Metal-Free Deep Eutectic Solvents: Preparation, Physical Properties, and Significance

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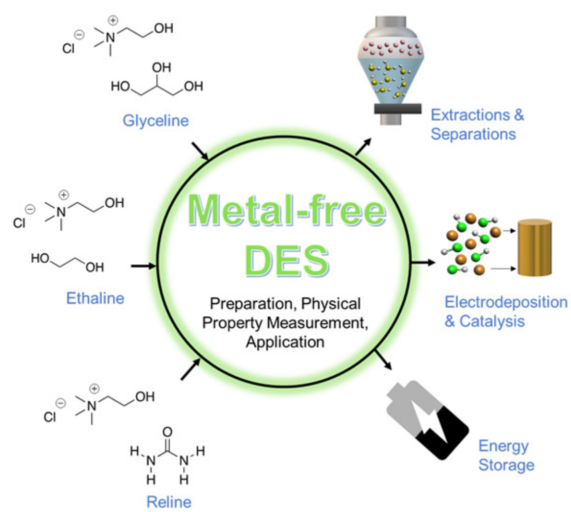


Abstract

In the past decade, reports detailing the preparation, characterization, and application of deep eutectic solvents (DESs) have grown in number significantly, showing signs of increased interest and attention. Indeed, these systems provide tunable polar environments attractive for their ease of synthesis and lack of need for purification. DESs are homogeneous systems composed of two or more components having a depressed melting point compared to either constituent material. As interest and application of DESs grow, the need for a common understanding of their preparation and characterization is required. In this perspective, we discuss metal-free DESs, focusing on their preparation, characterization of physical properties, and considerations for their application. We highlight inconsistencies or omissions in literature reports, as well as factors for researchers to consider when investigating these systems.

Deep eutectic solvents (DESs) are a relatively new class of liquids that have emerging interest for many chemical,[1] catalytic,[2-3] and separation processes,[4] including electrochemical energy storage.[5] Since coinage of the name DES in 2001 by Abbott et al.,[6] fundamental properties and applications of these systems have been investigated. A search on the Web of Science with the keyword "deep eutectic solvent" yields about 3,035 publications with total citations of about 54,014 (as of June 24, 2019), clearly showing a trajectory for continued growth and interest (**Figure 1**). The term "DES" has been used freely and widely to describe eutectic mixtures. As with all eutectics, DESs are mixtures of two or more components that have a melting point (mp) lower than either constituent material. However, eutectic and deep eutectic mixtures are distinct in that DESs have a eutectic point significantly below that of an ideal mixture, as established by a solid-liquid phase diagram. The constituent materials of DESs, their ratio, and purity (e.g., water content) dictate not only the mp, but other physical properties such as viscosity and conductivity, and thus enable tailoring of DESs for specific applications.

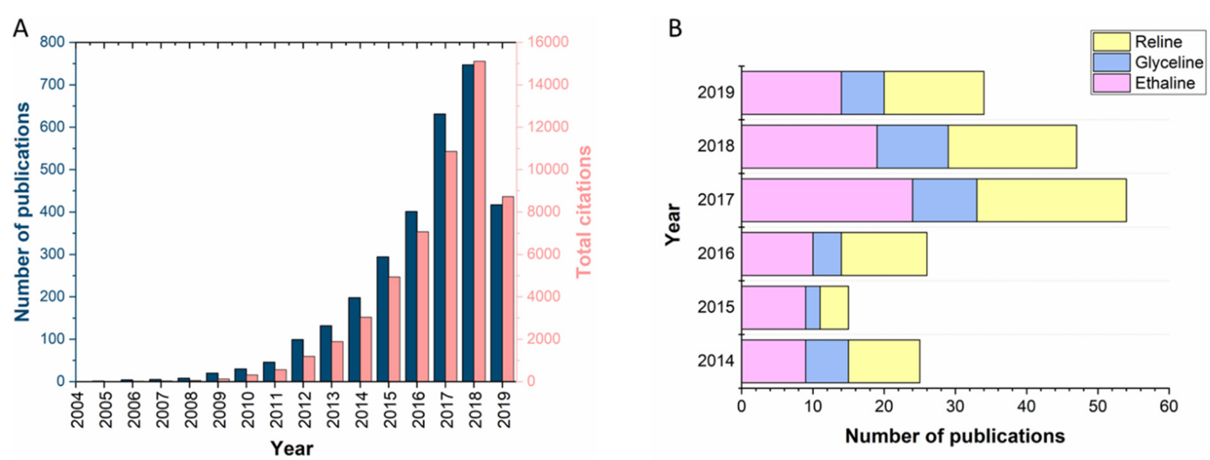


Figure 1. A) Number of publications and total citations for "deep eutectic solvent" by year; B) Number of publications for "reline," "ethaline," and "glyceline" along with the keyword "deep

