

Eutectic mixtures based on polyalcohols as sustainable solvents: Screening and characterization

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Abstract

Despite some promising potential applications of eutectic systems containing choline chloride and a polyalcohol, a detailed investigation of the thermodynamic behavior of these systems is still missing. In this work, the solid-liquid equilibria phase diagrams of binary systems containing choline chloride, and one from six different polyalcohols (ethylene glycol, 1,3-propanediol, glycerol, *meso*-erythritol, xylitol and sorbitol), were measured in the full composition. Excepting the mixtures with glycerol or ethylene glycol a quasi-ideal behavior in the [Ch]Cl solubility curve is observed. In the polyalcohol solubility curve, the mixtures present small negative deviations from ideality, excepting [Ch]Cl+ethylene glycol, which is slightly positive. The solid–liquid phase diagrams show a large liquidus composition window, and not a fixed stoichiometry for the eutectic points, where the mixtures can be used as solvents close, or below, room temperature. Aiming at their application, viscosities and densities were measured at the eutectic point in the temperature range from 278.15 to 373.15 K. All systems present densities and viscosities higher than water, which are directly related to the strong interactions between the components. Solvatochromic parameters were measured to characterize the solvents and they show how to achieve solvent tunability by varying the polyalcohol mole fraction.

Keywords: Eutectic solvents, solid-liquid equilibrium, phase diagrams, density, viscosity, solvatochromic parameters.

Introduction

Over the years, volatile organic compounds have been widely used as solvents. These are mainly composed of low molecular weight petrochemical derivatives and alcohols, which show often drawbacks such as volatility, flammability, toxicity, and in many cases, poor biodegradability.¹ In the last decade, the concept of sustainable development has impacted different industries and the way of thinking processes and methods, especially due to the properties of the solvents used. Alternative solvents such as ionic liquids, supercritical fluids, and biomass-based solvents, among others, have been sought.^{2,3} However, these also present several drawbacks regarding the large-scale use, such as their thermal and chemical instability, high cost, advanced equipment requirements, and/or life-cycle assessment. In this sense, the replacement of traditional organic solvents is crucial, and mixtures of natural compounds have emerged as a green sustainable alternative. The potential solvent character of eutectic and deep eutectic solvents (ES and DES, respectively) have been investigated as an alternative to conventional organic solvents due to their promising properties and industrial applications.^{4,5} The possibility of having solvents of lower viscosity at room temperature, or relatively low operating temperatures, led researchers to investigate different combinations of hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD) as constituents of ES.⁶

Regarding the interest of the industrial and scientific communities for new greener solvents, the eutectic systems present several advantages: low toxicity, high biodegradability, negligible volatility, and can be considered as having less impact on the environment than other solvents.^{1,6} However, the green character of any eutectic mixtures relies on the use of environmentally friendly components. These include non-toxic quaternary ammonium salts as HBA and HBD such as amines, sugars, alcohols, sugar alcohols, polyalcohols, and organic acids.^{4,7}

One of the most ubiquitous HBA is choline chloride ([Ch]Cl), an essential nutrient and additive in animal feed. Mixtures containing [Ch]Cl are generally biodegradable. Being a strong HBA presenting a relatively small (4300 J mol^{-1})⁶ melting enthalpy, it usually shows a very steep solid-liquid equilibrium curve.⁸ On the other hand, polyalcohols are widespread materials derived from natural sources presenting non-corrosive and non-toxic characteristics and are often used as HBD.¹¹ Among them, glycerol and ethylene glycol (EG) are widely studied due to their ability to form liquid mixtures in a large composition range namely with choline chloride, or urea.¹⁰⁻¹⁴

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3 Sustainable ES composed of cheap biodegradable polyalcohols and choline chloride have been
4 commonly used in DES formulations, as they allow numerous applications namely on
5 chemical, pharmaceutical, and material fields. These eutectic solvents were proposed as
6 extraction media for azeotropic mixtures,¹⁵ to extract flavonoids as well as purification agents
7 of biodiesel.¹⁶ In this respect, Abbott and co-workers¹⁶ reported glycerol-based DES as an
8 efficient extraction media for glycerol from biodiesel based on rapeseed or soybean oil, while
9 Hayyan et al.¹⁷ showed that a cheap quaternary ammonium-salt can be successfully used as a
10 solvent to extract the glycerol from palm oil-based biodiesel in a continuous separation process.
11 In the pharmaceutical area Morrison et al.¹⁸ used ethylene glycol-based DES to increase the
12 solubility of very low water solubility compounds favoring bioavailability in early drug
13 development studies. Shekaari et al.¹¹ studied the effect of using choline chloride/ethylene
14 glycol, or glycerol, as co-solvents on the acetaminophen solubility enhancement, showing that
15 interactions with acetaminophen became stronger by increasing the DES concentration.¹¹
16 Additionally, polyalcohols and their eutectic mixtures have been proposed as potential phase
17 change materials substitutes,^{19,20} which are an important class of modern materials that
18 contribute to the efficient use and storage of energy in processes such as solar thermal,
19 industrial waste heat recovery and thermal management of electronics.

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34 When selecting eutectic systems, many authors tend to study only fixed stoichiometric mole
35 ratios and report those at which the mixtures are visually liquid at room temperature.^{4,5,14}
36 However, to select the appropriate molar ratio of the ES components, and the operating
37 temperature for a specific application, the solid-liquid equilibria (SLE) phase diagrams must
38 be known,⁸ but very seldom in studies on eutectic systems the SLE phase diagrams were
39 characterized. Additionally, the physicochemical characterization of the resulting mixture is
40 also poor. Among the studies available in the literature involving eutectic mixtures of [Ch]Cl
41 and polyalcohols, only Abbott and co-workers¹⁶ have measured the SLE phase diagram for the
42 system [Ch]Cl+glycerol. This was later complemented with an extensive study of the
43 physicochemical properties of that system by the same group.¹⁴ It was shown it could be used
44 effectively at room temperature,¹⁶ in spite of its high viscosity¹⁴ that could be a limitation to
45 some applications of this solvent at an industrial scale.

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The number of applications and the performance of these mixtures can be enhanced and
optimized by an *a priori* knowledge on the phase equilibria and thermodynamic properties of
these mixtures. In parallel, this knowledge also contributes to a more profound understanding

of the type and magnitude of the interactions governing these mixtures that, subsequently, enables the development of theoretical models able to accurately correlate and predict the behavior of these mixtures under different conditions, avoiding a high number of experimental measurements.

In this work, eutectic binary mixtures of [Ch]Cl with polyalcohols are investigated. The SLE phase diagrams of six [Ch]Cl based-eutectic mixtures containing ethylene glycol, glycerol, 1,3-propanediol, meso-erythritol, sorbitol, or xylitol were measured in the full composition range. The main goal is to provide meaningful information on the compositions and temperature ranges for operating these alternative solvents. Additionally, densities, viscosities, and solvatochromic parameters were determined for each system at the eutectic composition.

Experimental Section

Chemicals

The source, purity, and melting properties of the compounds studied in this work are detailed in **Table 1**, while their chemical structures are illustrated in **Figure S1**. The [Ch]Cl was dried under vacuum, at room temperature and at atmospheric pressure with constant stirring, for at least 72 hours. For ethylene glycol, 1,3-propanediol, and glycerol, a purification was done through contact with zeolites (<45 μm) for 72 hours. All the remaining compounds were stored at room temperature and used as received from the supplier as they present a low hygroscopicity. The water content was measured using a Metrohm 831 Karl-Fischer coulometer, with the analyte Hydranal Coulomat AG from Riedel-de Haën and was found to be lower than 600 ppm for choline chloride and below 150 ppm for the remaining compounds.

Table 1. Source, purity (according to the supplier) and melting properties of the substances used in this work.

Compound	Supplier	Mass Purity %	T_m /K	$\Delta_m H$ /kJ·mol ⁻¹
Choline chloride ([Ch]Cl)	Acros Organics	98	597 ²¹	4.3 ²¹
Ethylene glycol (EG)	Sigma-Aldrich	99.5	256.6 ²²	9.5 ²²
1,3-propanediol (PD)	Sigma-Aldrich	99.5	249 ²³	11.4 ²³
Glycerol (Gly)	Fischer Chemical	99.88	293 ²³	18.28 ²³
Meso-erythritol (ME)	Alfa Aesar	99	391.2 ²⁴	38.9 ²⁴
Xylitol (Xyl)	Acros Organics	99	365.7 ²⁵	37.4 ²⁵
Sorbitol (Sor)	Fischer Bioreagents	98	366.5 ²⁵	30.2 ²⁵

Solid-Liquid Phase Diagrams Measurements

Due to the hygroscopic character of some polyalcohols and [Ch]Cl, all mixtures were prepared inside a dry-argon glove box at room temperature using an analytical balance from Kern (ALS 220-4N) with an accuracy of 0.2 mg. After the first heating to mix the compounds and immediate crystallization, three experimental methods were applied depending on the physical state of the mixture. *i)* For mixtures presenting a pasty consistency, samples were heated in an oil bath under stirring until complete melting. The melting temperatures, measured using a Pt100 probe (± 0.1 K), correspond to the last solid disappearance. *ii)* For mixtures showing complete recrystallization, the samples were ground in the glove box, and the powder was filled into a glass capillary. The melting point was then measured in a device model M-565 from Büchi, with a temperature resolution of 0.1 K. Each procedure was repeated at least three times. *iii)* For mixtures liquid at room temperature, a Hitachi DSC7000X model working at atmospheric pressure was applied. Samples of approximately 2–5 mg tightly sealed in aluminum pans were prepared inside the dry-argon glovebox and submitted to one repeated cooling-heating cycles at 5 K min^{-1} (cooling) and 2 K min^{-1} (heating). The thermal transition temperatures were taken as the peak temperature. The equipment was previously calibrated with several standards with weight fraction purities higher than 99%.

