].

DESs have also emerged as beneficial solvents for recycling lithium-ion batteries (LIBs) by extracting valuable metals from used batteries [160], [161], [162]. Tran et al. used the ethaline DES to extract metals from lithium cobalt oxide (LCO; $LiCoO_2$) and lithium nickel manganese cobalt oxide (NMC; $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) batteries. Leaching efficiencies as high as 99.3% were attained for cobalt were obtained in LCO battery, while efficiencies of 71% for lithium and 32% for cobalt were reported in NMC batteries [160]. Peeters et al. explored several DESs comprised of $[Ch^+][Cl^-]$ HBA and carboxylic acid HBDs for the recovery of cobalt from LIBs [161]. The highest leaching efficiency of 99.6% was achieved by using the $[Ch^+][Cl^-]$: citric acid DES [161]. In another investigation, Roldan-Ruiz et al. utilized p-TSA-based DESs and reported excellent cobalt recovery up to 94%, with lower temperature, shorter times, and lower amounts of solvent required compared to previous reports [162]. Moreover, Riano et al. as well as Liu et al. have

investigated the use of DESs for recovery of metals from NdFeB magnets [163], [164]. Nd_2O_3 and Dy_2O_3 were recovered with a purity of 99.87% and 99.94%, respectively [163]. Liu et al. reported a separation factor greater than 1300 between neodymium and iron through simple dissolution of their oxides in a DES comprised of guanidine hydrochloride and lactic acid [164]. Figure 9 shows the scheme of NdFeB recovery by selective leaching with DES. The roasted NdFeB magnet powder (mixture of Nd_2O_3 and Fe_2O_3 with a mole ratio of 1:7, respectively) was dissolved in the DES at a solid to liquid ratio of 1/10 at 40 °C for 6 hours. The DES selectively dissolved Nd_2O_3, and Fe_2O_3 was removed after centrifugation. Oxalic acid was added to the DES solution containing Nd_2O_3 for regeneration of the DES and formation of insoluble $Nd_2(C_2O_4)_3$ precipitates. $Nd_2(C_2O_4)_3$ was calcinated to yield Nd_2O_3 with a recovery rate of 83.1 wt%. The regenerated DES was further reused for 3 cycles [164].

DESs have also been extensively utilized for the efficient extraction and recovery of metals from ores and industrial process residues [165], [166], [167], [168], [169], [170], [171], [172], [173], [174]. Abbott et al. used DESs to recover Zn and Pb from electric arc furnace dust and achieved extraction efficiencies of 34% and 26% for Zn and Pb, respectively [165]. In a similar approach, Bakkar et al. extracted up to 38 wt% of Zn from cupola furnace dust by using DESs [166]. Soldner et al. accumulated up to 31% phosphorus from incinerated sewage sludge ash by employing a DES comprised of dimethyl urea and mannose [167]. In an attempt to extract Cu from copper sulfide mineral (CuS, Cu_2S, and $CuFeS_2$), Anggara et al. achieved 99% selective recovery of copper from $CuFeS_2$ using a combination of the ($[Ch^+][Cl^-]$: oxalic acid and $[Ch^+][Cl^-]$: ethylene glycol) DESs [168]. An extraction efficiency of 96.8% from 1 mM Au(III) solution was demonstrated by Geng et al. [169]. Zhu et al. achieved an 85.2% extraction efficiency of Zn from zinc oxide dust [170]. Other studies have reported extraction of indium, tin, tungsten, arsenic,

yttrium, and europium by using DESs comprised of [Ch^+][Cl^-] and carboxylic acid [171], [172], [173].

4.3. DESs in the desulfurization of fuels

The sulfur content in fuels has been a major cause of environmental pollution [23]. DESs have been extensively employed for removal of both aliphatic and aromatic sulfur compounds from fuels and are potential alternative solvents in the hydrodesulfurization process [23], [175]. Li et al. reported the extraction of benzothiophene from n-octane model fuel using ammonium-based DESs [23]. The tetrabutylammonium chloride : polyethylene glycol-based DES was found to extract up to 82.83% per cycle of extraction [23]. Since desulfurization is achieved in multiple cycles, a 99.48% total extraction efficiency over 5 cycles was reported with sulfur content in fuels reduced to as low as 8.5 ppm [23]. Unlike protic ionic liquids, the initial sulfur content had no effect on the extraction efficiencies and it was concluded that the DES had a much higher extraction capability than traditional ILs [23]. The study revealed that hydrogen bonding between the chloride anion of HBA and the active proton of HBD was disrupted by the addition of benzothiophene. Additionally, hydrogen bonding between DES components and benzothiophene was deemed responsible for the high extraction efficiency of the system [23]. The DESs were regenerated after washing with diethyl ether.

In a separate study involving benzothiophene and n-octane as a model fuel, hydrogen peroxide was employed to promote oxidative extraction of benzothiophene using acid-based DESs [175]. While extraction without hydrogen peroxide resulted in an extraction efficiency less than 40%, the addition of hydrogen peroxide resulted in extraction efficiencies of up to 99.99%. The mechanism indicated that the dissolution of benzothiophene was enhanced by its oxidation

resulting in a shift in equilibrium in the forward direction to promote further dissolution of the undissolved part [175]. The DESs were regenerated by washing with water.

Since the first few publications describing the desulfurization of fuels using DESs, a number of studies have been published on these extraction systems [23], [175], [176], [177]. A study by Macos et al. investigated the desulfurization efficiency for thiophene (Th), benzothiophene (BT) and dibenzothiophene (DBT) for which they reported the efficiencies of 91.5%, 95.4% and 99.2%, respectively, using phenol HBDs in choline-based DESs [176]. Desulfurization is done in consecutive runs or cycles. Lima et al. screened sixteen different PEG-based DESs to identify the most efficient DES that would result in maximum extraction efficiency per cycle [177]. The tetrabutylammonium chloride ($[N_{4444}^+][Cl^-]$) : 2 PEG-400 DES was found to be the best eutectic mixture and resulted in extraction efficiencies of 85% and 68% for DBT and Th, respectively, and yielded a sulfur content of less than 10 ppm in 2-3 cycles [177]. Shah et al. investigated the most important component of a ternary DES of $[N_{4444}^+][Cl^-]$, polyethylene glycol (PEG-200), and ferric chloride ($FeCl_3$) (4:1:0.05) responsible for sulfur extraction from model oil [178]. Simulations related to the interaction energy between n-octane/DBT and DBT/DES showed that the addition of DES weakened interactions between DBT and n-octane [178]. Between DBT and DES, the ammonium cation had the highest interaction energy, followed by the chloride anion, PEG with a small interaction energy value, and finally ferric chloride having negligible interaction energy. Removing ferric chloride in another simulation resulted in the interaction energy for n-octane/DBT being higher than that of DBT/DES, implying that ferric chloride was essential. Removing PEG and simulating an unreported 2 $[N_{4444}^+][Cl^-]$: $FeCl_3$ DES resulted in even higher interaction energy for DBT/DES than n-octane/DBT [178].

973 Liu et al. investigated an unconventional DES desulfurization system involving dual-acidic
974 DES of [L-Pyroglutamic acid] : [trifluoroacetic acid (L-Pyro:TFA)] [179]. This non-ionic DES,
975 coupled with oxidative extraction, resulted in very high extraction efficiencies of 99.7%, 99.6%,
976 and 99.2% for DBT, 4,6-dimethyldibenzothiophene and BT, respectively [179]. Razavian et al.
977 reported the conversion of low-value residual fuel oil to light fuels with the tetrapropylammonium
978 bromide (TPAB) : ethylene glycol DES which resulted in 36% asphaltene and 12.8% sulfur content
979 reduction [180]. Jha et al. demonstrated that (DBT), 2-methylthiophene (2-MT), and thiophene (T)
980 could be easily extracted using the tetrabutylammonium bromide (TBAB) : diglycol DES with
981 extraction efficiencies of 92%, 86%, and 71%, respectively [181]. Majid et al. reported that the
982 [Ch][Cl] : 1,2-ethanediol DES resulted in a desulfurization efficiency of up to 60.27% [182]. DESs
983 with shorter chain lengths were found to have lower viscosities, and this resulted in a higher
984 solvation power [182].

985 Simultaneous denitrogenation and desulfurization of fuels using DESs was reported by
986 Lima et al. [183]. Unlike the conventional industrial scale method, the study demonstrated that the
987 two processes could be done simultaneously using DESs without adversely affecting each other
988 [183]. The $[P_{4444}^{+}][Br^{-}]$: 4 sulfolane DES was used for extraction and three different systems
989 containing thiophene (Th), DBT, pyridine (Py) and carbazole (Carb) were tested. The first
990 consisted of solely n-heptane along with the four compounds while the other two contained extra
991 hydrocarbons to mimic model gasoline and model diesel [183]. In the case of sole n-heptane,
992 extraction efficiencies of Py and Carb were enhanced from 99% and 97% to 100% in the presence
993 of other compounds. On the other hand, extraction efficiencies of Th and DBT were reduced from
994 67% and 88% to 63% and 86%, respectively, by the presence of other species [183]. In the case of
995 model diesel and model gasoline, no impact was observed in the extraction of nitrogen-containing

compounds in the presence of other substances. The extraction efficiency of Th increased from 63% to 68% in gasoline while for DBT it decreased from 86% to 83% in diesel [183].

Desulfurization of fuels is not limited to liquid-based fuels [184], [185], [186]. Biogas often contains sulfur-based moieties that result in sulfuric acid production within the internal combustion engine and may reduce the life of the engine [184]. Slupek et al. developed an absorptive method to desulfurize model gas. Nitrogen, being the model biogas, was mixed with dimethyl disulfide (DMDS), and the stream was passed through a column that was saturated with choline-based DESs [184]. The content of DMDS was monitored using gas chromatography-flame ionization detector (GC-FID). The optimized parameters were reported to be 50 mL of the $[Ch^+][Cl^-]$: 2 phenol DES, temperature of 25 °C and a flow rate of 50 mL/min under which saturation of this particular DES was achieved rapidly between 800 minutes and 1100 minutes of gas exposure [184]. The regeneration efficiency of the $[Ch^+][Cl^-]$: 2 phenol DES was between 84.5% and 87.8% [184]. Unlike desulfurization of liquid fuels, the absorptive method has its own challenges as certain parameters, such as the flow rate, can vastly affect the saturation of DESs. As such, there is a need to understand the absorptive mechanism of DESs. Karibayev et al. aimed to establish an understanding of the absorptive mechanism of DESs involved in hydrogen sulfide extraction from natural gas, in order to corroborate existing experimental findings in literature, so as to better design such DESs in future studies [185].