eutectic solvent" by year for the last five years. Data collected from Web of Science on June 24, 2019.

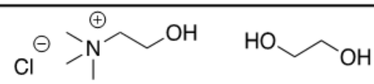
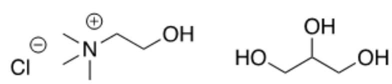
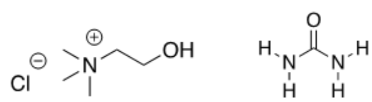
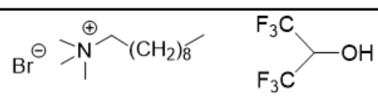
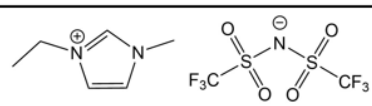
DESs are widely likened to ionic liquids (ILs), and at times considered an "environmentally friendly" sub-category, although the "green-ness" of a DES is dependent on the constituent materials. Modern ILs are salts that melt below 100 ˚C, which is an arbitrary temperature to differentiate ILs from molten salts.[7-9] Parallels are often drawn between DESs and ILs due to the similarity of their properties:[6] a wide liquidus range, high viscosity, low-to-negligible volatility, and high thermal stability. In contrast to ILs, the constituent components of a DES are not necessarily ionic. Additionally, the preparation of a DES is 100% atom economical, producing no byproducts and requiring no purification.[10] Varying the constituent materials of a DES allows the tailoring of the polar environment, enabling novel materials and innovative processes.[11-12]

DESs can be broadly separated into two categories: those that contain a metal salt and those that do not. DESs that contain metal salts can be further categorized depending on whether the metal salt is hydrated or not, following a system set forth by Smith, Abbott, and Ryder in a 2014 review.[13] "All organic" DESs, or those without metal salts, are comprised of a halide salt or hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD), mixed together to form a homogeneous system with a mp below that of an ideal mixture. As such, a vast number of DESs with a wide variety of properties can be prepared using common, commercially available compounds.[13] Metal-free DESs have been formulated from HBDs like polyols, carboxylic acids, and sugars[14] and HBAs like ammonium salts, phosphonium salts[15], and viologens[16]. While some

DESs have been known and investigated for over a decade[17], recent reports have detailed new DESs for bio-applications[18] and those composed of redox active components with potential application in flow batteries[16, 19] and two-phase aqueous DESs for use in extraction of organics such as anthraquinones.[14, 20]

In this perspective, we discuss methods to prepare and characterize metal-free DESs, focusing on ethaline, glyceline, and reline. **Table 1** shows the chemical structures and summarizes the essential physical properties of these three DESs: ethaline (2:1 ethylene glycol:choline chloride), glyceline (2:1 glycerol:choline chloride), and reline (2:1 urea:choline chloride). Each of these DESs contain the same HBA, choline chloride (often abbreviated ChCl), but differ in HBD. These DESs are among the most commonly investigated in literature and a wide variety of data on these systems is therefore available. The selected DESs demonstrate the ability to tune physical properties by the type (-OH *vs* $-NH_2$) and number of functional groups (2 –OH in ethylene glycol *vs* 3 –OH in glycerol). Additionally, their favorable properties like low viscosity when compared to other DESs (e.g., those based on phosphonium salts[15]), make ethaline, glyceline, and reline a good case study for this perspective. Morevover, metal-free DESs are chosen due to the availability of their constituent components and ease of handling without change in oxidation state, as most metal salts undergo during heat treatment in preparation of DESs. We write this perspective to provide a roadmap for researchers interested in exploring the preparation, physical properties, and application of metal-free DESs. Many reports detailing the use of these DESs are vague when describing preparation procedures and many simply state that the components were mixed together until a clear and transparent liquid was obtained, and then used without further characterization. Given that variables like water content can affect physical properties, we propose standards for the preparation and characterization of metal-free DESs.