Preparation of Eutectic Mixtures

To further characterize the eutectic systems, a certain number of compositions per system were selected (**Table S1**) and prepared in a larger quantity (2 batches of 5 g), following the procedure described above. After melting and immediate cooling at room temperature, mixtures were stored for 2 days in the glove box to check their stability.

Density and Viscosity Measurements

Densities and viscosities were measured at atmospheric pressure in the temperature range from 278.15 to 373.15 K using an SVM 3001 Anton Paar viscometer-densimeter (temperature uncertainty: ± 0.03 K; absolute density uncertainty: $1 \times 10^{-4} \text{ g cm}^{-3}$, relative viscosity uncertainty: 0.35%). Mixtures with compositions close to the eutectic point were used (**Table S1**). The water content of each mixture was measured using a Karl-Fischer coulometer (described above) and the results are presented in **Table S2**.

Kamlet-Taft Solvatochromic Parameters

The Kamlet-Taft solvatochromic parameters, α , β , and π^* were measured at 298 K for α parameter and at 323.15 K β and π^* parameters, in mixtures with compositions close to the eutectic point (**Table S1**). For the systems [Ch]Cl+EG and [Ch]Cl+glycerol, the solvatochromic parameters were measured over the entire composition range in which the system is in a liquid state at 323.15 K (**Table S1**). The measurements of π^* , β , and α were performed by adding small amount of the probes *N,N*-diethyl-4-nitroaniline, 4-nitroaniline or pyridine-*N*-oxide, respectively, to the mixtures, that were immediately stirred at 323.15 K and 1400 rpm using an Eppendorf Thermomixer Comfort until complete dissolution. Whereas α was obtained by ^{13}C nuclear magnetic resonance (NMR) spectra, using a Bruker Avance 300 apparatus at 75 MHz, π^* and β parameters were obtained using the longest wavelength absorption band determined by UV-Vis spectroscopy (BioTeck Synergy HT microplate reader) at 323.15 K. Trimethylsilyl propanoic acid (TSP) and deuterium oxide (D_2O) were respectively used as internal reference and solvent in the NMR measurements. The procedure was repeated at least three times for parameters π^* and β . The equations used to calculate the parameters are available in SI.

Soli-liquid equilibrium

After some assumptions, the solubility of a solid solute in a liquid solvent, can be obtained from the following expression:²⁶

$$\ln(x_i \cdot \gamma_i) = \frac{\Delta_m H_i}{R} \cdot \left(\frac{1}{T_{m,i}} - \frac{1}{T} \right) + \frac{\Delta_m C p_i}{R} \cdot \left(\frac{T_{m,i}}{T} - \ln \frac{T_{m,i}}{T} - 1 \right) \quad (1)$$

where x_i is the mole fraction of the solute i in the liquid phase, γ_i its activity coefficient in the liquid phase, $\Delta_m H_i$ and $T_{m,i}$ its melting enthalpy and temperature, respectively, and $\Delta_m C p_i$ represents its heat capacity change upon melting, R is the ideal gas constant, and T is the absolute temperature of the system. The heat capacity change upon melting is often not known (e.g. [Ch]Cl), but its contribution to the second term of **Equation 1** is typically negligible,²⁷ allowing **Equation 1** to be simplified as:²⁸

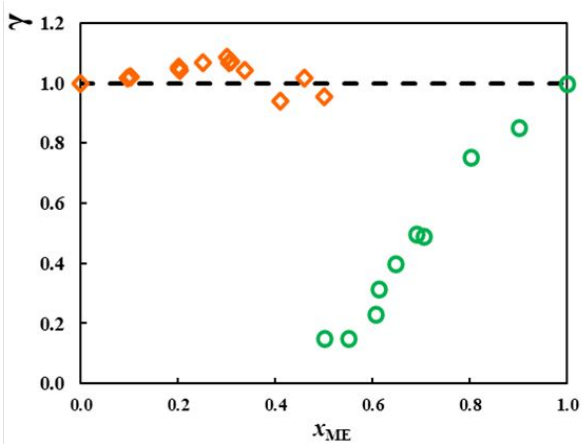
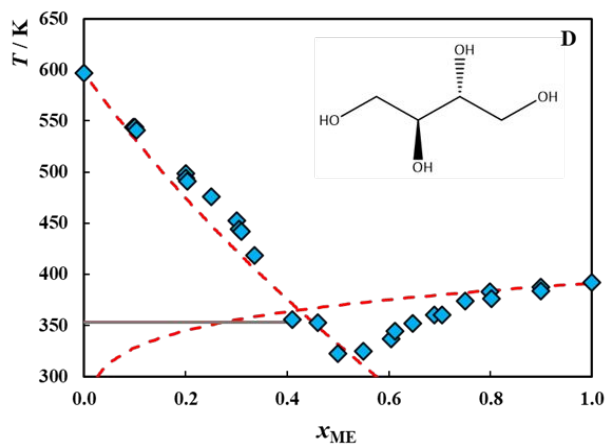
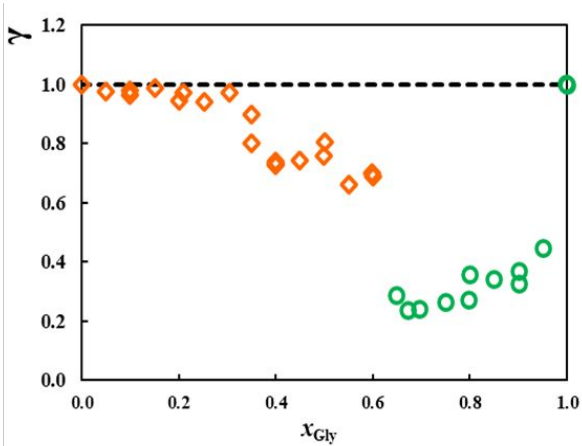
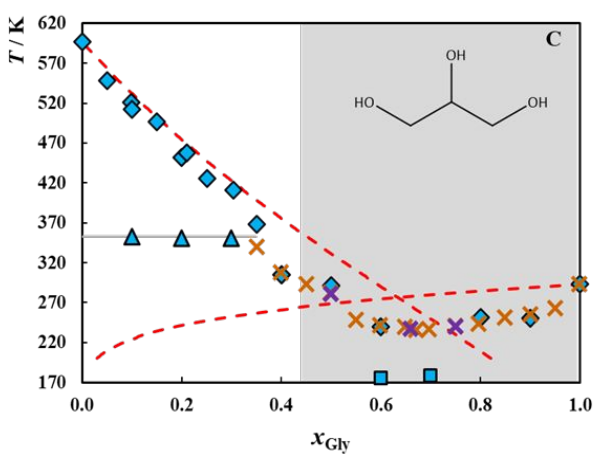
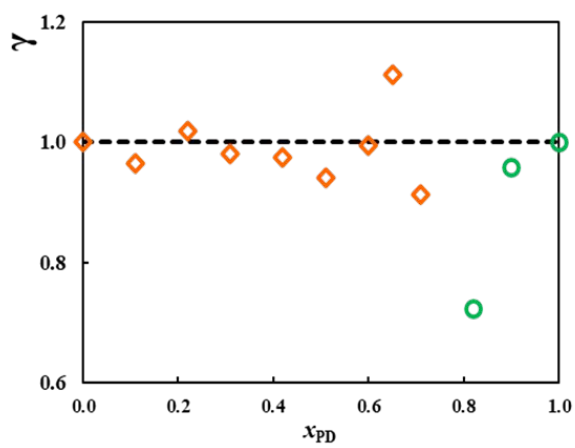
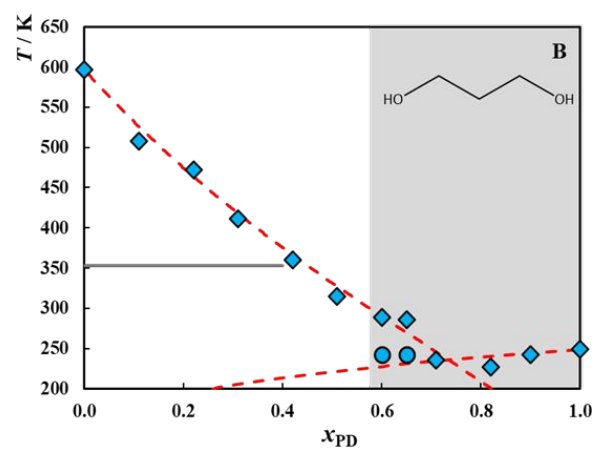
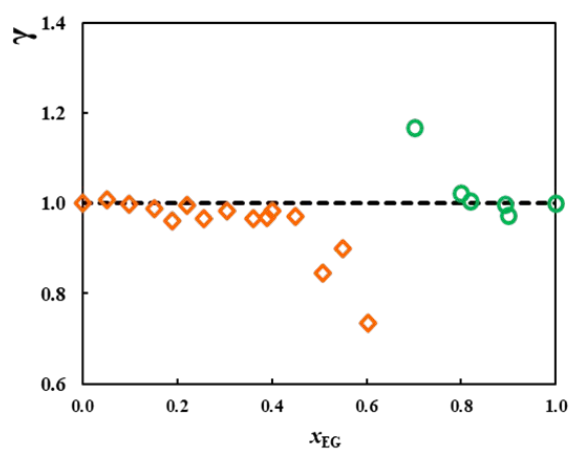
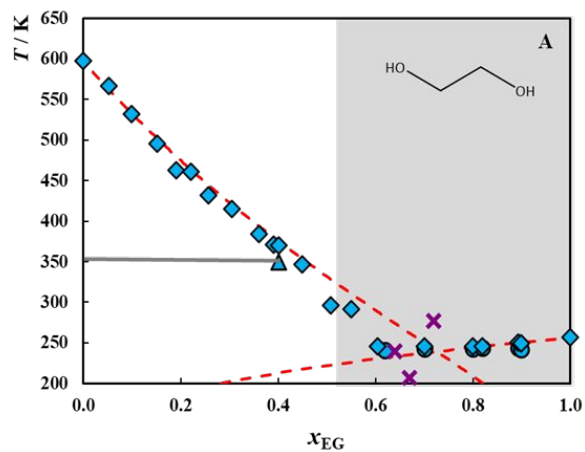
$$\ln(x_i \cdot \gamma_i) = \frac{\Delta_m H_i}{R} \cdot \left(\frac{1}{T_{m,i}} - \frac{1}{T} \right) \quad (2)$$