4.4. DESs in the extraction of proteins

DESs have been particularly useful in protein extractions [44], [187], [188], [189], [190], [191], [192], [193], [194], [195], [196], [197], [198], [199], [200]. The three-dimensional tertiary or quaternary structure of proteins can be stabilized by a number of intermolecular forces such as disulfide bridges, hydrogen bonding, and dispersion forces. In order to preserve protein structure

during extractions, the stability of proteins needs to be ensured [195]. DESs are very well-suited to extract proteins while providing structural stability through a multitude of different interactions. Aqueous biphasic systems (ABSs) based on DESs have been used in a number of partitioning-based protein extraction studies [187], [188], [189], [190], [191], [195], [200]. While DES integrity is believed to be compromised in ABSs, their extraction capabilities in these systems are remarkable [173], [200]. Zeng et al. reported the extraction of bovine serum albumin (BSA) using $[Ch^+][Cl^-]$: urea, $[N_{4444}^+][Cl^-]$: urea, $[N_{3333}^+][Br^-]$: urea and $[Ch^+][Cl^-]$: methylurea DESs [187]. The extraction was performed using a conventional shaker and the concentration of protein was determined using spectrophotometry. The $[Ch^+][Cl^-]$: urea DES exhibited the best extraction of BSA with average extraction efficiencies of 99.94%, 99.72%, 100.05%, and 100.05% over four different trials [187]. Circular dichroism (CD) spectra confirmed no conformational change of BSA post extraction. While the study achieved good extraction efficiencies, back-extraction of target proteins from the DES was largely unexplored. Xu et al. reported the back-extraction of BSA in a study involving the extraction of BSA and trypsin using the $[Ch^+][Cl^-]$: glycerol (1:1) DES [188]. The extraction was performed at 25 °C on a temperature-controlled shaker set at 2000 rpm. Although the extractions efficiencies were 98.16% for BSA and 94.36% for trypsin, only 32.96% of BSA was back-extracted into the NaCl salt-rich phase [188]. Pang et al. reported extraction of BSA and papain using ABS [189]. An extraction efficiency of 95.16% for BSA and 90.95% for papain was reported under the optimum conditions. While an attempt to back-extract the protein from DES was made, the BSA back-extraction efficiency did not exceed 34.35% [189].

A study by Zhang et al. compared ternary and binary DESs in aqueous two phase systems (ATPSs) for the extraction of BSA [190]. Using the $[N_{1111}^+][Cl^-]$: urea and $[N_{1111}^+][Cl^-]$: glycerol : urea DESs resulted in extraction efficiencies of up to 99.31% and 98.95%, respectively. While

the efficiencies were comparable for both ternary and binary DESs, the ternary DES provided back-extraction efficiencies of up to 71.89% compared to 21.02% for the binary DES system [190]. A recent study by Meng et al. examined the extraction of chymotrypsin, BSA, and lysozyme with various ABSs composed of binary DESs mixed with either amino acids or polyols, as well as to ABSs prepared by mixing two different DESs [191]. The phase-forming abilities of $[N_{4444}^+][Cl^-]$: polypropylene glycol / [amino acids] : [polyols] were found to lie between those of $[N_{4444}^+][Cl^-]$: polypropylene glycol / amino acids and $[N_{4444}^+][Cl^-]$: polypropylene glycol / polyols. Extraction efficiencies ranged from 52.72% to 85.73% for the $[N_{4444}^+][Cl^-]$: polypropylene glycol / amino acids ABSs and 60.16% to 98.85% for $[N_{4444}^+][Cl^-]$: polypropylene glycol / polyols ABSs, while the extraction efficiencies for $[N_{4444}^+][Cl^-]$: polypropylene glycol / [amino acids] : [polyols] ranged from 72.87% to 99.15% [191]. Fourier transform infrared spectroscopy (FT-IR) and CD spectroscopy revealed that no conformational changes were observed.

Protein extraction from a diverse range of matrices have been reported with DESs. The extraction of collagen peptides from cod skins was reported by Bai et al. using a heat and stir method [192]. Acidic DESs generally exhibited higher extraction efficiencies. The $[Ch^+][Cl^-]$: oxalic acid DES extracted higher and lower molecular weight collagens with extraction efficiencies of 91.57% and 96.01%, respectively, corresponding to a purity of 93.14% and 100% [192]. The extraction efficiency and purity of collagen peptides varied significantly with the relative ratios of HBA to HBD in the $[Ch^+][Cl^-]$: oxalic acid DES, as shown in Figure 10 [192]. The HBA:HBD ratio was varied from 1:0.6 to 1:1.2. Maximum extraction efficiency (44.60% w/v) was observed at 1:1.0 mole ratio, while highest purity of collagen (63.1%) was achieved at 1:0.6 mole ratio [192]. Lopez et al. reported the extraction of free seleno-amino acids from powdered and lyophilized milk [193]. The nonionic lactic acid : glucose (5:1) DES exhibited the highest

relative percentage recoveries of 100% and 94.46% for lyophilized biofortified sheep milk and cow powder milk, respectively. Seleno-amino acids were analyzed by ICP-MS and the LODs for selenocysteine, selenomethionine, and seleno-methyl-selenocysteine were 7.37, 8.63, and 9.64 μg/kg, respectively [193].

Utilization of brewer's spent grain (BSG) as a protein source for food products was reported using urea-based DESs [194]. The sodium acetate : urea (1:2) DES mixed with 10 wt% water provided a 79% extraction efficiency compared to a 41% extraction efficiency using the conventional alkaline extraction method [194]. The higher extraction efficiency was attributed to its specific ability to solvate the bulk of the denatured BSG protein along with prolamin aggregates and glutelins that are not easily dissolved [194]. Similarly, a study involving extraction of proteins from rapeseed cakes was reported [195]. The $[Ch^+][Cl^-]$: 2 glycerol DES was able to selectively extract and enrich the protein cruciferin and omit napin, as confirmed by sodium dodecyl sulfate–polyacrylamide gel electrophoresis (SDS-PAGE) [195]. Water was employed as the antisolvent to precipitate the proteins. The extraction of cruciferin was achieved up to a temperature of 140 °C beyond which the protein was believed to be denatured [195].

The simultaneous deproteinization and demineralization of black soldier fly (Hermetia illucens, BSF) prepupae to yield chitin for mass-rearing of insects has been reported with NADES [196]. DESs composed of either an acidic HBA or an acidic HBD were found to be best suited for chitin products. A mechanistic study found that low pH DESs were better at decalcification due to release of a large amount of H^+ that reacts with calcium carbonate while deproteinization was better achieved with high pKa-based HBDs of DESs, as this led to stronger hydrogen bonding [196]. The dissolution of gluten by NADES for its determination in food products as an alternative to ethanol-water solution has been reported using UAE [197]. While the ethanol-water solution is

1088 inefficient at protein extraction from processed food and also requires the addition of reducing
1089 agents, NADES were found to not require the addition of 2-mercaptoethanol or tris(2-
1090 carboxyethyl)-phosphine. Hence, gluten determination by enzyme-linked immunosorbent assay
1091 (ELISA) was achieved without interference from reducing agents using citric acid-based NADES.
1092 The sensitivity was enhanced by a factor of ten [197].

1093 The role of DESs in protein enrichment and partitioning studies is not only limited to their
1094 use as an extractant. DESs as a recyclable and efficient energy resource in forward osmosis (FO)
1095 membrane technology for protein enrichment has been reported [198]. BSA solutions concentrated
1096 after 20 hours of FO using isopropanol treated thin-film composite polyamide (TFC-PA)
1097 membranes were subjected to SDS-PAGE analysis. The $[Ch^+][Cl^-]$: 2 ethylene glycol DES was
1098 able to increase protein concentration by more than 6 times while the DES was easily regenerated
1099 by cooling it below -5 ℃ to facilitate its separation from water [198].

1100 Marchel et al. reported the simultaneous extraction and recovery of pepsin using ABS of
1101 polypropylene glycol (PPG) and DESs composed of betaine hydrochloride (BeHCl) as HBA and
1102 glucose, fructose, sucrose, and urea as HBDs [199]. Pepsin was found to have a higher affinity
1103 towards the BeHCl-enriched phase in all ABSs and extraction efficiencies between 96.6% and
1104 99.5% were reported. Increased enzymatic activity of pepsin on BSA was observed in these ABSs
1105 [199]. The enzyme lysozyme was extracted from chicken egg white using ammonium-based DESs
1106 and evaluated for pharmaceutical use [200]. The ABS composed of $[N_{4444}^+][Br^-]$: glycolic acid
1107 and Na_2SO_4 was able to transfer more than 98% of lysozyme into the DES-rich layer [200]. The
1108 enzyme retained 91.73% of its enzymatic activity post extraction indicating that the enzyme was
1109 not denatured, and its active and allosteric sites were vastly conserved [200].

1110 **4.5. DESs in the extraction of carbohydrates**

DESs have been widely used in the extraction of carbohydrates such as cellulose and lignin [201], [202], [203], [204], [205], [206], [207], [208], [209], [210], [211], [212], [213], [214], [215], [216], [217]. The ability of DESs to cleave lignin-carbohydrate complexes by disrupting covalent linkages as well as participate in hydrogen bonding between the target analyte and its matrix makes them ideal for biomass fractionation [203], [210]. Alvarez-Vasco et al. reported the extraction of low molecular weight lignin from poplar and Douglas fir (D. fir) using choline-based DESs [201]. The $[Ch^+][Cl^-]$: lactic acid DES extracted lignin from poplar and D. fir with a percentage yield of 78% at 120 °C and 58% at 145 °C, respectively, with purity up to 95% [201]. Hemicellulose was found to co-extract with lignin indicating that the DESs were selective to both hemicellulose and lignin. The addition of deionized water to a solution of lignin and hemicellulose in ethanol resulted in lignin precipitation. Liu et al. reported microwave-assisted cleavage of lignin-carbohydrate complexes using the $[Ch^+][Cl^-]$: oxalic acid dihydrate DES [202]. Low molecular weight lignin oligomers were obtained with a purity of 96% while other dissolved materials included glucose, xylose, and hydroxymethylfurfural. The undissolved material consisted of cellulose with a crystallinity of 75% [202]. The successful cleavage of lignin-carbohydrate complexes using the $[Ch^+][Cl^-]$: oxalic acid dihydrate DES was attributed to reported the hydrogen-bond acidity [202]. In the same year, Liu et al. explored the cleavage of strong hydrogen bonds between cellulose chain units in cotton fibers to yield nanocellulose [203]. The $[Ch^+][Cl^-]$: oxalic acid dihydrate (1:1) DES was achieved fabrication of nanocellulose crystals with a yield of 74.2% and a relative crystallinity of 82% [203].

Tan et al. reported the fractionation and delignification of oil palm empty fruit bunch using both acidic and basic DESs [204]. The $[Ch^+][Cl^-]$: lactic acid (1:5) DES resulted in 100% hemicellulose extraction, 50% lignin pellet extraction, and 88% delignification of oil palm empty

fruit bunch [204]. Subsequently, Tan et al. explored the extraction of lignin from lignocellulosic oil palm empty fruit bunch using acidic DESs [205]. The $[Ch^+][Cl^-]$: lactic acid (1:15) and $[Ch^+][Cl^-]$: formic acid (1:2) DESs provided extraction percentage yields of more than 60%. Nevertheless, the content of phenolic hydroxyl group for lignin extracted with the $[Ch^+][Cl^-]$: lactic acid (1:15) DES was higher (3.33–3.72 mmol/g) than that of lignin extracted with the $[Ch^+][Cl^-]$: formic acid (1:2) DES (2.66 mmol/g) [205]. Increasing the mole ratio of HBD was found to further decrease the phenolic hydroxyl group content. Chen et al. demonstrated the isolation of lignin from poplar wood meal using the $[Ch^+][Cl^-]$: lactic acid (1:9) DES [206]. The extraction efficiency of extracted lignin was 95% while the purity was 98%. FTIR and NMR analysis confirmed that the DES was able to selectively cleave ether bonds in lignin [206]. Ling et al. reported the pretreatment of moso bamboo using the levulinic acid-based DES for efficient deconstruction of lignocellulosic biomass [207]. The $[Ch^+][Cl^-]$: levulinic acid (1:2) DES yielded the highest lignin removal as well as morphological disruption of biomass that resulted in a glucose percentage yield of 79.07% [207].