Table 1. Chemical composition, melting point, density, viscosity, and ionic conductivity of the three common DES systems ethaline, glyceline, and reline.[10,13] All three DESs have a 2:1 molar ratio of choline chloride (ChCl) to HBD. For comparison, the structure and properties of an additional DES, DeTAB-HFIP[20], and representative IL, [EMIM][TFSI][21], are given. Reported densities, viscosities, and ionic conductivities are at 25 °C.

	Structures	Mp (˚C)	Density (g/cm^3)	Viscosity (cP)	Ionic Conductivity (mS/cm)
Ethaline		-66	1.12	36 – 52	7.61
Glyceline		-40	1.18	259 – 376	1.05
Reline		12	1.25	632 – 750	0.75
DeTAB-HFIP*		-25	1.28	40	----
[EMIM][TFSI]		-16	1.52	36	9

*DeTAB-HFIP: decyltrimethylammonium bromide (HBA) and hexafluoroisopropanol (HBD) in 1:2 molar ratio

Compared to traditional synthetic chemistry, such as that used to produce ILs, the preparation of DESs is relatively simple, only requiring mixing components and heating for a short time. Thus, DESs are prepared, not synthesized, producing no byproducts. For example, ethaline is prepared by combining a 2:1 molar ratio of EG:ChCl and heating until a transparent liquid is obtained (within few minutes for small gram-scales). To ensure reproducibility and consistent properties, the purity and water content of the components should be considered, as well as the environment in which the DES is prepared and stored. Ideally, high purity compounds are dried before use to remove absorbed water, then mixed together and heated under an inert atmosphere, such as an Ar-filled glove box or a flask under an inert atmosphere (i.e., prepared using Schlenk technique).[2,3] Across the protocols reported for the preparation of ethaline, the level of detail with respect to materials and technique varies widely,[2] with many reports providing little-to-no detail on the drying of components or the water content of the DESs produced.

HBAs tend to be more hygroscopic than HBDs, though both compounds may require drying before use.[2] If ChCl (or other HBA) is used as received (no additional drying or purification),[5] the resulting DES often has a relatively high and/or inconsistent water content (>2,000 ppm vs. <100 ppm), likely dependent on the relative humidity of the lab. Solids that are not prone to sublimation, such as ChCl and urea, can be dried under reduced pressure, heating at <120°C. Alternatively, if impurities in addition to water are present, the solid can be recrystallized, isolated by vacuum filtration, and then dried.[3,4] Most commonly, EG with a low water content is purchased and used as received; it cannot be easily dried under reduced pressure due to its volatile nature but can be dried by storage over activated molecular sieves.[2,6] Once the components of the DES have been purified and dried, they are then combined and agitated using a magnetic stir bar while heating (typically between 60°C and 100°C).[1-7] The time reported for heating varies widely, with some reporting heating "until a colorless, homogenous liquid is obtained" while others report specific heating times (for ethaline, typically 30 minutes to 2 hours at 80 °C). Additionally, some reports detail drying the prepared DES in a vacuum oven[8] or storing over activated molecular sieves.[6] Molecular sieves are preferred to vacuum oven drying, as reduced pressure can lead to a change in DES composition[6] by evaporation of volatile components before a stable DES is obtained.

An interesting phenomenon our groups have observed during the preparation of the DES ethaline is the formation of long, thin crystals after cooling the mixture to room temperature. We have not observed this with glyceline or reline. Analysis of these crystals by single crystal X-ray diffraction (XRD) reveals they are composed of alpha phase ChCl (CCDC Number: 1937745).[22] The formation of crystals is more frequently observed if the EG/ChCl mixture is heated at too low of a temperature or for too short of a time (e.g., heated to 50 °C or for only 10 minutes). Interestingly, crystals disappear when the mixture is re-heated for an appropriate amount of time, and do not re-form upon slow cooling to room temperature. Ibrahim et al.[23] reported formation of solid precipitates in solutions of EG and ChCl mixed in a molar ratio of 1:1 (i.e., not at the DES composition), though we are not aware of published reports disclosing crystal formation during preparation of ethaline itself (1:2 molar ratio). We hypothesize that the formation of ChCl crystals is due to incomplete homogenization of the EG and ChCl, thus leading to ChCl-rich domains which, upon cooling, expel EG leading to ChCl crystallization. Thus, to prepare ethaline (a homogeneous mixture of ChCl and EG), researchers are suggested to heat a stirring solution to 80 °C for 2 hours, and reheat if crystals are observed.