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3 Therefore, knowing the melting properties of the solute, using **Equation 2** one can estimate
4 the activity coefficients from the experimental data, allowing to evaluate the non-ideality of
5 the liquid phase. Furthermore, the experimental solubilities can also be compared with those
6 obtained assuming an ideal solution by setting the activity coefficients to unity.
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10 **Results & Discussion**

11 *Solid-liquid phase diagrams*

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14 The six SLE phase diagrams measured in this work are depicted in **Figure 1**, along with the
15 ideal liquid phase curves and the experimental activity coefficients. The detailed experimental
16 data and experimental activity coefficients are listed in **Table S3** of Supporting Information.
17 The experimental activity coefficients were calculated using Eq. (2), without considering the
18 solid-solid transition of choline chloride. Other relevant thermic events as eutectic temperatures
19 and solid-solid and glass transitions are reported in **Table S4**. In the eutectic region of
20 [Ch]Cl+glycerol it was not possible to measure the melting temperatures due to crystallization
21 problems and in these cases, only the glass transitions were observed and reported.
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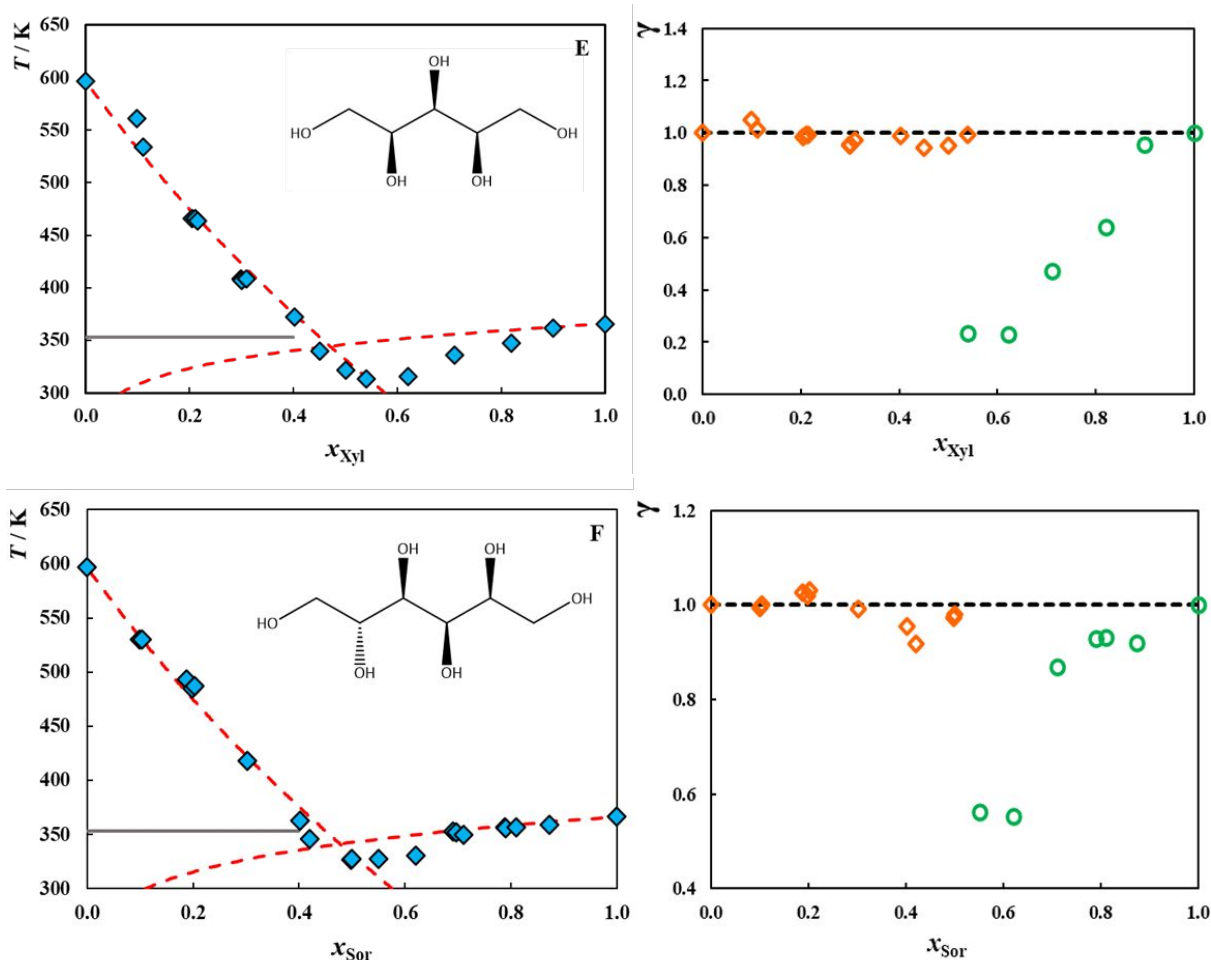


Figure 1. Solid-liquid phase diagrams (left) and activity coefficients (right) for binary mixtures composed of choline chloride and a polyalcohol: A) EG; B) PD; C) Gly; D) ME; E) Xyl and F) Sor. Legend: \blacklozenge , experimental melting temperatures measured in this work; \blacksquare , glass transitions temperatures; \bullet , eutectic temperatures; \blacktriangle , $-$, [Ch]Cl solid-solid transition ($T_{SS} = 352.93$ K, $\Delta H_{SS} = 17.19$ kJ mol $^{-1}$);²⁹ Literature: \times , Abbott et al.¹⁶; \times , Bagh et al.³⁰; $- -$, ideal solubility curve; \diamond , \circ , experimental activity coefficients, $--- \gamma = 1$. Gray regions represent the concentration range for which the mixture is liquid at room temperature ($T = 298.15$ K).