Smink et al. explored the role of choline chloride in biomass delignification using Eucalyptus globulus [208]. The $[Ch^+][Cl^-]$: lactic acid (1:250) DES was employed to demonstrate that the chloride anion was the active component that provided results similar to $[Na^+][Cl^-]$. The presence of choline chloride in DES form with lactic acid resulted in a faster rate of pulping of Eucalyptus globulus [208]. Chen et al. reported the pretreatment of lignocellulosic biomass consisting of corn stover, switchgrass, and Miscanthus using MAE coupled with the $[Ch^+][Cl^-]$: lactic acid DES [209]. The technique assisted the extraction of lignin and xylan with an enrichment of 65-67%, while most of the cellulose remained part of the pretreated solids. Lignin was recovered with a purity of 85-87% [209]. Lou et al. investigated the extraction of lignin nanoparticles from

wheat straw using the [Ch^+][Cl^-] : lactic acid (1:2) DES [210]. Lignin was extracted with a purity of up to 94.8% with a yield of 81.5% from air-dried wheat straw and 85.9% from oven-dried material. The DES was found to cleave ether linkages in lignin as well as bonds between lignin and hemicelluloses [210] as well as exhibit higher affinity to lignin in the absence of water.

Fang et al. explored the possibility of increasing the enzymatic digestibility of lignocellulosic date palm residues for samples that were pretreated with DESs [211]. It was revealed that a hydrothermal treatment of the sample prior to its pretreatment with [Ch^+][Cl^-] : glycerol (1:2) DES increased the enzymatic digestibility of date palm residues by 1.7 times. Moreover, xylan and lignin removal efficiencies were reported to be 25% and 22%, respectively [211]. Li et al. investigated the extraction of lignin from willow (Salix matsudana cv. Zhuliu) using choline-based DESs [212]. The [Ch^+][Cl^-] : lactic acid (1:10) DES provided the highest lignin yield of 91.82% with a purity of 94.46%. FT-IR, ^{13}C-NMR, and ^{31}P-NMR revealed that the extracted lignin was mainly composed of syringyl and guaiacyl units [212]. Xia et al. demonstrated the use of a ternary DES to enhance the cleavage of lignin-carbohydrate complexes in lignocellulose [213]. The [Ch^+][Cl^-] : glycerol (1:2) DES was coordinated with $AlCl_3 \cdot 6H_2O$ in various ratios. The ternary DES resulted in a lignin fractionation efficiency of 95.46% with a purity of 94% [213].

Das et al. reported the extraction of k-carrageenan from Kappaphycus alvarezii using choline-based DESs [214]. The quality and physico-chemical properties of extracted polysaccharides were benchmarked against conventional extraction methods as well as water-based extraction. Hydrated DESs generally provided higher extraction efficiency with 10% hydrated [Ch^+][Cl^-] : glycerol (1:2) DESs offering the highest percentage yield of 60.25% [214]. Traces of DESs were found in the extracted polysaccharide, but these were generally deemed non-hazardous for most combinations of DESs given the low toxicity of their starting materials. Cicci

et al. explored the extraction of microalgal metabolites using NADES [215]. A ternary DES comprised of 1,2-propanediol : [Ch^+][Cl^-] : water (1:1:1) was employed with both UAE and ball mill-based mechanical disruption. Extraction efficiencies using UAE for proteins, carbohydrates, lipids, chlorophylls, and carotenoids were 27%, 12%, 1.8%, 3.4%, and 0.11%, respectively [215]. On the other hand, extraction efficiencies using ball mill-based extraction for proteins, carbohydrates, lipids, chlorophylls, and carotenoids were 10%, 7%, 0.7%, 2.8%, and 0.06%, respectively [215]. Zhu et al. investigated the extraction of chitin from lobster shells using choline-based DESs [216]. The [Ch^+][Cl^-] : malonic acid (1:2) DES extracted chitin with the highest purity and resulted in a yield of 20.63%, which is higher than that of artificially prepared chitin reported at 16.53%. The obtained chitin had two different forms with a crystallinity of 67.2% and 80.6% [216]. Saravana et al. reported the extraction of chitin from shrimp shells (Marsupenaeus japonicas) [217]. A extraction yield of 19.41% was reported using the [Ch^+][Cl^-] : malonic acid DES compared to only 16.08% using conventional methods. Chitin films prepared with the extracted chitin exhibited similar properties to standard chitin films available otherwise [217].

Zuo et al. demonstrated the reduction of fructose to 5-hydroxymethylfurfural (5-HMF) in DESs [218]. Reduction of fructose to 5-HMF was previously reported with a 90% yield using the [Ch^+][Cl^-] : citric acid DES by Hu et al. [218], [219]. However, this new study demonstrated the conversion and in-situ extraction of fructose into 5-HMF from [Ch^+][Cl^-] : fructose DES, with a product yield of 90.3% and purity of 98% [218]. Gomes et al. demonstrated the reduction of carbohydrates to 5-HMF using a ternary composition of betaine hydrochloride : malic acid : water (1:1:1) [220]. MAE was employed and a 5-HMF yield of 94% from fructose and 72% from sucrose was achieved. Sert et al. attempted to convert cellulose from sunflower stalk into value-added products such as 5-HMF, formic acid, levulinic acid, and furfural using DESs coupled with MAE

[221]. Using the [Ch^+][Cl^-] : oxalic (1:1) DES resulted in production of 76.2% of levulinic acid, 5.57% of furfural, 4.07% of 5-HMF, and 15.24% of formic acid.

4.6. DESs in solid-phase extraction (SPE) and solid-phase microextraction (SPME)

DESs, particularly those that are hydrophobic, have been widely used in SPE and SPME for the analysis of a wide variety of analytes [47], [222], [223], [224], [225], [226], [227], [228], [229], [230], [231], [232], [233]. Shen et al. reported a DES-based graphene oxide (GO) incorporated monolithic chip for the analysis of aromatic hydrocarbons by SPE using alcohol-based DESs [222]. Compared to the monolithic chip without GO, the carboxylated GO incorporated chip of poly(butylmethacrylate-co-ethylene glycol dimethyl methacrylate) provided higher than 90% recoveries of anthracene, pyrene, and fluoranthene [222]. Wang et al. reported DES-modified GO and graphene as SPE absorbents for the preconcentration of 2,4,6-trichlorophenol (2,4,6-TCP), 4-chlorophenol (4-CP), and 2,4-dichlorophenol (2,4-DCP) in aqueous samples using choline-based DES [223]. The SPE method coupled to HPLC resulted in recoveries ranging between 88.49% and 89.70% for chlorophenols and were higher than that of commercially-available aminosilica and silica adsorbents [223]. Li et al. reported extraction of ferulic acid from wheat bran by SPE using DES modified silica gel [224]. The [Ch^+][Cl^-] : glycerol (1:2) DES provided the highest yield (5.86 mg/g) for ferulic acid. The recovery for ferulic acid using DES-modified silica gel was 89.7% compared to 64.1% using silica gel and 80.3% using IL modified silica gel [224].

Li et al. reported the preparation of DES modified molecularly imprinted polymers (MIPs) for SPE of laminarin and fucoidan [225]. The [Ch^+][Cl^-] : urea (1:2) DES provided the highest extraction efficiencies for laminarin and fucoidan at 87.6% and 95.5%, respectively, with interday and intraday RSD values lower than 4.23% [225]. Li et al. reported the preparation of DES-based

MIPs as SPE absorbents for the purification of levofloxacin [226]. A ternary caffeic acid : $[Ch^+][Cl^-]$: formic acid (1:3:1.5) DES was used as a functional monomer to impart good recognition ability for levofloxacin from a millet extract that resulted in a recovery of 91.4% [226]. Li et al. reported DES-based MIPs and mesoporous silica materials (MSMs) used as SPE absorbents for the extraction of levofloxacin from green bean extract [227]. Betaine-based DESs were used for the modification of MIPs and MSMs resulting in excellent recognition ability of levofloxacin. The LOD and LOQ for levofloxacin were 0.01 and 0.03 ug/mL, respectively, with method recoveries between 97.2% and 100.2% and RSD values less than 1.8% [227]. Li et al. examined the magnetic SPE (M-SPE) of theophylline and theobromine from green tea using Fe_3O_4/MIPs modified with DESs [228]. Compared to IL modified Fe_3O_4/MIPs, DES modified Fe_3O_4/MIPs gave higher recoveries of theophylline and theobromine at 87.51% and 92.27%, respectively [228].

Jeong et al. developed a fast and convenient method for analyzing volatile phenolic compounds and monoterpenes in peppermint leaves (Mentha piperita L.) using DESs [229]. Analytes from peppermint leaves were directly extracted into the $[Ch^+][Cl^-]$: D-(+)-glucose (5:2) DES in sufficient concentration for analysis by headspace solid-phase microextraction (HS-SPME) coupled to GC. The total phenolic content, antioxidant activity, and total flavonoid content of phenolics were assessed along with the quantification of monoterpenes using this one-step sample preparation technique [229]. Nie et al. investigated volatile compounds in tobacco using MAE with DESs coupled with HS-SPME and GC-MS [230]. The $[Ch^+][Cl^-]$: ethylene glycol (1:3) DES was used to extract analytes from the matrix using SPME coupled with MAE and provided higher responses in the analysis of more volatile compounds compared to conventional SPME [230].

Li et al. examined the modification of a sol-gel sorbent coating of poly(dimethylsiloxane) (PDMS) fiber using DESs [231]. Hydrophobic DESs composed of ethyl 4-hydroxybenzoate and methyltrioctylammonium chloride at various ratios were added to the sol-gel sorbent coating and resulted in the formation of more pores on the surface of PDMS fiber. Analysis of toluene, ethylbenzene and o-xylene using HS-SPME and GC-FID revealed that a LOD between 0.005 and 0.025 µg/L [231].. Wang et al. reported a DES-based polymer monolithic column for in-tube SPME of non-steroidal anti-inflammatory drugs (NSAIDs) in aqueous matrices [232]. The $[Ch^+][Cl^-]$: itaconic acid (1:1.5) DES was used as a functional monomer to prepare a polymeric monolith inside a polydopamine-functionalized poly(ether ether ketone) (PEEK) tube. The PEEK tube was connected to a HPLC system and yielded enrichment factors of around 100, small relative standard deviation values lower than 4.32% and good linearity. The reported LODs ranged between 0.05 and 0.25 ng/mL [232].

5. DESs in capillary electrochromatography

The use of DESs in capillary electrochromatography (CEC) has given rise to a new approach to vary the selectivity of the separation method [234], [235], [236], [237], [238], [239], [240], [241]. Typically, CEC combines the high separation efficiency of capillary electrophoresis (CE) and high selectivity of high-performance liquid chromatography (HPLC) [238], [242]. Monolithic columns form a crucial component of CEC. The in-situ polymerization of a mixture of radical initiators, monomers and porogens in a glass capillary produces a monolithic column that generally has long life, fast mass transfer kinetics and high reproducibility [235], [236]. Traditionally, organic solvents such as toluene-isooctane and toluene-isooctane-dimethyl sulfoxide have served as porogens in pure organic monolithic columns [236]. However, these organic solvents are volatile, toxic, and are not environmentally-friendly [236], [240]. Pure

monolithic columns are often plagued by poor efficiencies due to low surface area resulting from a lack of pores and insufficient interaction sites [235], [236], [237]. This results in their inability to separate small molecules [236]. Good column permeability permitting high flow rates ensures low backpressures and high mass transfer rates in polymer monolithic columns [234]. There is growing interest in developing hybrid monolithic columns involving carbon nanotubes (CNT), hydroxyapatite, GO, metal-organic frameworks, metal oxides and mesoporous molecular sieves in order to provide greater surface area and a denser network of pores within the polymer matrix [234].