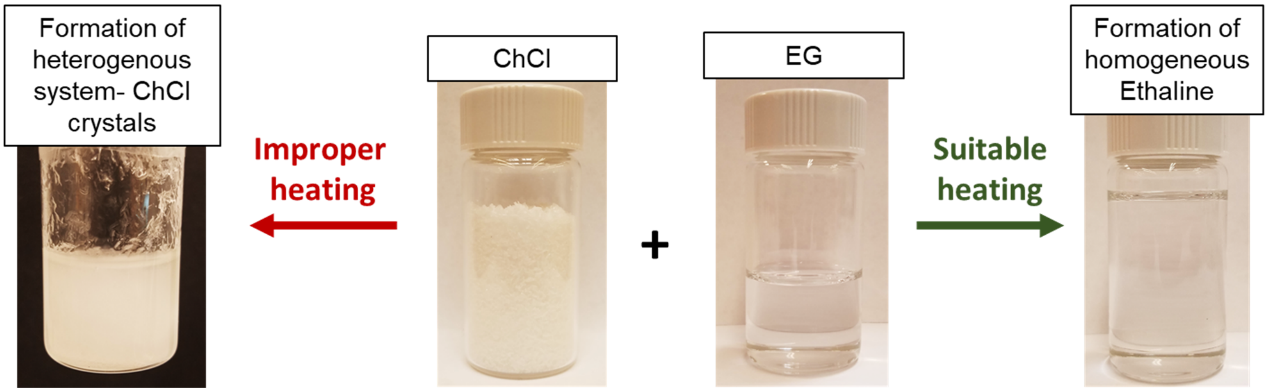


Figure 2. Preparation of the DES ethaline: dried choline chloride (ChCl) and ethylene glycol (EG) are mixed together in a controlled atmosphere (Ar-filled glovebox), heated to 80 ˚C for 2 hours, then cooled to room temperature. Improper heating can lead to formation of choline chloride crystals (i.e., precipitation from solution).

One of the most exciting prospects of DESs is their tailorable physical properties based on HBA or HBD structures and composition. For example, the DES of ChCl and malonic acid has a viscosity of 721 cP and ionic conductivity of 0.55 mS/cm, whereas a DES of ChCl with EG (ethaline) has a viscosity of only 36 cP and ionic conductivity of 7.61 mS/cm (at 25 ˚C).[13, 24] Physical properties of ChCl-based DESs are believed to be primarily governed by hydrogen bonding and charge delocalization. Computational[25-27] and spectroscopic techniques[28] have provided insight into dynamics and structural interactions in these complex fluids. While charge spreading does occur in DESs with ionic species, it remains unclear if the deep eutectic melting point originates from charge delocalization via H-bonding.[27] Abbott and co-workers suggested that changes in entropy might cause the melting point depression seen in DESs.[29] Biswas and co-workers performed a series of experimental and theoretical research on DESs to examine intermolecular H-bonding and the impact of charged components on relaxation dynamics.[30-35] These studies showed that

DESs containing ionic species are spatially and temporally heterogeneous while those consisting of uncharged components are homogenous. Very recently, these heterogeneities have been confirmed by 2D infrared spectroscopy[36] and scattering techniques.[26] DES nanostructure and dynamics (e.g., ionic interactions and H-bonding) have been probed by neutron techniques including quasi-elastic neutron scattering and neutron diffraction.[37-40] Despite increasing interest, molecular-level structures of DESs have not been thoroughly explored to link structure to physicochemical properties. To encourage the collection of quality data to establish the structure-property relations (i.e., so comparisons between different studies can be made), we summarize the basic characterization methods below.