To the best of our knowledge, literature data is only available for [Ch]Cl + glycerol and [Ch]Cl + EG systems. For the system [Ch]Cl+glycerol, Abbott et al.¹⁶ reported the freezing temperatures in a considerable composition range for $x_{\text{glycerol}} > 0.3$, while Bagh et al.³⁰ reported only 3 melting temperatures near the eutectic composition. Small discrepancies between both sets of data are observed – **Figure 1C**. For the system [Ch]Cl+EG, there are discrepancies between our results and those reported in the literature by Bagh et al.³⁰ as can be seen in **Figure 1A**. [Ch]Cl+EG phase diagram was reported by us before,²⁹ showing a considerable different SLE phase diagram than the one reported here for $x_{\text{EG}} > 0.4$, composition intersecting the solid-solid transition temperature of choline chloride (**Figure S2**). The discrepancies in the results

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3 obtained are attributed to the metastability of [Ch]Cl. The polymorphism of choline chloride
4 was previously reported by Shanley and Collin^{31,32} that identified two forms: α and β , the latter
5 observed for temperatures higher than the [Ch]Cl solid-solid transition. This has an impact on
6 the SLE phase diagram depending on choline chloride solid phase. Considering the temperature
7 levels observed in both works, it indicates that here choline chloride remains in the α form,
8 while in our previous work, it changes from α to β at the SS transition temperature shifting the
9 slope in the SLE phase diagram. The temperature and enthalpy for the solid–solid transition of
10 [Ch]Cl, 352.92 K and 17.19 kJ·mol⁻¹, respectively, were measured in this work using DSC.
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18 The high hygroscopicity of choline chloride can lead to a significant decrease in the melting
19 temperature due to absorbed water. As shown by Meng et al.,³³ after 48 hours in contact with
20 atmosphere samples containing [Ch]Cl can absorb 5.5 wt% of water leading to a decrease of
21 more than 15 °C in the melting temperature.³³ This result can contribute to explaining the
22 discrepancies observed in the literature on the melting temperatures of different eutectic
23 systems.³³ However, in this work, the pure components were carefully dried (water content of
24 [Ch]Cl less than 600 ppm), and the preparation of all samples was made in a water-free
25 environment (< 1 ppm), as described in the experimental section. Thus, it is improbable that
26 the measured SLE phase diagrams here reported are significantly affected by the presence of
27 undesired water.
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36 As shown in **Figure 1**, all the studied systems exhibit a phase diagram characterized by a single
37 eutectic point – as expected for systems where the constituents are immiscible in the solid
38 phase. Additionally, the eutectic temperatures observed are much lower than those of pure
39 [Ch]Cl (597 K)²¹ as common in other [Ch]Cl-based eutectic mixtures.⁸ On the other side, the
40 lowering of the melting point of the polyalcohol is in general small for systems containing
41 ethylene glycol (-11.1K), propanediol (-6.91 K) and xylitol (- 18.8 K) and large for glycerol (-
42 57.64 K), erythritol (-47.67 K) and sorbitol (-39.7 K).
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49 Assuming an ideal behavior in the liquid phase ($\gamma = 1$), ideal solubility curves are also depicted
50 in **Figure 1**, and evidence a quasi-ideal behavior in [Ch]Cl solubility curve with activity
51 coefficients close to 1 (**Table S3**) for all systems excepting for ethylene glycol and glycerol
52 containing systems (**Figures 1A and 1C**) where some deviations to ideality are observed in the
53 region below the solid-solid transition point.
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58 Excepting the system [Ch]Cl+EG, in the polyalcohol rich region all systems display negative
59 deviations to ideality, indicating the existence of stronger interactions between [Ch]Cl and the
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3 polyalcohol, than those observed in the pure polyalcohol. The non-ideality in the polyalcohol
4 rich side seems to increase with the increasing number of hydroxyl groups and chain length till
5 [Ch]Cl+sorbitol, where the activity coefficients are close to one at high sorbitol mole fractions.
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7 Thus, the increase in the number of hydroxyl groups increases the possibility of cross-
8 interactions with choline chloride favoring the non-ideality, to the extent where steric effects
9 and strong interactions in the pure compound become dominant like in the case of sorbitol,
10 leading to a significant deviation to the ideality.
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16 The experimental eutectic point coordinates (x_{Polyol}^E , T^E) are represented in **Figure 2** and
17 reported in **Table S5**, along with those calculated assuming an ideal behavior. The
18 experimental eutectic points were determined from the interception between the two $\ln(x)$ vs
19 $1/T$ curves (using **Equation 2**) and are plotted in **Figure S3**. **Eq. (2)** shows a linear relationship
20 between $\ln(x)$ and $1/T$ and thus, a linear regression of a set of experimental data that can
21 provide an indirect estimation of the experimental eutectic point for these systems. Due to the
22 lack of experimental points observed for the system [Ch]Cl+glycerol due to recrystallization
23 difficulties in the eutectic region, and as the SLE phase diagram measured here is in agreement
24 with the one reported by Abbot et al.,¹⁶ the two experimental sets of data were used to calculate
25 the experimental eutectic point for this system.
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34 As can be seen in **Figure 2**, with the exception of the systems involving ethylene glycol and
35 propanediol where $T_{exp}^E \approx T_{ideal}^E$, the eutectic temperatures obtained in this work are lower than
36 those predicted assuming an ideal solution, due to the negative deviations from ideality of these
37 systems. Regarding the eutectic compositions, in almost all systems $x_{exp}^E > x_{ideal}^E$ due to those
38 negative deviations being present in the HBD, the [Ch]Cl showing a near ideal behavior as
39 discussed above.
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45 Both x_{exp}^E and T_{exp}^E depend strongly on the number of functional groups present in the polyol
46 chemical structure. These can be divided into two groups: those that present up to 3 OH groups
47 – ethylene glycol, propanediol, and glycerol; and those having more than 3 OH groups in their
48 structure (erythritol, xylitol, sorbitol). In each group, the experimental eutectic coordinates are
49 similar. This means that the eutectic coordinates are mainly controlled by the HBD chemical
50 structure, specifically the number of functional groups and their interaction with the HBA. This
51 can be seen in the eutectic temperature of the mixture [Ch]Cl+erythritol that is lower than that
52 observed for the system [Ch]Cl+sorbitol, although the melting temperature of erythritol is 25
53 K higher than that of sorbitol. Although sorbitol has two more -OH group able to interact with
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[Ch]Cl the intermolecular interactions between [Ch]Cl and erythritol are stronger, as the activity coefficients suggest, and the temperature depression confirms, showing that the two additional -OH groups present in sorbitol do not contribute for stronger interactions with [Ch]Cl, but for more interactions with other sorbitol molecules. These results suggest that additional hydroxyl groups in the HBD, and their configuration on the chemical structure play an important role in the interactions with [Ch]Cl. This is in agreement with our previous work,³⁴ where we investigated mixtures composed of [Ch]Cl and sugars. In that work it was observed that the interactions with the chloride anion seem to be favored by some sugar configurations, as demonstrated by the difference in the values of the activity coefficient between the two isomers reported there, arabinose and xylose.³⁴

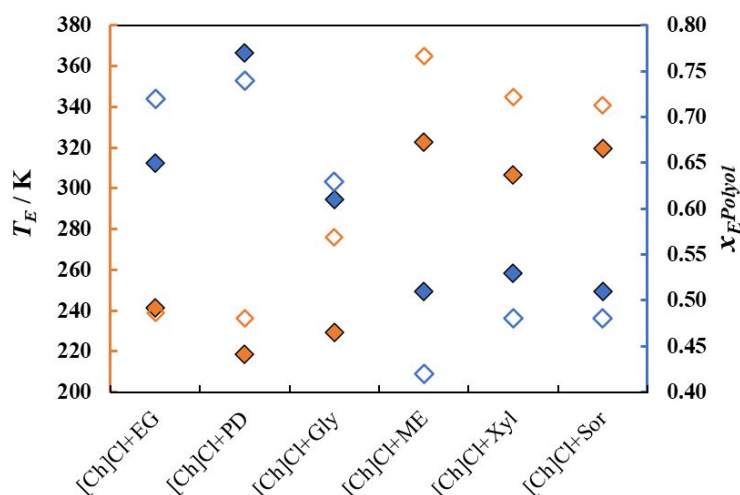


Figure 2. Eutectic coordinates for the systems measured in this work. Legend: \blacklozenge, \diamond Eutectic composition (polyol mole fraction) and \blacklozenge, \diamond eutectic temperature. The full marks correspond to the experimental data, while the open marks are calculated assuming ideality. For the system [Ch]Cl+glycerol the experimental coordinates were reported by Abbott et al.¹⁶

Although the systems studied are often reported as DES,^{4,5,12,13,16,35–38} it is here demonstrated that in some mixtures the eutectic temperature is very close to that predicted assuming ideality ([Ch]Cl+ethylene glycol or propanediol). The absence of favourable interactions on these systems is further supported by the excess enthalpy measurements reported by Lopez-Porfiri et al.³⁷ showing these mixtures to be endothermic. Moreover, almost all systems studied present a quasi-ideal behavior in the [Ch]Cl solubility curve. This means that the interactions between the components are not significantly different from those present in the pure compound to induce negative deviations from ideality and the temperature depressions associated with them. Nevertheless, systems composed of [Ch]Cl and ethylene glycol, propanediol or glycerol,

present a wide compositions range at which the mixtures are liquid at room temperature. One cannot help noticing that the formulation of liquid mixtures at room temperature with the compounds here studied only occurs when the HBD used is already liquid at room temperature (ethylene glycol, propanediol, or glycerol), and thus they should more appropriately be considered solutions of [Ch]Cl on these solvents rather than DES.

Densities and Viscosities

In general, a useful solvent should have a low viscosity allowing for fast mass transfer, and a density sufficiently different from water for good phase demixing. Therefore, these two physicochemical properties were studied to further characterize the mixtures herein investigated.

Densities of the polyalcohol-based mixtures at a composition near the eutectic point composition (see **Table S1**), were measured at atmospheric pressure in the temperature range from 278.15 to 373.15 K, and are presented in **Figure 3**, and reported in the tabular form in **Table S6**.