With the use of the aforementioned multifunctional polymer nanocomposites, studies have explored the use of RTILs as suspension media and porogens [234], [235], [236], [237]. The separation efficiency of a monolithic column is dependent on the pore size and pore structure within the polymer matrix, which can be tuned with the type of porogen used [235]. While RTILs alone can offer the high viscosity needed for the suspension of nanocomposites as well as negligible vapor pressure, the biodegradability and ease of synthesis of DESs has resulted in a number of studies involving the binary mixtures of RTILs and DESs as porogens [234], [235]. Zhang et al. reported the incorporation of single-walled carbon nanotubes (SWCNTs) in a binary mixture of $[Ch^+][Cl]$: ethylene glycol (1:2) and $[HMIM^+][BF_4^-]$ as porogen [234]. Compared to SWCNT-free columns, the SWCNT-based hybrid monolith columns produced higher column efficiencies of up to 251,000 plates/meter using CEC and were thermally stable up to 270 °C [234]. Scanning electron microscopy (SEM) revealed that SWCNTs-based hybrid columns possessed relatively denser monolithic structures with a lower interstitial porosity than SWCNTs-free columns. The binary porogen mixture of RTILs and DESs eliminated the need for oxidative cutting of CNTs using sulfuric and nitric acids prior to their use [234]. Conventionally, oxidative cutting

of CNTs prevents their aggregation and sedimentation. The ratio of RTIL to DES was found to dictate the morphology of the columns. The lack of [$HMIM^+$][BF_4^-] resulted in a block monolith while using [$HMIM^+$][BF_4^-] alone in the absence of DES made it difficult to dissolve the polar electroosmotic flow (EOF) modifier [234]. The column coated with 60% of [$HMIM^+$][BF_4^-] and 40% DES gave the best separation of small molecules while the column coated with 40% of [$HMIM^+$][BF_4^-] and 60% DES provided the highest EOF [234].

Apart from carbon nanotubes, Zhang et al. reported hybrid monolith columns of uniform pore-sized mesoporous molecular sieves MCM-41 using a binary mixture of porogen comprised of the [$HMIM^+$][BF_4^-] IL and [Ch^+][Cl^-] : alcohol-based DESs [235]. MCM-41 was silanized with 3-(trimethoxysilyl)propyl methacrylate (γ-MPS) and MCM-41-MPS-based columns attained efficiencies of up to 209,000 plates/meter [235]. The high viscosity of [Ch^+][Cl^-] : alcohol-based DESs decreased the interfacial tension of polymer microparticles and prevented the aggregation of polymer oligomers [235]. SEM images revealed smaller interstitial porosity and comparatively dense structures with rough micro globular surface in the case of MCM-41-MPS-based columns as opposed to the MCM-41-MPS-free columns. The lack of [$HMIM^+$][BF_4^-] resulted in a block monolith while using [$HMIM^+$][BF_4^-] alone in the absence of DES made it difficult to dissolve the polar radical initiator and the electroosmotic flow (EOF) modifier. The column coated with 60% of [$HMIM^+$][BF_4^-] and 40% DES gave the best separation of small molecules while the column coated with 40% of [$HMIM^+$][BF_4^-] and 60% DES gave the highest column permeability and EOF [235]. Similarly, Li et al. published the incorporation of GO in monolithic columns using a binary mixture of [$HMIM^+$][BF_4^-] and alcohol-based DESs by modifying GO with 3-(trimethoxysilyl)propyl methacrylate (γ-MPS) [236]. Both GO-MPS-based and GO-MPS-free columns were prepared under identical conditions, with GO-MPS-based columns achieving

efficiencies of up to 147,000 plates/meter using CEC [236]. The [Ch^+][Cl^-] : 1,2-propane diol (1:3) DES-based porogen gave the highest column efficiencies and permeabilities. A RTIL to DES ratio of 3:2 generally gave higher column efficiencies and permeabilities while using neat DESs or RTILs provided poor baseline separation and low efficiencies [236].

Zhou et al. reported hybrid monolithic columns involving stellated mesoporous silica nanoparticles (SMSNs) with good structural uniformity and permeability prepared with binary mixtures of RTILs and DESs [237]. Silanization of SMSNs was carried out with γ-MPS and SMSN-based columns having efficiencies up to 266,000 plates/meter when a binary porogen mixture of 65% (v/v) of [$HMIM^+$][BF_4^-] and 35% (v/v) of [Ch^+][Cl^-] : 1,2-propylene glycol DES was used [237]. Baseline separation of alkylbenzenes, phenols, anilines, naphthalenes, nonsteroidal anti-inflammatory drugs (NSAIDs), and hydroxybenzoic acid isomers was achieved with CEC using SMSN-based columns.

In a recent study by Wang et al., the DES served as a functional monomer instead of being a part of the porogen [238]. A DES composed of chlorocholine chloride and itaconic acid was used along with ethylene glycol dimethacrylate as crosslinker and a binary mixture of isopropanol and PEG-400 as porogen. The hybrid monolithic column preparation method was similar to previously reported methods [234], [235], [236], [237]. The polymeric DES-based column provided good separation of phenols, nucleosides, toluidines, alkaloids and nucleotide bases [238]. The migration time relative standard deviation (RSD) from batch-to-batch was 3.08% for the DES-based columns while the RSD for columns of the same batch was 4.26% [238].

Recently, DESs were used as auxiliary additives to beta-cyclodextrins (β-CD) as chiral selectors to expand the scope of DESs in chiral electrochromatography [239]. Moufawad et al. have shown the formation of inclusion complexes between analytes and β-CD in the presence of

DES as a cosolvent [243]. Pretreated fused-silica capillaries were coated with mixtures of β-CD and four different choline-based DESs ([Ch^+][Cl^-] : urea, [Ch^+][Cl^-] : ethylene glycol, [Ch^+][Cl^-] : propylene glycol and [Ch^+][Cl^-] : butylene glycol) [239]. Enantiomeric separation of chiral drugs rac-Zopiclone (rac-Zop), rac-salbutamol (rac-Sal), and rac-amlodipine (rac-Aml) were achieved using DESs as an auxiliary additive [239]. Figure 11 shows that the separation of all three racemic drugs improved upon the addition of [Ch^+][Cl^-]-based DESs. For all three drugs, the best resolution was with 1.0% (v/v) [Ch^+][Cl^-] : urea-based DES and the highest retention was generally achieved with urea-based DESs [239]. Columns of different concentrations up to 2.0% (v/v) of urea-based DESs were evaluated; resolution and retention times generally increased for each drug with increasing concentration of DES. Nevertheless, DES concentrations over 2.0% (v/v) were not tested due to increased Joule heating [239].

A study by Zhao et al. explored the possibility of preparing monolithic columns with DESs to immobilize enzyme microreactors using thiol-ene click reaction [240]. A binary mixture of [$BMIM^+$][BF_4^-] and [Ch^+][Cl^-] : ethylene glycol (1:3) was used to immobilize the enzyme trypsin in a polymer structure of poly(butyl methacrylate-co-α-methacrylic acid-co-ethylene glycol dimethacrylate). The immobilized enzyme reactor (IMER) was observed to digest BSA in under 50 seconds, making it up to 864 times faster than in-solution digestion that normally takes 12 hours [240]. Comparison of protein extracts fragments from rat liver to a protein database resulted in identification of 1034 protein groups [240].

6. Conclusions and outlook

DESs have gained significant interest in the field of separations due to their tunable physico-chemical properties, sustainability, low cost, and ease of preparation. The various preparation methods afford a number of different advantages and limitations. The heating and

stirring method is most common, but prolonged heating at high temperatures can lead to thermal degradation. The vacuum evaporation method uses comparatively lower temperatures, but evaporation of water at low temperatures is often time consuming and energy intensive. The freeze-drying method allows for the incorporation of biological moieties within the DES while the grinding method uses a mechanical approach for preparation at room temperature. The twin screw extrusion process is an efficient and scalable route for DES preparation, while the microwave irradiation method and ultrasonication methods are faster approaches that consume less energy. As the popularity of DESs continues to grow, more attention should be focused on thorough characterization to ensure that only high purity products are used. Relevant physico-chemical properties such as viscosity, water content, density, and thermal stability should be reported when applicable. It should be recognized that some HBA/HBD combinations can give rise to unwanted side reactions, such as esterification, that can result in the solvent's chemical structure evolving over time. It is important to understand the potential challenges and limitations of various preparation methods of DESs. Limitations such as degradation and formation of by-products upon heating at high temperature and/or for prolonged periods of times should be considered before employing them in various applications.

DESs have been extensively used in many extraction processes. Phenolic extractions have been reported for various food samples including olive oil, orange peels, rosemary, and walnut leaves. DESs have been employed in the dissolution of metal oxides, extraction of metals from their ores, and quantitative determination of metals in food samples. DESs have been utilized for removal of both aliphatic and aromatic sulfur moieties from fuels with nearly 99.48% desulfurization of model fuels being achieved using the $[N_{4444}^{+}][Cl^{-}]$: PEG-based DES. Aqueous biphasic systems have been demonstrated for partitioning-based protein extractions. The use of

DESs as additives in capillary electrochromatography reveals a more recent application in the field of separation science. It can be expected that DESs will continue to be widely incorporated into large scale and microextraction systems where the regeneration and reuse of the solvent can have greater utility compared to conventional organic solvents. In these systems, it is very important that the structure/composition of the DES be carefully studied to ensure long-term stability of the solvent. Since DESs are much less thermally stable compared to ILs, it is important to monitor the stability of the solvent when elevated temperatures are used.

Solvent polarity scales have been used to characterize DESs. The betaine polarity scale has revealed that the polarities of most DESs are similar to that of methanol (E_T^N = 0.76) and higher than acetonitrile (E_T^N = 0.49) and dimethylsulfoxide (E_T^N = 0.46). Since DESs are capable of undergoing multiple simultaneous solvation interactions, Kamlet-Taft parameters have provided additional insight towards individual solute-solvent interactions of DESs. The nile red polarity scale has mostly been used to characterize the polarity of NADESs. The literature is currently void of chromatographic approaches to measure solvent properties of DESs. Such information, when combined with data reported from polarity and solvatochromic dye scales, would greatly enhance our understanding of these solvent systems. Significant opportunities exist in studying the effects of DES nanoscale ordering on various aspects of the separation process.

Acknowledgements

The work performed by the authors was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through the Ames Laboratory. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University of Science and Technology under contract No. DE-AC02-07CH11358.

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Figure Legends:

Figure 1. a) Chemical structures and abbreviations of commonly used HBAs and HBDs for the preparation of DESs. b) Nomenclature of common DESs used in separations. Chemical structures of the HBA/HBD highlight hydrogen bonding interactions between the two components.

Figure 2. Preparation of $[Ch^+][Cl^-]$: ethylene glycol (1:2) DES, where the homogenous eutectic on the right is prepared by heating the HBA and HBD mixture for 2 hours at 80 °C. Crystallization occurs (left) over time when inappropriate heating or short stirring times are utilized for DES preparation. Reprinted with permission from [42]. Copyright (2020) American Chemical Society.