The 100 % atom economy of DES preparation means DESs are typically not purified. Thus, common chemistry characterization techniques like nuclear magnetic resonance spectroscopy (NMR) or mass spectrometry are not performed. However, some researchers have used infrared spectroscopy to probe hydrogen bonding[41-42] and used thermal gravimetric analysis (TGA) to probe thermal stability.[43] As such, most characterization of DESs has centered on physical properties of density, viscosity, and melting point. Additional properties like polarity, surface tension, ionic conductivity, and electrochemical window have also been investigated but to a lesser extent. In this section, we focus on techniques used to characterize these properties and provide guiding principles for sample preparation and handling, as summarized in **Table 2**.

Table 2. Overview of the techniques used to characterize the physical properties of DESs and considerations for sample preparation and evaluation.

Property	Measurement Technique	Notes
Phase transformations	Thermal Gravimetric Analysis (TGA)	Requires a few drops of sample (e.g., 5 mg); used to determine thermal stability which defines the max working fluid temperature
	Differential Scanning Calorimetry (DSC)	Requires a few drops of sample (e.g., 5 mg); used to determine temperature of glass transition (T_g), crystallization (T_c), and melting (T_m). Crystals and melts may co-exist in the same temperature range. Attention should be given to the control of temperature: confirm that heating/cooling ramp is maintained by the instrument.
	Temperature bath	Requires >0.2 g of sample; Used to approximate mp
Density	Vibrating U-tube densitometer; pycnometer	Sample size is ~1 mL. Liquid should be free of air bubbles.
Rheology	Parallel plate or cone & plate rheometer	Sample size varies depending on plate and gap sizes (~ 1 mL)
	Falling ball viscometer	1 – 1.5 mL sample
	Microfluidic channel	Sample size is about 100 µL, eliminates air exposure
Ionic conductivity	2-probe or preferably 4-probe conductivity cell with fixed high frequency measurement by a conductivity meter; electrochemical impedance spectroscopy (multiple frequency option)	Sample size varies (500 µL to 5 mL).
Electrochemical stability	Cyclic voltammetry (CV), linear sweep voltammetry	Sample size varies depending on the electrochemical cell; screen printed cells (a drop) to glass cell vials (500 µL to 5 mL).
Surface tension	Capillary, Wilhemy plate and pendant drop methods	Sample size varies depending on the method chosen: drop size (pendant drop method) to 1 mL (Wilhelmy plate)
Polarity	Broadband dielectric spectroscopy (BDS) gives dielectric constant; UV-Vis with Reichardt’s dye 30 (Kamlet-Taft parameters)	BDS requires a minimum amount (few drops), UV-Vis method requires the filled cuvette (~3 mL)

Characterization of the mp (or freezing point (fp)) of a DES is important as it distinguishes DESs from normal eutectics; however, many reports do not provide this data. The ideal method for determining the mp of a DES is differential scanning calorimetry (DSC), as only a small amount of sample (~ 5 mg) is required. In an inert environment, the DES is put into an oxide-free hermetically sealed aluminum pan (achieved by heating Al pans to >330 ˚C). The sample is either cooled to liquid nitrogen temperature and then heated, or heated to well below decomposition temperature then cooled, using temperature change rates of 1 - 20 ˚C/min. Of note, if the DSC instrument is not able to accommodate fast heating/cooling rates (e.g., 20 ˚C/min), a slope or step in the baseline DSC curve occurs. In the DSC profile, T_m and T_c are observed as endothermic and exothermic peaks, respectively, while the T_g is observed as an inflection point on a heat versus temperature plot. DES phase transformations can be complex and crystals may melt as they form which may result in overlapping exothermic and endothermic peaks in the DSC trace. An example of a rarely reported DSC curve can be found in a study by Morrison et al. [44] where the thermal behavior of eutectic mixtures of ChCl + malonic acid and ChCl + urea (i.e., reline) were studied. While crystallization and melting were observed for reline, they reported that no nucleation was captured by DSC in the case of ChCl + malonic acid DES. They attributed this to the high viscosity and rapid formation of eutectic melt. As the required thermal window may not be available on all DSC equipment, alternative methods like salt baths can be used to approximate mp.[45] In this approach, two salt baths with temperatures that bracket the expected mp of the DES are used such that solidification is observed in one bath, but not the other. For example, for ethaline (reported mp of -66 ˚C) solid is not observed in a chloroform/liquid nitrogen bath (-63 ˚C), but is observed in an acetone/liquid nitrogen bath (-68 ˚C). With this method, the sample should be prepared and sealed in an inert environment, the salt baths should be properly prepared, and appropriate time allowed for equilibration.