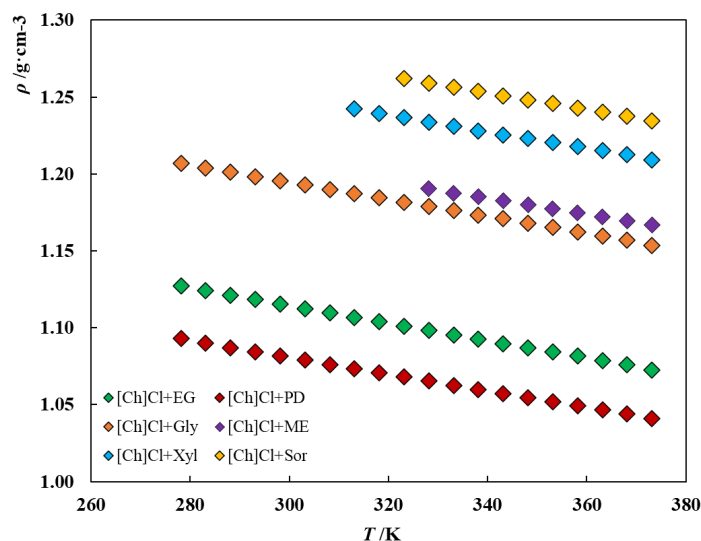


Figure 3. Density of the binary systems [Ch]Cl(1)+polyalcohol(2) at different temperatures and a mole fraction of component 2 of: EG) 0.67; PD) 0.75; Gly) 0.68; ME) 0.50; Xyl) 0.55 and Sorb) 0.50.

All systems present densities higher than water being [Ch]Cl+propanediol and [Ch]Cl+sorbitol mixtures the less and more denser, respectively. As expected, density decreases linearly with increasing temperature due to thermal expansion. Similarly to the density of pure polyalcohols, at a fixed temperature, density increases with the increase of the alkyl chain length and the

number of -OH group in the polyalcohol structure.³⁹ Ethylene glycol and 1,3-propanediol both have 2 OH groups in their structures and at the same temperature $\rho_{[\text{Ch}]\text{Cl}+\text{EG}} > \rho_{[\text{Ch}]\text{Cl}+\text{PD}}$. The organic salt/HBD molar ratio also has a strong effect on the densities of ES. Analyzing the mole fraction of choline chloride in each mixture, one can say that density increases with the amount of [Ch]Cl in the mixture for systems involving ethylene glycol, propanediol and glycerol, as can be seen comparing the systems [Ch]Cl+propanediol with $x_{[\text{Ch}]\text{Cl}} \approx 0.25$, and system [Ch]Cl+EG with $x_{[\text{Ch}]\text{Cl}} \approx 0.33$, where the amount of [Ch]Cl influences the density of the mixtures. The remaining systems, all have approximately the same mole fraction of choline chloride, $x_{[\text{Ch}]\text{Cl}} \approx 0.5$.

Differences in density can be explained in terms of the molecular arrangement or packing of the ES. This was previously analyzed by Garcia et al.,³⁶ who reported that the molecular characteristics of the HBD and the molar ratio at which the ES is formed have a large effect on their density and its temperature variation. In this work, the system [Ch]Cl+sorbitol is denser due to the higher intermolecular packing of the mixture structure. The volume packing indicates that systems with larger molecules of polyalcohol, or that present more functional groups in their structure, are arranged in a more packed arrangement than systems containing smaller polyalcohol molecules. Also, bigger polyalcohols are able to occupy a part of the space between the polar heads of the [Ch]Cl cation and anion which cannot be occupied by the pure compounds or small species.³⁶

The experimental density data measured in this work is plotted against literature data for the same systems at the same composition (1:2, HBA:HBD) and the respectively pure polyalcohol density (**Figure S4**). The percentage average relative deviations, %ARD, were calculated through:

$$\%ARD(X) = 100 \left| \frac{X^{lit} - X^{exp}}{X^{exp}} \right| \quad (3)$$

where X^{lit} and X^{exp} are the literature and the experimental quantities, respectively.

A good agreement between the data reported in this work and those reported in the literature for [Ch]Cl+EG and [Ch]Cl+glycerol is observed, with an %ARD in the range of 0.3%. Overall, small and non-systematic deviations were found between the different sets of data. An exception is the density reported by Leron et al.⁴⁰ for the mixtures with glycerol, and for

temperatures above 320 K, where the density values reported are significantly lower than those measured in this work. Differences may be attributed to the presence of water on their samples.

Comparing the density between the mixtures, and the corresponding pure polyalcohol, one can realize that for ethylene glycol and propanediol, the densities of the mixtures are higher than those reported to the pure compounds.²² Like ionic liquids, in ES a lattice containing holes or empty vacancies is structured in the solution. It seems that when ethylene glycol or propanediol are mixed with [Ch]Cl, the average hole radius is decreased⁴¹ resulting in a slight increase of the ES density as compared to that of the pure solvent.¹⁶ On the contrary, the ES containing glycerol presents a smaller density than reported for the respective pure polyalcohol.²² These differences can be associated with the free volume in the system and the number of -OH groups in the polyalcohol structure, since ethylene glycol and propanediol both have one OH group less than glycerol.^{13,35}

Viscosities of the same polyalcohol-based mixtures (compositions at **Table S1**) were measured at atmospheric pressure, in the temperature range from 278.15 to 373.15 K, and are presented in **Figure 4** and, and reported in the tabular form in **Table S7**.

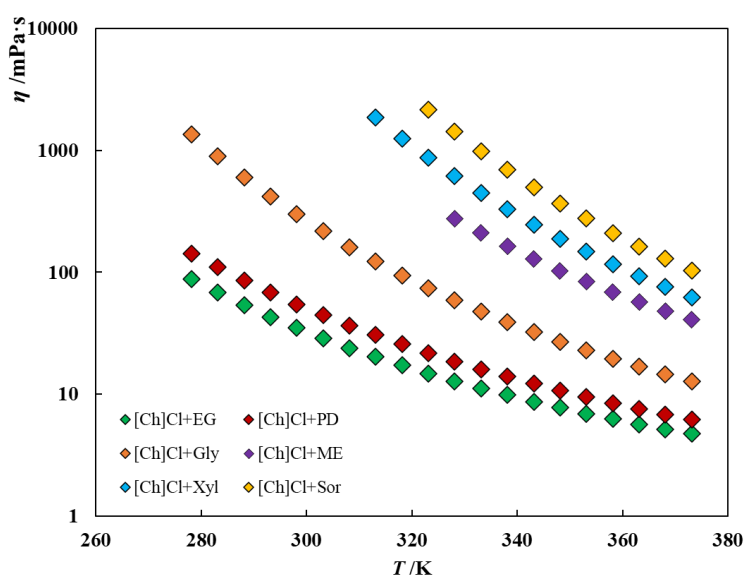


Figure 4. Viscosity of the binary systems [Ch]Cl(1)+polyalcohol(2) at different temperatures and a mole fraction of component 2 of: EG) 0.67; PD) 0.75; Gly) 0.68; ME) 0.50; Xyl) 0.55 and Sorb) 0.50.

The viscosities of the investigated systems are higher than water and decrease with increasing temperature. Moreover, the number and position of the functional groups strongly influence the behavior of these systems as, at a fixed temperature, viscosity increases with the number of

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3 -OH groups and number of carbons in the polyalcohol structure, as for pure polyalcohols. For
4 instance, [Ch]Cl+EG exhibits a viscosity of 34.96 mPa·s at 298 K, much lower than the
5 viscosity of [Ch]Cl combined with glycerol in the same proportion and at the same temperature
6 (298.57 mPa·s at 298 K). The higher viscosity of the later is due to the presence of a more
7 robust 3D intermolecular hydrogen-bond network, increasing the viscosity of the system. The
8 highest viscosity is observed for [Ch]Cl+sorbitol, where sorbitol has more -OH groups than the
9 other polyalcohols, forming more extensive H-bonds networks in the mixture. The activity
10 coefficients of the mixtures can support this evidence. Smaller activity coefficients indicate
11 greater molecular interactions between the species. Thus, mixtures comprising polyalcohol's
12 with less -OH groups, like EG, have greater activity coefficient in the eutectic point than
13 mixtures with a higher number of -OH groups, leading to lower viscosities, due to the less
14 robust intermolecular hydrogen-bond network. It was previously reported that increasing alkyl
15 chain length or the number of functional groups causes an increase in van der Waals
16 interactions and hydrogen bonds, which results in lower mobility of free species within the
17 ESs, making them more viscous.^{13,35,42} However, the effect of chain length is less relevant at
18 higher temperatures where viscosity values are closer among the various series.⁴³ Regarding
19 the mole fraction of choline chloride in each system, its increase seems to lead to an increase
20 in the viscosity values.