Figure 3. a) Photograph demonstrating a color comparison of $[Ch^+][Cl^-]$: D-fructose DES prepared via twin screw extrusion method (left) and conventional heating and stirring method (right), b) UV-vis spectra of $[Ch^+][Cl^-]$: D-fructose DES as prepared via twin screw extrusion method (red) and conventional heating and stirring method (green). Adapted from Ref. [58] with permission from The Royal Society of Chemistry.

Figure 4. Comparison of ^1H NMR spectra of $[Ch^+][Cl^-]$: glutaric acid (1:1) as prepared by heating and stirring method (top) and grinding method (bottom). The peaks at chemical shifts of 1.9, 2.4, 3.3, 3.6, and 4.5 ppm (highlighted by red circles) correspond to the ester formation between the $[Ch^+][Cl^-]$ and glutaric acid. Reproduced from Ref. [43] with permission from The Royal Society of Chemistry.

Figure 5. Chemical structures of various probes employed to measure the polarity and solute-solvent interactions of DESs.

Figure 6. Absorption spectra of betaine dye 33 dissolved in maline, ethaline, glyceline, and reline at 30 °C. Reproduced from Ref. [38] with permission from the PCCP Owner Societies.

Figure 7. Kamlet-Taft parameters (α, β, and π*) of DESs comprised of $[Ch^+][Cl^-]$, $[N_{4444}^+][Cl^-]$, and DL-menthol HBAs with carboxylic acid HBDs. Also included are the parameters for glyceline, ethaline, and reline DESs. Adapted from Ref. [84] with permission from the PCCP Owner Societies.

Figure 8. Ternary plot of Kamlet-Taft parameters (α, β, and π*) of DESs comprised of the $[Ch^+][Cl^-]$ HBA and carboxylic acid HBDs compared to organic solvents and ionic liquids.
The organic solvents plotted in the figure are acetonitrile, acetone, dichloromethane, toluene, methanol, 1,1,2,2-tetrachloroethane, nitrobenzene, 1,1,1-trichloroethane, benzene, acetophenone, 1,4-dioxane, cyclohexanone, DMSO, ethyl acetate, tetrahydrofuran, and ethanol. The ILs are $[BMIM^+][BF_4^-]$, $[BMIM^+][PF_6^-]$, $[BMIM^+][TfO^-]$, [BMIM$^+$][bis(trifluoromethylsulfonyl)imide] ($[NTf_2^-]$), [BMIM$^+$][hexafluoroantimonate], [1-butyl-2,3-dimethylimidazolium]($[BDMIM^+]$) $[BF_4^-]$, $[BDMIM^+][NTf_2^-]$, [1-butyl-3-methylpyrrolidinium]$[NTf_2^-]$, [1-ethyl-3-methylimidazolium]($[EMIM^+]$)$[PF_6^-]$, $[EMIM^+][NTf_2^-]$, [EMIM$^+$][perchlorate]($[ClO_4^-]$), [EMIM$^+$][nitrate]($[NO_3^-]$), [EMIM$^+$][acetate]($[CH_3COO^-]$), [EMIM$^+$][dicyanamide]($[N(CN)_2^-]$), [1-(2-hydroxyethyl)-3-methylimidazolium]([HOEMIM])$[PF_6^-]$, $[HOEMIM^+][NTf_2^-]$, $[HOEMIM^+][ClO_4^-]$, $[HOEMIM^+][N(CN)_2^-]$, $[HOEMIM^+][NO_3^-]$, $[HOEMIM^+][CH_3COO^-]$,

[$HOEMIM^+$][Cl^-], [1-butyl-3methylpyridinium][BF_4^-], and [1-butyl-4-methylpyridinium][BF_4^-]. Reprinted with permission from ([32]). Copyright (2020) American Chemical Society.

Figure 9. Scheme demonstrating recovery of NdFeB permanent magnet by selective leaching with DES comprised of guanidine hydrochloride HBA and lactic acid HBD. The roasted NdFeB powder was dissolved in the DES for selective dissolution of Nd_2O_3. DES was regenerated by addition of oxalic acid due to precipitation of $Nd_2(C_2O_4)_3$. Recovery of Nd_2O_3 was achieved after calcination of $Nd_2(C_2O_4)_3$ precipitate. Reprinted with permission from ([164]). Copyright (2020) American Chemical Society.

Figure 10. Effect of changing the molar ratio of [Ch^+][Cl^-] : oxalic acid DES on (a) the extraction efficiency (w/v), and (b) the purity of collagen peptides. The extraction efficiency increased when the mole ratio was increased from 1:0.6 to 1:1.0, and then slightly decreased at 1:1.2 mole ratio. The highest purity of collagen peptides was observed at 1:0.6 mole ratio and lowest purity was observed at 1:0.8. Reprinted with permission from ([192]). Copyright (2020) American Chemical Society.

Figure 11. Separation of three drugs including *rac*-Zop, *rac*-Sal, and *rac*-Aml, using different concentrations of alcohol-based and urea-based DESs. Chromatograms A-C show the effect of using different alcohol-based and urea-based DESs with DES concentration of 1.0% (v/v) for each drug while D-F show the effect of using different concentrations of urea-based DES for each drug. Reprinted with permission from reference [239].

Table 1. List of E_T^N polarity values for binary and ternary DESs as measured using betaine dye 30 and betaine dye 33. For comparison, E_T^N polarity values are also provided for water, and select organic solvents and ILs.

No.	HBA	HBD	Relative ratio HBA : HBD	$E_T(30)$ kcal mol^{-1}	$E_T(33)$ kcal mol^{-1}	E_T^N	Ref
1	[Ch$^+$][Cl$^-$]	Glycerol	1 : 1	58.49	-	0.858	[36]
2	[Ch$^+$][Cl$^-$]	Glycerol	1 : 1.5	58.21	-	0.849	[36]
3	[Ch$^+$][Cl$^-$]	Glycerol	1 : 2	58.58	-	0.860	[36]
				58.0	66.4	0.84	[38]
				-	-	0.845	[33]
				-	66.49	0.84	[84]
4	[Ch$^+$][Cl$^-$]	Glycerol	1 : 3	57.96	-	0.841	[36]
~~5~~	~~[Ch$^+$][Cl$^-$]~~	~~1,2-Ethanediol~~	~~1 : 2~~	~~57.3~~	~~65.7~~	~~0.82~~	~~[38]~~
~~6~~ 5	[Ch$^+$][Cl$^-$]	Urea	1 : 2	57.0	65.4	0.81	[38]
~~7~~ 6	[Ch$^+$][Cl$^-$]	Oxalic acid	1 : 1	47.78	-	0.527[a]	[101]
~~8~~ 7	[ATEAm$^+$][Cl$^-$]	Oxalic acid	1 : 1	56.40	-	0.793[a]	[101]
~~9~~ 8	[Ch$^+$][Cl$^-$]	Urea	1 : 2	-	-	0.835	[33]
				-	65.75	0.81	[84]
~~10~~	~~[Ch$^+$][Cl$^-$]~~	~~Glycerol~~	~~1 : 2~~	~~-~~	~~-~~	~~0.845~~	~~[33]~~

9				-	66.49	0.84	[84]
11 10	[Ch^+][Cl^-]	Ethylene glycol	1 : 2	57.3	65.7	0.82	[38]
				-	-	0.822	[33]
				-	65.91	0.83	[84]
12 11	[Ch^+][Cl^-]	Urea Glycerol	1 : 1 : 1	-	-	0.843	[33]
13 12	[Ch^+][Cl^-]	Urea Ethylene glycol	1 : 1 : 1	-	-	0.827	[33]
14 13	[Ch^+][Cl^-]	Urea Formamide	1 : 1 : 1	-	-	0.817	[33]
15 14	[Ch^+][Cl^-]	Urea Thiourea	1 : 1 : 1	-	-	0.844	[33]
16 15	[Ch^+][Cl^-]	Glycerol Ethylene glycol	1 : 1 : 1	-	-	0.830	[33]
17 16	[Ch^+][Cl^-]	Glycerol Formamide	1 : 1 : 1	-	-	0.829	[33]
18 17	[Ch^+][Cl^-]	Glycerol Thiourea	1 : 1 : 1	-	-	0.857	[33]
19 18	[Ch^+][Cl^-]	Ethylene glycol Formamide	1 : 1 : 1	-	-	0.814	[33]
20 19	[Ch^+][Cl^-]	Ethylene glycol Thiourea	1 : 1 : 1	-	-	0.842	[33]

~~21~~ 20	[Ch^+][Cl^-]	Formamide / Thiourea	1 : 1 : 1	-	-	0.833	[33]
~~22~~ 21	[Ch^+][Cl^-]	Urea / Acetamide	1 : 1 : 1	-	-	0.801	[97]
~~23~~ 22	[Ch^+][Cl^-]	Glycerol / Diethyleneglycol	1 : 1 : 1	-	-	0.806	[97]
~~24~~ 23	[Ch^+][Cl^-]	Glycerol / Triethyleneglycol	1 : 1 : 1	-	-	0.781	[97]
~~25~~ 24	[Ch^+][Cl^-]	Urea / Diethyleneglycol	1 : 1 : 1	-	-	0.787	[97]
~~26~~ 25	[Ch^+][Cl^-]	~~Urea~~ Glycerol / Acetamide	1 : 1 : 1	-	-	0.815	[97]
~~27~~ 26	[Ch^+][Cl^-]	Levulinic acid	1 : 2	-	50.26	0.35	[84]
27	[Ch^+][Cl^-]	Malonic acid	1 : 2	-	64.61	0.79	[84]
28	[Ch^+][Cl^-]	Glycolic acid	1 : 2	-	50.83	0.3~~3~~6	[84]
29	DL-Menthol	Acetic acid	1 : 1	-	62.45	0.72	[84]
~~29~~ 30	DL-Menthol	Levulinic acid	1 : 1	-	62.62	0.73	[84]
~~30~~ 31	DL-Menthol	Octanoic acid	1 : 1	-	63.10	0.74	[84]
~~31~~	DL-Menthol	Dodecanoic acid	2 : 1	-	62.90	0.73	[84]

32							
~~32~~ 33	$[N_{4444}^+][Cl^-]$	Octanoic acid	1 : 2	-	61.52	0.69	[84]
~~33~~ 34	$[N_{4444}^+][Cl^-]$	Decanoic acid	1 : 2	-	60.23	0.65	[84]
~~34~~ 35	$[N_{4444}^+][Cl^-]$	Dodecanoic acid	1 : 2	-	61.57	0.69	[84]
~~35~~ 36	$[MEA^+][Cl^-]$ [c]	Ethylenediamine	1 : 1	59.0	-	0.873 [a]	[102]
~~36~~ 37	$[MEA^+][Cl^-]$ [c]	Ethylenediamine	1 : 2	55.8	-	0.775 [a]	[102]
~~37~~ 38	$[MEA^+][Cl^-]$ [c]	Ethylenediamine	1 : 3	54.0	-	0.719 [a]	[102]
~~38~~ 39	$[MEA^+][Cl^-]$ [c]	Ethylenediamine	1 : 4	52.7	-	0.679 [a]	[102]
~~39~~ 40	$[MEA^+][Cl^-]$ [c]	Diethylenetriamine	1 : 4	51.3	-	0.636 [a]	[102]
~~40~~ 41	$[MEA^+][Cl^-]$ [c]	Tetraethylenepentamine	1 : 4	50.4	-	0.608 [a]	[102]
~~41~~ 42	$[MEA^+][Cl^-]$ [c]	Pentaethylenehexamine	1 : 4	50.2	-	0.602 [a]	[102]
~~42~~ 43	$[MEA^+][Cl^-]$ [c]	3-amino-1-propanol	1 : 1	59.7	-	0.895 [a]	[102]