The most commonly reported physical properties of DESs are density and viscosity, which impact potential application. Densities of most metal-free DESs are higher than water, and in most cases higher than that of the neat HBD, which is the majority component. This is often explained by hole theory[46] which predicts vacancies within the molecular organization of DES. Density can be accurately measured (± 0.0005 g/cm^3) with vibrating-tube densitometers:[47-48] a U-shaped tube inside a temperature control unit is filled with a small volume of sample, ~ 1 mL, ensuring the sample is free of bubbles. The ends of the tube are fixed and vibrated with a piezoelectric element, with the instrument measuring the frequency which is related to the DES density by modeling the system as a mass and spring. Viscosities of most DESs are >100 cP at room temperature[10] as a result of the extended H-bonding network. Viscosity can be measured with a variety of viscometers or rheometers, all of which rely on a well-defined fluid flow profile.[49] In these systems, fluid is forced to flow in a known profile while the instrument measures the resulting shear stress or pressure drop; this is then related to viscosity through different empirical relations depending on the exact flow conditions. To obtain reproducible results, the water content of the DES should be reported and exposure to air should be prevented since most DESs are hygroscopic.

Reported ionic conductivities for metal-free DES are typically 0.1 – 10 mS/cm at 25 ˚C. Conductivity is commonly measured by electrochemical impedance spectroscopy (EIS) with a two electrode cell in combination with a potentiostat equipped with a frequency response analyzer.[50] Complex impedance is measured by applying a potential wave with a small voltage amplitude at various frequencies. Solution resistance, *R*, is generally accepted to be the intercept of the EIS spectra on the real impedance axis of a Nyquist plot from which conductivity, k, can be calculated as: $k = C/R$ where C is the cell constant that is obtained by measuring a standard electrolyte with known conductivity.[51,52]

DESs usually have wider window of electrochemical stability than aqueous electrolytes and narrower than ILs. Electrochemical window (EW) can be determined with slow scan cyclic voltammetry (CV) using a potentiostat and an electrochemical cell.[53-54] The cell usually consists of three electrodes; working (e.g., Pt), counter (e.g., glassy carbon), and reference. The choice of electrode materials may influence EW with carbon inert electrodes able to acccess wider EWs compared to metal working electrodes. The area of the counter electrode should be at least two times larger than the area of the working electrode to ensure a uniform current distribution and the reference electrode should be carefully chosen to provide reproducible results. A silver/silver chloride reference electrode is common for DESs containing ChCl.[55] Alternatively, an internal reference such as ferrocene (Fc/Fc^+ redox couple) can be used.[56]

Similar to viscosity, surface tension is related to intermolecular interactions in DESs. While surface tensions of DESs are seldom measured, reported values are similar to some imidazolium-based ILs, e.g., 49 – 56 mN/m at 25 ˚C for ethaline, glyceline, and reline.[10] The pendant method can be used to determine surface tension by utilizing an optical contact angle tensiometer equipped with imaging capability.[57] With the geometry of the DES drop at the needle tip and application of the Laplace-Young equation, surface tension can be determined. Predictive methods have also been developed that can reasonably estimate surface tension within 3 to 6 %

error.[58] Polarity is an indicator of solvent strength and thus an important property for specific applications, e.g., separations. DESs are expected to be dipolar in nature, and thus UV-Vis spectroscopy and solvatochromic optical spectroscopic probes such as Reichardt's betaine dye (no. 30), pyrene, Nile red, and coumarin 153 are well suited to study their polarity. Probe-dependent dipolarities are dominantly controlled by the HBD component of DES.[59] To rank DES polarities and thus understand their different environments, choice of solvatochromic probe must be consistent.

The hygroscopic nature of DESs necessitates handling under inert atmosphere, as even storage in a non-air-free vial leads to an increase in water content of 10 wt% or higher. Water is significantly less viscous than ethaline, so even a small amount can drastically affect the physical properties of the DES. **Figure 3** shows the differences in dynamic viscosity of ethaline as a function of temperature with varying water content: published works with reported water content (145, 410, and 600 ppm), published works with un-reported water content, and two samples from our lab with known water content (100 and 1000 ppm). Measured viscosity of ethaline samples at 313.15 K are given in the legend of **Figure 3**. In general, viscosity values for ethaline with 100 ppm water match closely with those of Barrado et al.[6] (145 ppm water), and higher water content yields lower viscosities (compare Gajardo-Parra et al. (410 ppm) [2] and Harafi-Mood et al.[3] (600 ppm)). Our sample with the highest water content (1000 ppm) consistently had lower viscosity compared to samples with lower water content, though differences are smaller at higher temperatures.