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35 Although several authors reported viscosity data for the mixture of choline chloride with EG⁴⁴⁻
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46 and glycerol^{44,46,47}, to the best of our knowledge, no data were reported for the remaining ES
investigated. A comparison of the available literature data with the values measured in this
work for [Ch]Cl + EG or glycerol, at the same molar proportion (1:2, HBA:HBD), is plotted
in **Figure S5** together with the viscosities of the pure polyalcohols ethylene glycol, glycerol or
propanediol, showing considerable viscosity deviations between the different literature
sources, and with the data measured in this work, which can reach 90%. These differences may
arise from the experimental methodology used, sample preparation procedures, water content,
or even impurities. It has been already reported that the sample preparation substantially
influences the physicochemical properties of the ES. Florindo et al.⁴⁸ reported differences of
6.5% between the viscosity data of DES samples prepared by the traditional heating and stirring
method in comparison with a grinding approach. Although this effect is more significant for
viscosity than density, it should be considered in both properties. As in density, the viscosity
of mixtures of [Ch]Cl with ethylene glycol and propanediol are higher than the pure
corresponding polyalcohol, while the mixture with glycerol presents a lower viscosity than the

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3 pure HBD. Glycerol has strong cohesive energy due to the presence of an extensive
4 intermolecular hydrogen bond network. This drastic decrease of the viscosity upon the addition
5 of [Ch]Cl in the mixture was attributed to the partial rupture of the hydrogen bond network of
6 glycerol, which can be corroborated by analyzing the low activity coefficients of glycerol in
7 this mixture (close to 0.24) that reinforces the strong interaction between [Ch]Cl and glycerol.¹⁴
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12 The experimental viscosity data of the systems [Ch]Cl + glycerol or ethylene glycol was further
13 compared with literature data involving different^{49–51} HBAs and at the same HBD/HBA molar
14 ratio – **Figure S6**. The systems studied in this work have lower viscosities than the other
15 ammonium, or phosponium based ES. Within the ammonium group, and at the same
16 temperature, it was observed that the viscosities of the different ES increase as the HBA
17 molecular volume increases ([Ch]Cl < DAC < TEMA < BTMA < TBAB). Additionally, the salts
18 that have aromatic rings in their structure (like MTPB, BTPC, and BTMA) lead to ES with
19 higher viscosities. These results show that ES are tunable solvents with viscosities that can be
20 designed considering the structure of both the HBA and HBD.
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29 The viscosities of the studies ES are much larger than those of conventional liquid solvents,
30 which can be explained by a large ion-to-hole radius ration in these eutectic mixtures, since ES
31 are composed of roles holes or empty vacancies as reported by Abbott.^{13,41} One possibility to
32 reduce their viscosities, and their densities, is the addition of water. As shown before by us, in
33 systems with [Ch]Cl+sugars and hydrophobic terpene+terpene mixtures, and others [33,52–54]
34 the addition of water, can reduce by approximately half the viscosities of these systems.^{34,55}
35 However, this should be done with caution since it may affect and change other properties of
36 the system.
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44 The low toxicity and ready availability of the investigated polyalcohols make them very
45 interesting solvents. However, their properties, namely high viscosities and densities, limits
46 their use. The results reported in this work show that the addition of salt can be used to tune
47 the ES properties, leading to higher or lower densities and viscosities, depending on the molar
48 proportion of the mixture and the interaction between the components. The temperature has a
49 significant effect on viscosity, and if highly viscous mixtures are formed at room temperature,
50 which hampers its use for practical purposes, higher temperatures can be chosen instead. the
51 meso-erythritol, xylitol, and sorbitol melt, or decompose upon melting, at temperatures around
52 373.15 K and thus, comparisons between their pure densities and viscosities with the ones
53 measured in this work in mixtures with choline chloride are not possible.
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Solvatochromic parameters

The solvatochromic parameters give information about the dipolarity/polarizability (π^*), hydrogen bond donor (α) and acceptor (β) capacities of a compound, or mixture, thereby providing insights into the solvent nature. Here, the Kamlet-Taft solvatochromic parameters of the [Ch]Cl-polyalcohol systems were measured at the same compositions (**Table S1**), and at 323.15 K for both π^* and β , while α was measured at 298.15 K. The experimental data are presented in **Figures 5** and **6**, and **Table S8** (a brief description of the equations used is also available in **SI**). The parameters in the system [Ch]Cl+erythritol were not measured due to the fast crystallization of the eutectic mixture. This does not happen in all other systems due to supercooling, allowing the measurement of the KT parameters at a temperature lower to their melting points. At these temperatures, only pure ethylene glycol, glycerol and propanediol are in the liquid state, and thus only for those pure polyalcohols the KT parameters were found: ethylene glycol $\beta=0.554$, $\alpha=1.05$, $\pi^*=0.956$; glycerol $\beta=0.480$, $\alpha=1.14$, $\pi^*=1.089$; and propanediol $\beta=0.602$, $\alpha=0.96$, $\pi^*=0.913$.

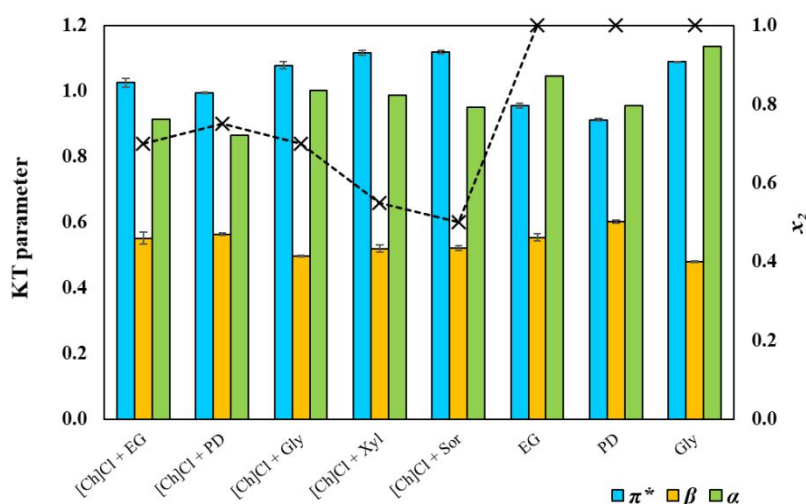


Figure 5. Kamlet-Taft solvatochromic parameter of some pure polyols and polyol + ChCl mixtures at compositions close to the eutectic point at 323.15 K (π^* and β) or 298.15 K (α). Clustered columns correspond to the KT parameters (left y-axis). The dotted line corresponds to the mole fraction of each polyalcohol in the respective mixture (right y-axis).

The parameter π^* provides a measure of the solvent polarizability/dipolarity and present values between 0.995 ([Ch]Cl+propanediol) and 1.119 ([Ch]Cl+sorbitolb), considerably higher than those of conventional organic solvents (**Table S8**), and very close to water. Moreover, there is a slight increase in the π^* value with the number of -OH groups in the alkyl chain length of the polyalcohol, which is probably connected to the simultaneous increase in the [Ch]Cl mole