~~43~~ 44	[MEA^+][Cl^-] [c]	3-amino-1-propanol	1 : 2	58.0	-	0.843 [a]	[102]
~~44~~ 45	[MEA^+][Cl^-] [c]	3-amino-1-propanol	1 : 3	57.2	-	0.818 [a]	[102]
~~45~~ 46	[MEA^+][Cl^-] [c]	3-amino-1-propanol	1 : 4	56.6	-	0.799 [a]	[102]
~~46~~ 47	[$HMIM^+$][Cl^-] [c]	Ethylenediamine	1 : 2	53.7	-	0.710 [a]	[102]
~~47~~ 48	[$HMIM^+$][Cl^-] [c]	Ethylenediamine	1 : 3	52.8	-	0.682 [a]	[102]
~~48~~ 49	[$HMIM^+$][Cl^-] [c]	Ethylenediamine	1 : 4	52.4	-	0.670 [a]	[102]
~~49~~ 50	[$HMIM^+$][Cl^-] [c]	Diethylenetriamine	1 : 4	51.3	-	0.636 [a]	[102]
~~50~~ 51	[$HMIM^+$][Cl^-] [c]	Tetraethylenepentamine	1 : 4	50.3	-	0.605 [a]	[102]
~~51~~ 52	[$HMIM^+$][Cl^-] [c]	Pentaethylenehexamine	1 : 4	49.9	-	0.593 [a]	[102]
~~52~~ 53	[$HMIM^+$][Cl^-] [c]	3-Amino-1-propanol	1 : 1	59.2	-	0.880 [a]	[102]
~~53~~ 54	[$HMIM^+$][Cl^-] [c]	3-Amino-1-propanol	1 : 2	58.0	-	0.843 [a]	[102]
~~54~~	[$HMIM^+$][Cl^-] [c]	3-Amino-1-propanol	1 : 3	57.2	-	0.818 [a]	[102]

55							
~~55~~ 56	[HMIM$^+$][Cl$^-$] [c]	3-Amino-1-propanol	1 : 4	56.7	-	0.802 [a]	[102]
~~56~~ 57	[N_{4444}^+][Br$^-$]	3-Amino-1-propanol	1 : 2	47.3	-	0.512 [a]	[102]
~~57~~ 58	[N_{4444}^+][Br$^-$]	3-Amino-1-propanol	1 : 3	48.1	-	0.537 [a]	[102]
~~58~~ 59	[N_{4444}^+][Br$^-$]	3-Amino-1-propanol	1 : 4	48.5	-	0.549 [a]	[102]
~~59~~ 60	[N_{4444}^+][Br$^-$]	Aminomethylpropanol	1 : 3	48.9	-	0.562 [a]	[102]
~~60~~ 61	[N_{4444}^+][Br$^-$]	Aminomethylpropanol	1 : 4	49.2	-	0.571[a]	[102]
~~61~~ 62	[Ch$^+$][Cl$^-$]	D-sorbitol	1 : 1	-	66.804	0.846 [a]	[35]
~~66~~ 63 [c]	[Ch$^+$][Cl$^-$]	Urea	1 : 2	-	67.355	0.863 [a]	[35]
~~67~~ 64 [c]	[Ch$^+$][Cl$^-$]	Oxalic acid	1 : 1	-	66.185	0.828 [a]	[35]
~~68~~ 65 [c]	[Ch$^+$][Cl$^-$]	Citric acid	1 : 1	-	67.433	0.866 [a]	[35]
~~69~~ 66 [c]	[Ch$^+$][Cl$^-$]	L-(+)-diethyl tartrate	1 : 1	-	65.880	0.818 [a]	[35]

~~70~~ 67 [c]	[Ch^+][Cl^-]	Zinc chloride	1 : 1	-	56.618	0.536 [a]	[35]
~~71~~ 68 [c]	[Ch^+][Cl^-]	Lactic acid	1 : 1	-	67.593	0.870 [a]	[35]
~~72~~ 69 [c]	[Ch^+][Cl^-]	Propanetriol	1 : 2	-	66.185	0.828 [a]	[35]
~~73~~ 70 [d]	[Ch^+][Cl^-]	Butanoic acid	1 : 2	-	-	0.619	[32]
~~74~~ 71 [d]	[Ch^+][Cl^-]	Butanoic acid	1 : 3	-	-	0.612	[32]
~~75~~ 72 [d]	[Ch^+][Cl^-]	Pentanoic acid	1 : 2	-	-	0.640	[32]
~~76~~ 73 [d]	[Ch^+][Cl^-]	Pentanoic acid	1 : 3	-	-	0.637	[32]
~~77~~ 74 [d]	[Ch^+][Cl^-]	Decanoic acid	1 : 2	-	-	0.682	[32]
~~78~~ 75 [d]	[Ch^+][Cl^-]	Decanoic acid	1 : 3	-	-	0.697	[32]
~~79~~ 76	[N_{2222}^+][Br^-]	Ethylene glycol	1 : 4	53.0	-	0.690	[98]
~~80~~ 77	[N_{2222}^+][Br^-]	1,3-propanediol	1 : 4	51.8	-	0.652	[98]
~~81~~	[N_{2222}^+][Br^-]	1,4-butanediol	1 : 4	51.3	-	0.63	[98]

78							
~~82~~ 79	$[N_{2222}^{+}][Br^{-}]$	1,5-pentanediol	1 : 4	51.3	-	0.635	[98]
~~83~~ 80	$[N_{3333}^{+}][Br^{-}]$	Ethylene glycol	1 : 4	54.2	-	0.725	[98]
~~84~~ 81	$[N_{3333}^{+}][Br^{-}]$	1,3-propanediol	1 : 4	53.2	-	0.696	[98]
~~85~~ 82	$[N_{3333}^{+}][Br^{-}]$	1,4-butanediol	1 : 4	51.9	-	0.654	[98]
~~86~~ 83	$[N_{3333}^{+}][Br^{-}]$	1,5-pentanediol	1 : 4	51.4	-	0.639	[98]
~~87~~ 84	$[N_{4444}^{+}][Br^{-}]$	Ethylene glycol	1 : 4	55.6	-	0.767	[98]
~~88~~ 85	$[N_{4444}^{+}][Br^{-}]$	1,3-propanediol	1 : 4	56.1	-	0.784	[98]
~~89~~ 86	$[N_{4444}^{+}][Br^{-}]$	1,4-butanediol	1 : 4	50.5	-	0.612	[98]
~~90~~ 87	$[N_{4444}^{+}][Br^{-}]$	1,5-pentanediol	1 : 4	49.6	-	0.584	[98]
~~91~~ 88	$[N_{5555}^{+}][Br^{-}]$	Ethylene glycol	1 : 4	53.0	-	0.688	[98]
~~92~~ 89	$[N_{5555}^{+}][Br^{-}]$	1,3-propanediol	1 : 4	52.0	-	0.658	[98]

~~93~~ 90	$[N_{5555}^{+}][Br^{-}]$	1,4-butanediol	1 : 4	52.1	-	0.662	[98]
~~94~~ 91	$[N_{5555}^{+}][Br^{-}]$	1,5-pentanediol	1 : 4	51.1	-	0.629	[98]
~~95~~ 92	$[N_{6666}^{+}][Br^{-}]$	Ethylene glycol	1 : 4	52.6	-	0.676	[98]
~~96~~ 93	$[N_{6666}^{+}][Br^{-}]$	1,3-propanediol	1 : 4	51.4	-	0.640	[98]
~~97~~ 94	$[N_{6666}^{+}][Br^{-}]$	1,4-butanediol	1 : 4	48.8	-	0.560	[98]
~~98~~ 95	$[N_{6666}^{+}][Br^{-}]$	1,5-pentanediol	1 : 4	50.5	-	0.612	[98]
~~99~~ 96	$[N_{7777}^{+}][Br^{-}]$	Ethylene glycol	1 : 4	52.6	-	0.677	[98]
~~100~~ 97	$[N_{7777}^{+}][Br^{-}]$	1,3-propanediol	1 : 4	51.0	-	0.627	[98]
~~101~~ 98	$[N_{7777}^{+}][Br^{-}]$	1,4-butanediol	1 : 4	50.6	-	0.613	[98]
~~102~~ 99	$[N_{7777}^{+}][Br^{-}]$	1,5-pentanediol	1 : 4	49.4	-	0.577	[98]
~~103~~ 100	$[N_{8888}^{+}][Br^{-}]$	Ethylene glycol	1 : 4	52.8	-	0.684	[98]
~~104~~	$[N_{8888}^{+}][Br^{-}]$	1,3-propanediol	1 : 4	52.3	-	0.666	[98]

101							
~~105~~ 102	$[N_{8888}^{+}][Br^{-}]$	1,4-butanediol	1 : 4	53.5	-	0.703	[98]
~~106~~ 103	$[N_{8888}^{+}][Br^{-}]$	1,5-pentanediol	1 : 4	50.9	-	0.624	[98]
	Miscellaneous Solvents (water, organic solvents and ILs)			$E_T(30)$ kcal mol^{-1}	$E_T(33)$ kcal mol^{-1}	E_T^N	Ref
~~107~~ 104	Glycerol			57.17	-	0.817	[36]
				-	-	0.813	[33]
~~108~~ 105	Dimethylsulfoxide			45.5	53.9	0.46	[38]
~~109~~ 106	Acetonitrile			46.5	54.8	0.49	[38]
~~110~~ 107	Ethanol			52.1	60.5	0.66	[38]
~~111~~ 108	Methanol			55.5	63.9	0.76	[38]
~~112~~ 109	Water			63.1	71.5	1.00	[38]
~~113~~ 110	2,2,2-Trifluoroethanol			59.9	68.4	0.90	[38]
~~114~~	Ethylene glycol			-	-	0.792	[33]

111						
~~115~~ 112	Acetone		-	-	0.787	[97]
	Cation	Anion	$E_T(30)$ kcal mol^{-1}	$E_T(33)$ kcal mol^{-1}	E_T^N	Ref
~~116~~ 113	$[BMIM^+]$ [e]	$[BF_4^-]$	53.2	61.6	0.69	[38]
			-	-	0.670	[33]
~~117~~ 114	$[BMIM^+]$ [e]	$[PF_6^-]$	53.2	61.6	0.69	[38]
~~118~~ 115	$[N_{1444}^+]$	$[NTf_2^-]$	~~53.2~~ 56.7	~~61.6~~ 65.1	~~0.69~~ 0.80	[38]
~~119~~ 116	$[BMIM^+]$ [e]	$[OTf^-]$ [e]	~~53.2~~ 53.7	~~61.6~~ 62.1	~~0.69~~ 0.71	[38]
~~120~~ 117	$[bmpyrr^+]$ [e]	$[NTf_2^-]$ [e]	~~53.2~~ 56.4	~~61.6~~ 64.9	~~0.69~~ 0.79	[38]
~~121~~ 118	$[Ch^+]$	$[Levulinate^-]$	-	58.94	0.61	[84]
~~122~~ 119	$[Ch^+]$	$[Malonate^-]$	-	66.69	0.85	[84]
~~123~~ 120	$[Ch^+]$	$[Glycolate^-]$	-	63.09	0.74	[84]

[a] E_T^N polarity values are calculated in this study by using equation 3 and equation 4, so that polarities of all the DESs can be compared by a normalized scale

[b] "-" corresponds to the values which have not been reported in literature

[c] DESs ~~65-72~~ 63-69 are 70 wt% aqueous solutions

[d] Polarity values of DESs ~~73-78~~ 70-75 are measured at 313 K

[e] [MEA^+][Cl^-]: Monoethanolammonium chloride, [$HMIM^+$][Cl^-]: 1-hexyl-3-methylimidazolium chloride, [$BMIM^+$][Cl^-]: 1-butyl-3-methylimidazolium chloride, [$bmpyrr^+$]: 1-butyl-1-methylpyrrolidinium, [NTf_2^-]: bis[(trifluoromethyl)sulfonyl]imide, [OTf^-]: trifluoromethanesulfonate, and [PF_6^-]: hexafluorophosphate.