At higher temperatures, the impact of water is less pronounced due to increased molecular motion which dominates intermolecular interactions between the HBD, HBA, and water. Across the temperatures measured, viscosity exponentially decreases with increasing temperature for most studies, as expected. A notable exception is reported by D'Agostino et al.[9], illustrating a more linear trend. While the reason for this discrepancy is unclear, the water content of the sample is not reported, nor are the handling/storage conditions, or experimental procedure for measuring viscosity.[9] From **Figure 3,** it can also be gleaned that systems with no reported water content have viscosity values that vary widely from the samples with reported water contents. As such, we emphasize that the water content of DES should be reported and special care should be taken to prevent changes water content to ensure accurate physical property determination.

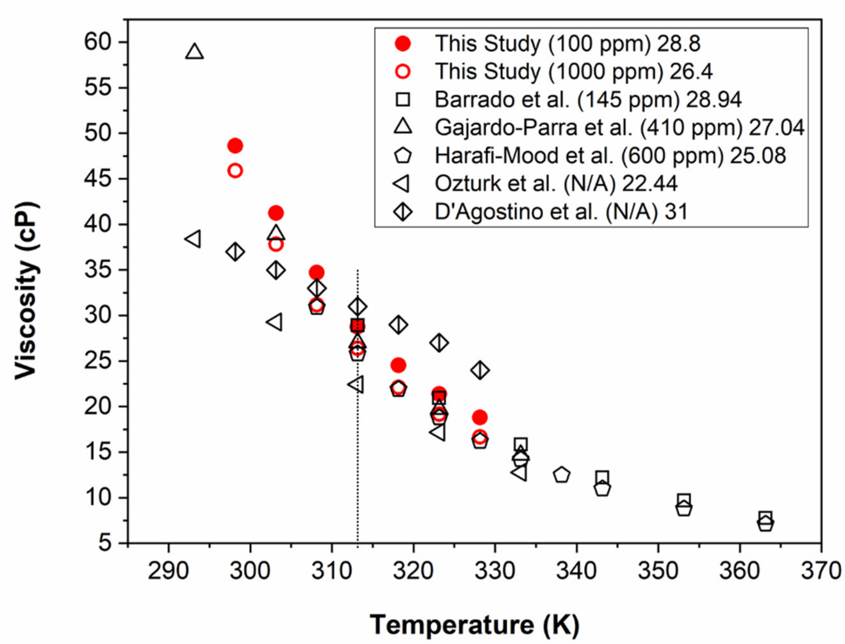


Figure 3. Viscosity of ethaline as a function of temperature. Numbers in the legend text are the viscosity of a sample at 313 K in units of cP as indicated by the dashed line.

While DESs show promise in various applications, their full potential has not been recognized in most cases since a concrete understanding of their physical, transport, and electrochemical properties is currently not available. **Table 3** summarizes particular DES properties that make them attractive for different uses. Most applications clearly take advantage of the low vapor pressures, suppressed or non-flammability, and wide liquidus range of DESs. Additionally, solvation strength is among the most appreciated traits of DESs as it allows solvation of various solutes in high concentrations. We believe metal-free DESs will find broad utility especially in biocatalysis where enzymes show great stability in DESs[60], gas separations[4] where high solubility of CO_2 can be obtained, and redox flow batteries[5, 61] in which electrolyte energy density can be increased by developing DESs formed from redox active HBAs or HBDs or with redox active additives.[16, 19]