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3 fraction at the eutectic point. The parameter π^* for the mixture studied in this work is always
4 higher than the respective pure polyalcohol, except for glycerol containing system.
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8 The β and α parameters describe the hydrogen bond acceptor and donor capacity, respectively.
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10 The β values obtained here for the mixtures are between 0.497 ([Ch]Cl+glycerol) and 0.563
11 ([Ch]Cl+propanediol), similar to methanol and acetone (**Table S8**), but smaller than the β of
12 ethanol. On the other hand, the α values are between 0.87 ([Ch]Cl+propanediol) and 1.12
13 ([Ch]Cl+glycerol), higher than most of the organic solvents used nowadays, but lower than
14 water (**Table S8**). The variation observed for parameter β is the opposite of α , as previously
15 reported.⁴³ Mixtures involving polyalcohols with 2 -OH groups in their structures (EG and
16 propanediol) present a higher capacity to accept hydrogen bonds (higher β) than mixtures
17 involving other polyalcohols. Additionally, this parameter tends to increase with the
18 polyalcohol mole fraction. The ability to act as hydrogen bond donor (α) is higher in mixtures
19 involving polyalcohols with more than 2 -OH groups (glycerol, xylitol, and sorbitol). The
20 values obtained for mixtures are lower than pure compounds in the case of the α parameter,
21 while, in the case of β , the values are close to the corresponding pure polyalcohol. In general,
22 mixtures with smaller polyalcohols, present a higher capacity to accept hydrogen bonds
23 meaning a higher ability to establish nonspecific interactions with a solute, while the capacity
24 to act as hydrogen bond donor is higher in mixture with higher polyalcohols.
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36 Aiming to explore the designer solvent character of these mixtures, the KT solvatochromic
37 parameters of [Ch]Cl+EG and [Ch]Cl+glycerol were measured as a function of the polyalcohol
38 mole fraction – **Figure 6**. For the system with ethylene glycol, π^* decreases with the increase
39 of ethylene glycol mole fraction, while β shows a smooth minimum at around 0.80 of
40 polyalcohol. In the case of [Ch]Cl+glycerol system, π^* increases with the increase of
41 polyalcohol in the mixture. β shows the opposite behavior. In both systems, parameter α
42 increases with the increase of polyalcohol mole fraction. These results suggest that the desired
43 properties of the final solvent can be tailored based on the mole fraction of the constituents
44 avoiding the typical use of fixed stoichiometric proportions.
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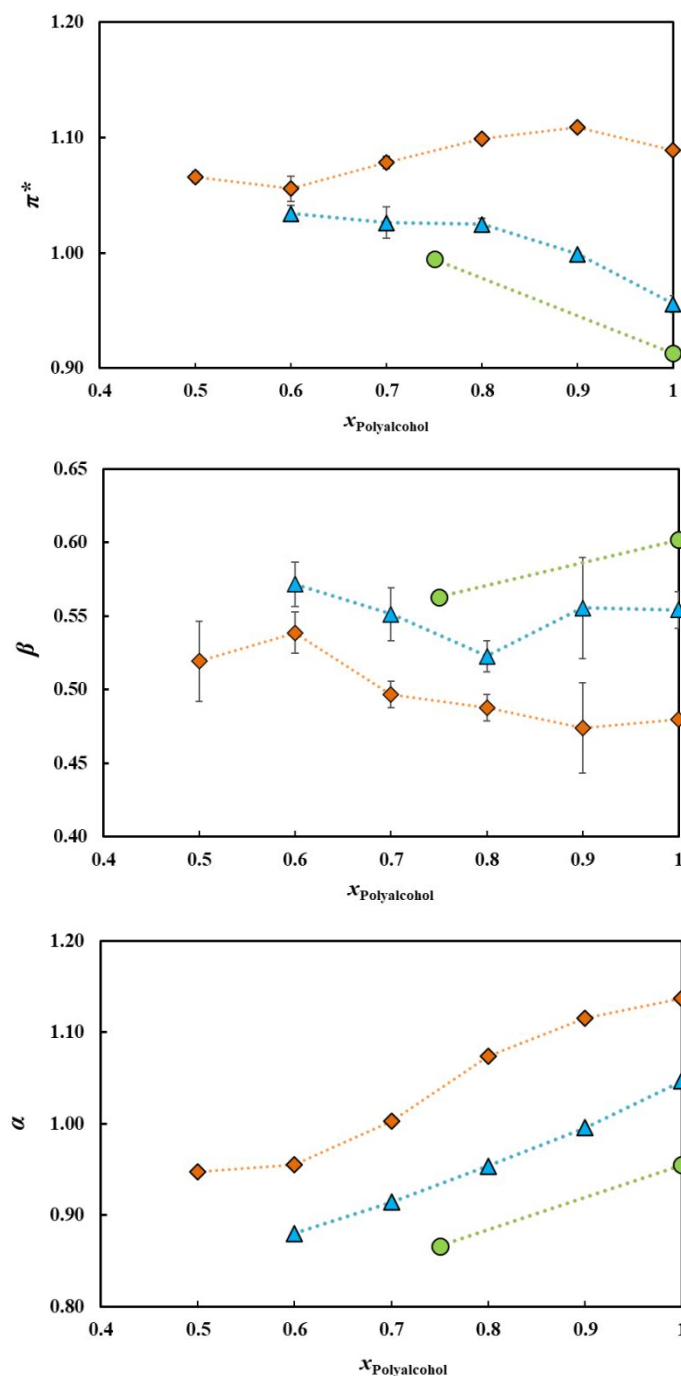


Figure 6. KT solvatochromic parameters of mixtures [Ch]Cl+EG and [Ch]Cl+glycerol at 323.15 K (π^* and β) and 298.15 K (α) as a function of the polyalcohol mole fraction. The dotted lines are guides for the eyes. Legend: \blacklozenge [Ch]Cl+glycerol; \blacktriangle [Ch]+EG; \bullet [Ch]Cl+propanediol.

In literature, some authors reported the KT solvatochromic parameters for [Ch]+EG and [Ch]+glycerol systems and the pure compounds (see **Table S9**). In general, significant discrepancies between the different sets, especially for parameter π^* can be observed being the results from literature larger than those here measured. However, it is important to highlight that the measurements were carried out at different compositions, inhibiting a direct

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3 comparison. Regarding the pure compounds, there are also some discrepancies in the KT
4 values, namely for glycerol, and generally the results from literature lower than those here
5 presented. Discrepancies can be attributed to the different probes used, different
6 methodologies, water content and temperature.^{55–57}
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11 The studied mixtures present KT parameters similar to [Ch]Cl-based DES, but higher than
12 those obtained for tetraalkylammonium-based DES,^{58,59} indicating that choline chloride plays
13 an important role in the polarizability of these mixtures. The results obtained here have lower
14 values than those of [Ch]Cl+sugars previously reported by us⁴⁷ for all parameters evaluated,
15 probably due to the presence of a ring-shaped structure in sugars.⁴³ Compared with
16 hydrophobic mixtures containing only terpenes, or terpenes and fatty acids, the mixtures
17 studied in this work present much higher values, except the π^* parameter.^{43,55} These are related
18 to the fact that cholinium based DES are constituted by charged moieties with polar groups,
19 more polar than the terpenes-based mixtures formed by non-charged compounds.
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28 **Conclusion**

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31 Herein mixtures involving natural compounds – polyalcohols and choline chloride – were
32 investigated, aiming to characterize their behavior and evaluate their potential as eutectic
33 solvents. The SLE phase diagrams of the mixtures were measured in the full composition range
34 using three different techniques. It is shown that in general choline chloride displays an ideal
35 behavior while the polyalcohol exhibit negative deviations from ideality, resulting in a
36 temperature depression that may lead to the formation of liquids at relatively low temperature.
37 Results suggest that the number and positions of functional groups, HBD:HBA eutectic ratio
38 and interactions in the pure HBD have a strong influence on the solubility of the HBD in the
39 ES and thus on the eutectic melting temperatures.
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46 Although these systems are often reported as DES, this works shows that this is somewhat
47 arbitrary: negative deviations from ideality are only observed in one side of the SLE phase
48 diagram and in some cases, small temperature depressions face to the pure polyalcohol are
49 found, along with eutectic points very close to the ideally predicted ones. It must, however, be
50 stressed that room temperature solvents can be obtained for some of these mixtures on a wide
51 composition range and not fixed to any particular stoichiometric relationship between the
52 hydrogen bond donor and acceptor, what reinforces the tunable character of the liquid phase
53 region of these mixtures.
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3 The densities and viscosities were measured in order to evaluate the potential of these systems
4 as solvents, and were found to be higher than water. Generally, both properties increase with
5 the increase of -OH groups, and the number of carbons in the polyalcohol structure, as well as
6 with the increase of [Ch]Cl mole fraction in the eutectic mixture.
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10 The mixtures investigated were further characterized measuring their solvatochromic
11 parameters, which are influenced by the number of -OH groups in the polyalcohol structure,
12 and vary with its mole fraction in the mixture. Mixtures involving ethylene glycol and
13 propanediol present a higher hydrogen-bond basicity character, while mixtures involving
14 polyalcohols with more than 2 -OH groups in their structure show a higher hydrogen-bond
15 acidity and higher nonspecific interactions. Moreover, it was shown that mixture properties can
16 be tailored changing the mole proportion of its constituents. The knowledge gathered here is a
17 contribution for the study of eutectic mixtures involving choline chloride and polyalcohols, and
18 their interactions, enhancing their attractiveness for practical applications.
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26 **Supporting Information**

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29 Supporting information is available free of charge on the ACS Publications website. Water
30 content of mixtures used in the density and viscosity measurements; experimental solid-liquid
31 phase diagrams and calculated activity coefficients; experimental and ideal eutectic points;
32 densities; viscosities; Kamlet-Taft solvatochromic parameters equations and experimental and
33 literature values.
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38 **Acknowledgments**

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55 **References**

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58 (1) Clarke, C. J.; Tu, W. C.; Levers, O.; Bröhl, A.; Hallett, J. P. Green and Sustainable
59
60