Table 2. Summary of reported Kamlet-Taft parameters (α, β, and π*) for binary and ternary DESs. For comparison, Kamlet-Taft parameters are also provided for water, and select organic solvents and ILs

No.	HBA	HBD	Relative ratio HBA : HBD	π*[a]	α[a]	β[a]	Ref
1	$[Ch^+][Cl^-]$	Glycerol	1 : 1	1.003	0.923	0.658	[36]
2	$[Ch^+][Cl^-]$	Glycerol	1 : 1.5	0.980	0.921	0.658	[36]
3	$[Ch^+][Cl^-]$	Glycerol	1 : 2	0.984	0.937	0.657	[36]
				1.161	0.903	0.554	[33]
				1.11	1.49	0.52	[84]
4	$[Ch^+][Cl^-]$	Glycerol	1 : 3	0.970	0.914	0.657	[36]
5	$[Ch^+][Cl^-]$	Urea	1:2	0.319	1.732[b]	0.821	[39]
				1.192	0.860	0.559	[33]
				1.14	1.42	0.50	[84]
				1.227[e]	2.253[e]	1.238[e]	[35]
6	$[Ch^+][Cl^-]$	Ammonium Thiocyanate	1:1	0.258	1.575[b]	0.810	[39]
7	$[Ch^+][Cl^-]$	Imidazole	3:7	0.382	1.869[b]	0.864	[39]
8	$[Ch^+][Cl^-]$	Oxalic acid	1:1	0.92	0.24	0.52	[101]
				1.288[e]	2.173[e]	0.825[e]	[35]
9	$[ATEAm^+][Cl^-]$[g]	Oxalic acid	1:1	1.10	0.41	0.89	[101]
10	$[Ch^+][Cl^-]$	Ethylene glycol	1 : 2	1.112	0.891	0.640	[33]

				1.07	1.47	0.57	[84]
11	$[Ch^+][Cl^-]$	Urea Glycerol	1 : 1 : 1	1.170	0.893	0.583	[33]
12	$[Ch^+][Cl^-]$	Urea Ethylene glycol	1 : 1 : 1	1.165	0.862	0.560	[33]
13	$[Ch^+][Cl^-]$	Urea Formamide	1 : 1 : 1	1.159	0.846	0.593	[33]
14	$[Ch^+][Cl^-]$	Urea Thiourea	1 : 1 : 1	1.245	0.840	0.486	[33]
15	$[Ch^+][Cl^-]$	Glycerol Ethylene glycol	1 : 1 : 1	1.127	0.897	0.625	[33]
16	$[Ch^+][Cl^-]$	Glycerol Formamide	1 : 1 : 1	1.131	0.891	0.598	[33]
17	$[Ch^+][Cl^-]$	Glycerol Thiourea	1 : 1 : 1	1.217	0.889	0.539	[33]
18	$[Ch^+][Cl^-]$	Ethylene glycol Formamide	1 : 1 : 1	1.113	0.872	0.657	[33]
18	$[Ch^+][Cl^-]$	Ethylene glycol Thiourea	1 : 1 : 1	1.207	0.864	0.601	[33]
19	$[Ch^+][Cl^-]$	Formamide Thiourea	1 : 1 : 1	1.209	0.843	0.549	[33]
20	$[Ch^+][Cl^-]$	Urea Acetamide	1 : 1 : 1	1.115	0.844	0.620	[97]

21	[Ch^+][Cl^-]	Glycerol Diethyleneglycol	1 : 1 : 1	1.057	0.896	0.627	[97]
22	[Ch^+][Cl^-]	Glycerol Triethyleneglycol	1 : 1 : 1	1.045	0.853	0.685	[97]
23	[Ch^+][Cl^-]	Urea Diethyleneglycol	1 : 1 : 1	1.089	0.833	0.661	[97]
24	[Ch^+][Cl^-]	~~Urea~~ Glycerol Acetamide	1 : 1 : 1	1.092	0.890	0.703	[97]
25	[N_{2222}^+][Cl^-]	Butanoic acid	1 : 2	0.92	0.99[c]	0.76	[40]
26	[N_{2222}^+][Cl^-]	Hexanoic acid	1 : 2	0.86	0.97[c]	0.85	[40]
27	[N_{2222}^+][Cl^-]	Octanoic acid	1 : 2	0.81	0.96[c]	0.87	[40]
28	[N_{3333}^+][Cl^-]	Butanoic acid	1 : 2	0.93	0.94[c]	0.84	[40]
29	[N_{3333}^+][Cl^-]	Hexanoic acid	1 : 2	0.85	0.91[c]	0.92	[40]
30	[N_{3333}^+][Cl^-]	Octanoic acid	1 : 2	0.80	0.90[c]	0.96	[40]
31	[N_{4444}^+][Cl^-]	Butanoic acid	1 : 2	0.86	0.92[c]	0.99	[40]
32	[N_{4444}^+][Cl^-]	Hexanoic acid	1 : 2	0.81	0.90[c]	1.02	[40]
33	[N_{4444}^+][Cl^-]	Octanoic acid	1 : 2	0.80	0.84[c]	1.19	[40]
				0.76	1.41	0.99	[84]
34	[N_{4444}^+][Cl^-]	Decanoic acid	1 : 2	0.69	0.85[c]	1.28	[40]
				0.73	1.36	0.97	[84]
35	[N_{4444}^+][Cl^-]	Decanoic acid	1 : 1	0.86	0.91[c]	1.21	[40]
36	[N_{3333}^+][Br^-]	Butanoic acid	1 : 2	0.93	1.07[c]	0.80	[40]

37	$[N_{3333}^{+}][Br^{-}]$	Hexanoic acid	1 : 2	0.87	1.02[c]	0.86	[40]
38	$[N_{4444}^{+}][Br^{-}]$	Butanoic acid	1 : 2	0.93	1.02[c]	0.81	[40]
39	$[N_{4444}^{+}][Br^{-}]$	Butanoic acid	1 : 1	0.90	1.09[c]	0.84	[40]
40	$[N_{4444}^{+}][Br^{-}]$	Butanoic acid	2 : 1	0.95	0.94[c]	0.82	[40]
41	$[N_{4444}^{+}][Br^{-}]$	Hexanoic acid	1 : 2	0.92	1.02[c]	0.93	[40]
42	$[N_{4444}^{+}][Br^{-}]$	Octanoic acid	1 : 2	0.84	0.98[c]	1.09	[40]
43	$[N_{4444}^{+}][Br^{-}]$	Decanoic acid	1 : 2	0.71	0.95[c]	1.05	[40]
44	$[Ch^{+}][Cl^{-}]$	Acetic acid	1 : 2	1.10	-	0.53	[84]
45	$[Ch^{+}][Cl^{-}]$	Levulinic acid	1 : 2	1.00	0.51	0.57	[84]
46	$[Ch^{+}][Cl^{-}]$	Malonic acid	1 : 2	1.08	1.39	0.42	[84]
47	$[Ch^{+}][Cl^{-}]$	Glycolic acid	1 : 2	1.08	0.49	~~1.08~~ 0.50	[84]
48	DL-Menthol	Acetic acid	1 : 1	0.53	1.64	0.60	[84]
49	DL-Menthol	Levulinic acid	1 : 1	0.66	1.56	0.58	[84]
50	DL-Menthol	Octanoic acid	1 : 1	0.41	1.77	0.50	[84]
51	DL-Menthol	Dodecanoic acid	2 : 1	0.37	1.79	0.57	[84]
52	$[N_{4444}^{+}][Cl^{-}]$	Levulinic acid	1 : 2	1.06	-	0.82	[84]
53	$[N_{4444}^{+}][Cl^{-}]$	Dodecanoic acid	1 : 2	0.71	1.45	1.04	[84]
54[d]	$[Ch^{+}][Cl^{-}]$	Xylose	-	1.13	-	0.23	[104]
55[d]	$[Ch^{+}][Cl^{-}]$	Fructose	-	1.07	-	0.42	[104]
56[d]	$[Ch^{+}][Cl^{-}]$	Mannose / Xylose	-	1.11	-	0.33	[104]
56[d]	$[Ch^{+}][Cl^{-}]$	Fructose	-	1.10	-	0.52	[104]

		Glucose					
57	L(-)-menthol	Octanoic acid	-	0.39	0.85[c]	0.43	[103]
58	L(-)-menthol	Decanoic acid	-	0.35	0.84[c]	0.45	[103]
59	L(-)-menthol	Dodecanoic acid	-	0.37	0.79[c]	0.54	[103]
60	L(-)-menthol	Tetradecanoic acid	-	0.38	0.75[c]	0.50	[103]
61	L(-)-menthol	Hexadecanoic acid	-	0.38	0.71[c]	0.57	[103]
62	L(-)-menthol	Octadecanoic acid	-	0.38	0.68[c]	0.64	[103]
63	Thymol	Octanoic acid	-	0.67	1.10[c]	0.05	[103]
64	Thymol	Decanoic acid	-	0.71	1.11[c]	0.05	[103]
65	Thymol	Dodecanoic acid	-	0.75	1.05[c]	0.02	[103]
66	Thymol	Tetradecanoic acid	-	0.84	1.13[c]	0.02	[103]
67	Thymol	Hexadecanoic acid	-	0.87	1.11[c]	0.01	[103]
68	Thymol	Octadecanoic acid	-	0.94	1.10[c]	0.05	[103]
69	$[MEA^+][Cl^-]^g$	Ethylenediamine	1 : 1	1.18	0.94	0.73	[102]
70	$[MEA^+][Cl^-]^g$	Ethylenediamine	1 : 2	1.17	0.76	0.80	[102]
71	$[MEA^+][Cl^-]^g$	Ethylenediamine	1 : 3	1.15	0.65	0.82	[102]
72	$[MEA^+][Cl^-]^g$	Ethylenediamine	1 : 4	1.13	0.57	0.86	[102]
73	$[MEA^+][Cl^-]^g$	Diethylenetriamine	1 : 4	1.06	0.54	0.90	[102]
74	$[MEA^+][Cl^-]^g$	Tetraethylenepentamine	1 : 4	1.00	0.52	0.87	[102]
75	$[MEA^+][Cl^-]^g$	Pentaethylenehexamine	1 : 4	0.83	0.63	1.03	[102]
76	$[MEA^+][Cl^-]^g$	3-amino-1-propanol	1 : 1	1.15	1.02	0.58	[102]
77	$[MEA^+][Cl^-]^g$	3-amino-1-propanol	1 : 2	1.13	0.92	0.68	[102]
78	$[MEA^+][Cl^-]^g$	3-amino-1-propanol	1 : 3	1.09	0.89	0.74	[102]