Table 3. Significance of DES properties for specific applications

Application	DES property of most interest	Examples
Catalysis	• Solvation strength • Recyclability of DES by liquid-liquid extractions • Lowered reactivity by H-bond network towards enzymes in biocatalysis	○ Acid-catalyzed dehydration of hexoses to 5-hydroxymethylfurfural[62] ○ Catalytic conversion of lignocellulosic biomass[63-64]
Drug solubilization	• Solvation strength • Low toxicity	○ Dissolution of several poorly soluble drugs (i.e., benzoic acid)[44] ○ Solvents for nucleic acids (DNA, RNA reversible secondary structures)[65]
Material synthesis	• Low/negligible vapor pressures • Thermal decomposition pathway • Liquid heterogeneity	○ Ionothermal synthesis of aluminophosphate and organophosphonate materials[66]
Extractions	• Low/negligible vapor pressures • Solvation strength	o Starch extraction from plants ○ Various micro extraction techniques possible[67]
Gas separations	• Density and free volume for gas solubility	○ CO_2 and SO_2 capture from flue gas[4, 68]

Electrochemical energy storage (i.e., flow battery)	• Electrochemical stability • Conductivity & viscosity • Solvate structure and coordination strength • Solubility of redox active species • Suppressed flammability	○ All-iron redox flow battery in ChCl+EG[69], hybrid-ion flow batteries[70] ○ Ferrocene[71] in metal-free DES and redox-active DES based on viologens in EG or malonic acid[16] ○
Other electrochemical processes	• Solvation strength • Electrode-electrolyte interface	○ Electrodeposition of conductive polymers for sensing[72] ○ Electrochromic devices[73]

The field of DESs is relatively young, yet the diversity of chemical structures provides an exciting landscape for researchers to explore from fundamental property evaluation to application in various processes. Metal-free DESs are particularly attractive due to their simplicity (readily available, abundant components, ease of preparation) and prospects for greener, all-organic electrolytes. The major benefits of metal-free DESs include the atom efficiency of preparation, accessibility of starting materials, and most importantly, the ability to access different polar environments simply by varying composition. Inconsistent preparation and characterization methods currently limit the full exploration of these DESs. Foremost, fundamental structure-property relation understanding of DESs must be built. To date, data scarcity and the complexity of molecular interactions in DESs have hampered efforts to connect their structure to function. These systems are further complicated by piecemeal and incomplete data reported in literature. Consistent standards must be established for the preparation of DESs, including heating method, storage conditions, baseline characterization, and purity and water content of constituent components. This ensures trends between studies can be identified and established.

Metal-free DESs have great potential due to their tunability allowing for possible advances in applications[10] like separations, catalytic synthesis, and various electrochemical processes including electrodeposition[74-76] and electrochemical energy storage[5, 19] otherwise not possible with traditional solvents. For electrochemical processes, the electrode-electrolyte interfacial structure, solvate structure, and solvation strength play an important role in electron transfer kinetics. Taking a cue from the existing body of literature on ILs near electrode surfaces, the interfacial structures of DESs are expected to be similarly complex, since the ionic component of DESs are not point charges. Therefore, DES behavior at electrode-electrolyte interfaces cannot be described by classical theories that are applicable to ideal, aqueous electrolytes. Interfacial studies on ILs suggest that a complex re-arrangement of ions occurs near electrified interfaces driven by potential, adsorption-desorption hysteresis, and slow restructuring.[77] This phenomenon has been investigated by X-ray reflectometry,[78-79] atomic force microscopy,[80-81] surface force measurements,[82-83] and various spectroscopy techniques including sum frequency generation,[84-85] surface enhanced infrared spectroscopy,[86-87] and surface enhanced Raman spectroscopy.[88-91] While there is some consensus about the existence of alternating ion layers in ILs near the electrode surface, the extent of ordering remains unclear. Conventional electrochemical techniques traditionally applied to aqueous systems to study electron transfer kinetics must be reevaluated for DESs. Dai et al.[55] recently highlighted the importance of IR compensation and use of reliable reference electrodes when carrying out polarization experiments in resistive electrolytes such as DESs. For aqueous electrolytes, the breakdown species produced as a result of an applied potential are simply hydrogen and oxygen gas, yet the breakdown species of DESs are not known. Fundamental studies investigating the relation between interfacial DES structure, solvate structures, and redox kinetics are almost non-existent and are crucial for wide spread adaptation of DESs in electrochemical devices. With standardized procedures and tools for preparation, storage, and characterization of metal-free DESs in hand, their unique polar environments will ensure transformative advances are made in, for example, safe and efficient flow batteries, difficult and dangerous chemical separations, and efficient and selective chemical catalysis reactions, among other systems.

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