79	$[MEA^+][Cl^-]^g$	3-amino-1-propanol	1 : 4	1.07	0.87	0.74	[102]
80	$[HMIM^+][Cl^-]$	Ethylenediamine	1 : 2	1.11	0.66	0.77	[102]
81	$[HMIM^+][Cl^-]$	Ethylenediamine	1 : 3	1.13	0.58	0.56	[102]
82	$[HMIM^+][Cl^-]$	Ethylenediamine	1 : 4	1.13	0.56	0.86	[102]
83	$[HMIM^+][Cl^-]$	Diethylenetriamine	1 : 4	1.08	0.53	0.90	[102]
84	$[HMIM^+][Cl^-]$	Tetraethylenepentamine	1 : 4	0.98	0.53	0.92	[102]
85	$[HMIM^+][Cl^-]$	Pentaethylenehexamine	1 : 4	0.91	0.55	0.94	[102]
86	$[HMIM^+][Cl^-]$	3-Amino-1-propanol	1 : 1	1.11	1.01	0.65	[102]
87	$[HMIM^+][Cl^-]$	3-Amino-1-propanol	1 : 2	1.11	0.93	0.67	[102]
88	$[HMIM^+][Cl^-]$	3-Amino-1-propanol	1 : 3	1.11	0.88	0.76	[102]
89	$[HMIM^+][Cl^-]$	3-Amino-1-propanol	1 : 4	1.08	0.88	0.72	[102]
90	$[N_{4444}^+][Br^-]$	3-Amino-1-propanol	1 : 2	1.08	0.27	0.88	[102]
91	$[N_{4444}^+][Br^-]$	3-Amino-1-propanol	1 : 3	1.08	0.32	0.85	[102]
92	$[N_{4444}^+][Br^-]$	3-Amino-1-propanol	1 : 4	1.02	0.39	0.90	[102]
93	$[N_{4444}^+][Br^-]$	Aminomethylpropanol	1 : 3	0.99	0.43	0.94	[102]
94	$[N_{4444}^+][Br^-]$	Aminomethylpropanol	1 : 4	0.98	0.46	0.89	[102]
95[f]	$[Ch^+][Cl^-]$	D-sorbitol	1 : 1	1.244	2.216	0.493	[35]
96[f]	$[Ch^+][Cl^-]$	Citric acid	1 : 1	1.373	2.248	0.714	[35]
97[f]	$[Ch^+][Cl^-]$	L-(+)-diethyl tartrate	1 : 1	1.770	2.118	0.840	[35]
98[f]	$[Ch^+][Cl^-]$	Zinc chloride	1 : 1	1.406	1.543	1.253	[35]
99[f]	$[Ch^+][Cl^-]$	Lactic acid	1 : 1	1.305	2.263	1.025	[35]
100[f]	$[Ch^+][Cl^-]$	Propanetriol	1 : 2	1.253	2.175	0.599	[35]
101[g]	$[Ch^+][Cl^-]$	Butanoic acid	1 : 2	0.945	0.775	0.514	[32]

102[g]	[Ch^+][Cl^-]	Butanoic acid	1 : 3	0.914	0.847	0.526	[32]
103[g]	[Ch^+][Cl^-]	Pentanoic acid	1 : 2	0.830	0.703	0.495	[32]
104[g]	[Ch^+][Cl^-]	Pentanoic acid	1 : 3	0.785	0.752	0.557	[32]
105[g]	[Ch^+][Cl^-]	Decanoic acid	1 : 2	0.421	0.667	0.853	[32]
106[g]	[Ch^+][Cl^-]	Decanoic acid	1 : 3	0.327	0.620	0.955	[32]
	Miscellaneous Solvents (water, organic solvents and ILs)			π^*[a]	α[a]	β[a]	Ref
107	Acetone			0.71	0.08	0.48	[97]
108	Water			1.14	1.23 [c]	0.49	[40]
109	Butanoic acid			0.47	1.06 [c]	0.22	[40]
110	Hexanoic acid			0.43	1.05 [c]	0.21	[40]
111	Octanoic acid			0.38	0.94 [c]	0.23	[40]
112	Glycerol			1.014	0.898	0.620	[33]
				0.956	0.882	0.658	[36]
113	Ethylene glycol			1.046	0.626	0.446	[33]
114	L(-)-menthol			0.42	0.53	0.66	[103]
115	Octanoic acid			0.30	0.91	0.14	[103]
116	Decanoic acid			0.27	0.86	0.17	[103]
117	Dodecanoic acid			0.25	0.85	0.26	[103]
118	Water			1.09	1.17	0.14	[103]
119	Ethanol			0.51	0.83	0.75	[103]
120	Methanol			0.58	0.93	0.66	[103]
121	Acetone			0.71	0.08	0.48	[103]
122	Heptane			-0.08	0.00	0.00	[103]

123	Cyclohexane		0.00	0.00	0.00	[103]
124	*o*-xylene		0.48	0.00	0.16	[103]
	Cation	Anion	π^{*a}	α^a	β^a	Ref
125	$[AMIm^+]^g$	$[Cl^-]$	0.298	2.189^b	0.830	[39]
126	$[BMIM^+]$	$[BF_4^-]$	1.046	0.626	0.446	[97]
127	$[Ch^+]$	$[Levulinate^-]$	1.00	1.07	1.03	[84]
128	$[Ch^+]$	$[Malonate^-]$	1.04	1.55	0.62	[84]
129	$[Ch^+]$	$[Glycolate^-]$	1.08	1.29	0.79	[84]

[a] π^* is the dipolarity/polarizability, α is the hydrogen bond acidity, and β is the hydrogen bond basicity

[b] The hydrogen bond acidity of DESs is measured via Hammett acidity function (H_o)

[c] The hydrogen bond acidity of DESs is measured via ^{13}C NMR and pyridine-*N*-oxide probe

[d] Kamlet-Taft solvatochromic parameters are measured at 323 K

[e] DESs 75-82 are 70 wt% aqueous solutions

[f] Kamlet-Taft solvatochromic parameters are measured at 313 K

[g] $[ATEAm^+][Cl^-]$: allyl triethyl ammonium chloride, $[AMIm^+]$: 1-allyl-3-methylimidazolium chloride, $[MEA^+][Cl^-]$: Monoethanolammonium chloride

[h] "-" corresponds to the values which have not been reported in literature

Table 3. List of E_{NR} polarity values for binary and ternary DESs as measured using nile red. For comparison, E_{NR} polarity values are also provided for water and select organic solvents and ILs.

No.	HBA	HBD	Relative ratio HBA : HBD	E_{NR}	Ref
1	$[Ch^+][Cl^-]$	Malic acid / Water	1 : 1 : 2	44.81	[37]
2	$[Ch^+][Cl^-]$	Glycerol / Water	1 : 2 : 1	49.55	[37]
3	β-alanine	Malic acid / Water	1 : 1 : 3	48.05	[37]
4	Proline	Malic acid / Water	1 : 1 : 3	48.3	[37]
5	$[Ch^+][Cl^-]$	Fructose / Water	5 : 2 : 5	49.81	[37]
6	$[Ch^+][Cl^-]$	Xylose / Water	2 : 1 : 2	49.81	[37]
7	$[Ch^+][Cl^-]$	Sucrose / Water	4 : 1 : 4	49.72	[37]
8	$[Ch^+][Cl^-]$	Glucose / Water	5 : 2 : 5	49.72	[37]
9	$[Ch^+][Cl^-]$	1,2-propanediol / Water	1 : 1 : 1	50.07	[37]

10	Glucose	Lactic acid Water	1 : 5 : 3	44.81	[37]
11	$[Ch^+][Cl^-]$	Sorbitol Water	5 :2 : 6	49.98	[37]
12	$[Ch^+][Cl^-]$	Xylitol Water	2 : 1 : 3	49.72	[37]
13	$[Ch^+][Cl^-]$	Xylose	2 : 1	50.69	[109]
14	$[Ch^+][Cl^-]$	Xylose	3 : 1	50.34	[109]
15	$[Ch^+][Cl^-]$	Glucose	1 : 1	50.43	[109]
16	$[Ch^+][Cl^-]$	Sucrose	1 : 1	49.72	[109]
17	$[Ch^+][Cl^-]$	Sucrose	4 : 1	50.16	[109]
18	Citric acid	Sucrose	1 : 1	49.72	[109]
19	$[Ch^+][Cl^-]$	Citric acid	1 : 1	47.97	[109]
20	$[Ch^+][Cl^-]$	Citric acid	2 : 1	48.30	[109]
21	$[Ch^+][Cl^-]$	Tartaric acid	2 : 1	48.13	[109]
22	Citric acid	Glucose	1 : 1	47.81	[109]
23	Tartaric acid	Glucose	1 : 1	47.73	[109]
24	$[Ch^+][Cl^-]$	1,2-propanediol	1 : 2	50.7	[34]
25	$[Ch^+][Cl^-]$	Glycerol	1 : 2	49.6 ~~49.29~~	[34]
26	$[Ch^+][Cl^-]$	Malic acid	1 : 1	46.9	[34]

27	[Ch^+][Cl^-]	Glycerol	1 : 1	50.91	[106]
28	[Ch^+][Cl^-]	Glucose	2 : 5	50.07	[106]
29	[Ch^+][Cl^-]	Xylitol	1 : 2	49.81	[106]
30	l-Proline	Glycerol	1 : 3	49.55	[106]
31	l-Alanine	Glycerol	1 : 3	49.82	[106]
32	l-Threonine	Glycerol	1 : 3	50.01	[106]
33	[Ch^+][Cl^-]	Diethyleneglycol	1 : 3	50.80	[56]
34	[Ch^+][Cl^-]	Triethyleneglycol	1 : 3	~~51.17~~ 50.92	[56]
35	[Ch^+][Cl^-]	Polyethyleneglycol (200)	1 : 3	~~49.15~~ 51.17	[56]
36	Citric acid	1,2-Propanediol	1 : 4	49.34	[107]
37	[Ch^+][Cl^-]	Urea	1 : 1	49.25	[107]
38	[Ch^+][Cl^-]	Glucose	5 : 2	49.29 [a]	[107]
39	[Ch^+][Cl^-]	Xylitol	4 : 1	49.25	[107]
40	*N*-methylmorpholine-*N*-oxide	Phenylacetic acid	1 : 1	50.93 [b]	[108]
41	*N*-dodecylmorpholine-*N*-oxide	Phenylacetic acid	1 : 1	52.01 [b]	[108]
42	*N*,*N*-dimethyldodecyl-*N*-amine oxide	Phenylacetic acid	1 : 1	52.29 [b]	[108]

	Miscellaneous Solvents (water, organic solvents and ILs)		E_{NR}	References
43	Water		48.20	[56]
			48.21	[37]
44	Diethyleneglycol		51.18	[56]
45	Triethyleneglycol		51.55	[56]
46	Polyethyleneglycol (200)		51.71	[56]
47	Methanol		51.80	[106]
			51.89	[37]
48	70% Ethanol		50.83	[107]
	Cation	Anion	E_{NR}	References
49	$[BMIM^+]$	$[BF_4^-]$	51.42	[109]
50	$[BMIM^+]$	$[PF_6^-]$	52.22 [b]	[108]

[a] DES contains 30% water

[b] The E_{NR} values are calculated in this review article from the reported λ_{max} (nm) of Nile Red [108], by using equation 11