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2
3 Solvents in Chemical Processes. *Chem. Rev.* **2018**, *118*, 747–800.
4 <https://doi.org/10.1021/acs.chemrev.7b00571>.
5
6
7 (2) Zhao, H.; Xia, S.; Ma, P. Use of Ionic Liquids as “green” Solvents for Extractions. *J.*
8 *Chem. Technol. Biotechnol.* **2005**, *80*, 1089–1096. <https://doi.org/10.1002/jctb.1333>.
9
10
11 (3) Chemat, F.; Vian, M. A.; Ravi, H. K.; Khadhraoui, B.; Hilali, S.; Perino, S.; Tixier, A.
12 S. F. Review of Alternative Solvents for Green Extraction of Food and Natural
13 Products: Panorama, Principles, Applications and Prospects. *Molecules* **2019**, *24*, 1–
14 26. <https://doi.org/10.3390/molecules24163007>.
15
16
17
18 (4) Dai, Y.; van Spronsen, J.; Witkamp, G. J.; Verpoorte, R.; Choi, Y. H. Natural Deep
19 Eutectic Solvents as New Potential Media for Green Technology. *Anal. Chim. Acta*
20 **2013**, *766*, 61–68. <https://doi.org/10.1016/j.aca.2012.12.019>.
21
22
23
24 (5) Paiva, A.; Craveiro, R.; Aroso, I.; Martins, M.; Reis, R. L.; Duarte, A. R. C. Natural
25 Deep Eutectic Solvents – Solvents for the 21st Century. *ACS Sustain. Chem. Eng.*
26 **2014**, *2*, 1063–1071. <https://doi.org/10.1021/sc500096j>.
27
28
29
30 (6) Abbott, A. P.; Boothby, D.; Capper, G.; Davies, D. L.; Rasheed, R. K. Deep Eutectic
31 Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile
32 Alternatives to Ionic Liquids. *J. Am. Chem. Soc.* **2004**, *126*, 9142–9147.
33 <https://doi.org/10.1021/ja048266j>.
34
35
36
37 (7) Faggian, M.; Sut, S.; Perissutti, B.; Baldan, V.; Grabnar, I.; Acqua, S. D. Natural Deep
38 Eutectic Solvents (NADES) as a Tool for Bioavailability Improvement :
39 Pharmacokinetics of Rutin Dissolved in Proline / Glycine after Oral Administration in
40 Rats : Possible Application in Nutraceuticals. *Molecules* **2016**, *21*, 1–11.
41 <https://doi.org/10.3390/molecules21111531>.
42
43
44
45 (8) Martins, M. A. R.; Pinho, S. P.; Coutinho, J. A. P. Insights into the Nature of Eutectic
46 and Deep Eutectic Mixtures. *J. Solution Chem.* **2018**, *48*, 962–968.
47 <https://doi.org/10.1007/s10953-018-0793-1>.
48
49
50
51 (9) Wang, H.; Liu, S.; Zhao, Y.; Wang, J.; Yu, Z. Insights into the Hydrogen Bond
52 Interactions in Deep Eutectic Solvents Composed of Choline Chloride and Polyols.
53 *ACS Sustain. Chem. Eng.* **2019**, *7* (8), 7760–7767.
54 <https://doi.org/10.1021/acssuschemeng.8b06676>.
55
56
57
58 (10) Chen, J.; Li, S.; Yao, Z.; Yang, D.; Zhang, L. Improved Stability of Salvianolic Acid B
59
60

- 1
2
3 from Radix Salviae Miltiorrhizae in Deep Eutectic Solvents. *Anal. Methods* **2016**, *8*
4 (11), 2502–2509. <https://doi.org/10.1039/C5AY03351A>.
5
6
7 (11) Shekaari, H.; Zafarani-Moattar, M. T.; Shayanfar, A.; Mokhtarpour, M. Effect of
8 Choline Chloride/Ethylene Glycol or Glycerol as Deep Eutectic Solvents on the
9 Solubility and Thermodynamic Properties of Acetaminophen. *J. Mol. Liq.* **2018**, *249*,
10 1222–1235. <https://doi.org/10.1016/j.molliq.2017.11.057>.
11
12
13
14 (12) Manurung, R.; Simanjuntak, G. C.; Perez, R. N.; Syahputra, A.; Alhamdi, M. A.;
15 Siregar, H.; Syahputri Zuhri, R. R. Production of Choline Chloride-Based Deep
16 Eutectic Solvent with Hydrogen Bond Donor D-Glucose and Ethylene Glycol. *IOP*
17 *Conf. Ser. Mater. Sci. Eng.* **2019**, *505*, 1–20. [https://doi.org/10.1088/1757-](https://doi.org/10.1088/1757-899X/505/1/012134)
18 [899X/505/1/012134](https://doi.org/10.1088/1757-899X/505/1/012134).
19
20
21
22
23 (13) Troter, D. Z.; Todorović, Z. B.; Đokić-Stojanović, D. R.; Đorđević, B. S.; Todorović,
24 V. M.; Konstantinović, S. S.; Veljković, V. B. The Physicochemical and
25 Thermodynamic Properties of the Choline Chloride-Based Deep Eutectic Solvents. *J.*
26 *Serbian Chem. Soc.* **2017**, *82*, 1039–1052. <https://doi.org/10.2298/JSC170225065T>.
27
28
29
30 (14) Abbott, A. P.; Harris, R. C.; Ryder, K. S.; D'Agostino, C.; Gladden, L. F.; Mantle, M.
31 D. Glycerol Eutectics as Sustainable Solvent Systems. *Green Chem.* **2011**, *13*, 82–90.
32 <https://doi.org/10.1039/c0gc00395f>.
33
34
35
36 (15) Oliveira, F. S.; Pereiro, A. B.; Rebelo, L. P. N.; Marrucho, I. M. Deep Eutectic
37 Solvents as Extraction Media for Azeotropic Mixtures. *Green Chem.* **2013**, *15* (5),
38 1326–1330. <https://doi.org/10.1039/C3GC37030E>.
39
40
41
42 (16) Abbott, A. P.; Cullis, P. M.; Gibson, M. J.; Harris, R. C.; Raven, E. Extraction of
43 Glycerol from Biodiesel into a Eutectic Based Ionic Liquid. *Green Chem.* **2007**, *9*,
44 868–872. <https://doi.org/10.1039/b702833d>.
45
46
47 (17) Hayyan, M.; Mjalli, F. S.; Hashim, M. A.; AlNashef, I. M. A Novel Technique for
48 Separating Glycerine from Palm Oil-Based Biodiesel Using Ionic Liquids. *Fuel*
49 *Process. Technol.* **2010**, *91*, 116–120. <https://doi.org/10.1016/j.fuproc.2009.09.002>.
50
51
52
53 (18) H.G. Morrison; Sun, C. C.; Neervannan, S. Characterization of Thermal Behavior of
54 Deep Eutectic Solvents and Their Potential as Drug Solubilization Vehicles. *Int. J.*
55 *Pharm.* **2009**, *378*, 136–139.
56
57
58 (19) Gunasekara, S. N.; Pan, R.; Chiu, J. N.; Martin, V. Polyols as Phase Change Materials
59
60

- 1
2
3 for Surplus Thermal Energy Storage. *Appl. Energy* **2016**, *162*, 1439–1452.
4 <https://doi.org/10.1016/j.apenergy.2015.03.064>.
5
6
7 (20) Wahid, M. A.; Hosseini, S. E.; Hussien, H. M.; Akeiber, H. J.; Saud, S. N.;
8 Mohammad, A. T. An Overview of Phase Change Materials for Construction
9 Architecture Thermal Management in Hot and Dry Climate Region. *Appl. Therm. Eng.*
10 **2017**, *112*, 1240–1259. <https://doi.org/10.1016/j.applthermaleng.2016.07.032>.
11
12
13
14 (21) Fernandez, L.; Silva, L. P.; Martins, M. A. R.; Ferreira, O.; Ortega, J.; Pinho, S. P.;
15 Coutinho, J. A. P. Indirect Assessment of the Fusion Properties of Choline Chloride
16 from Solid-Liquid Equilibria Data. *Fluid Phase Equilib.* **2017**, *448*, 9–14.
17 <https://doi.org/10.1016/j.fluid.2017.03.015>.
18
19
20
21 (22) Daubert, T. E.; Sibul, H. M.; Stebbins, C. C.; Danner, R. P.; Rowley, R. L.; Adams, M.
22 E.; Wilding, W. V.; Marshall, T. L. *Physical and Thermodynamic Properties of Pure*
23 *Chemicals: DIPPR: Data Compilation: Core + Supplements 1-10*; Taylor & Francis,
24 2000.
25
26
27
28 (23) Jabrane, S.; Létoffé, J. M.; Claudy, P. Study of the Thermal Behaviour of 1,3-
29 Propanediol and Its Aqueous Solutions. *Thermochim. Acta* **1998**, *311*, 121–127.
30 [https://doi.org/10.1016/S0040-6031\(97\)00416-4](https://doi.org/10.1016/S0040-6031(97)00416-4).
31
32
33
34 (24) Jesus, A. J. L.; Tomé, L. I. N.; Eusébio, M. E.; Redinha, J. S. Enthalpy of Sublimation
35 in the Study of the Solid State of Organic Compounds. Application to Erythritol and
36 Threitol. *J. Phys. Chem. B* **2005**, *109*, 18055–18060.
37 <https://doi.org/10.1021/jp051621n>.
38
39
40
41 (25) NIST Chemistry WebBook <http://webbook.nist.gov/cgi/cbook>.
42
43
44 (26) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of*
45 *Fluid-Phase Equilibria*; 1970; Vol. 2. [https://doi.org/10.1016/0021-9614\(70\)90078-9](https://doi.org/10.1016/0021-9614(70)90078-9).
46
47
48 (27) Elliott, J. R.; Lira, C. T. *Introductory Chemical Engineering Thermodynamics*, 2nd
49 editio.; Prentice Hall.
50
51
52 (28) Coutinho, J. A. P.; Andersen, S. I.; Stenby, E. H. Evaluation of Activity Coefficient
53 Models in Prediction of Alkane Solid-Liquid Equilibria. *Fluid Phase Equilib.* **1995**,
54 *103* (1), 23–39. [https://doi.org/10.1016/0378-3812\(94\)02600-6](https://doi.org/10.1016/0378-3812(94)02600-6).
55
56
57 (29) Crespo, E. A.; Silva, L. P.; Lloret, J. O.; Carvalho, P. J.; Vega, L. F.; Llorell, F.;
58 Coutinho, J. A. P. A Methodology to Parameterize SAFT-Type Equations of State for
59
60

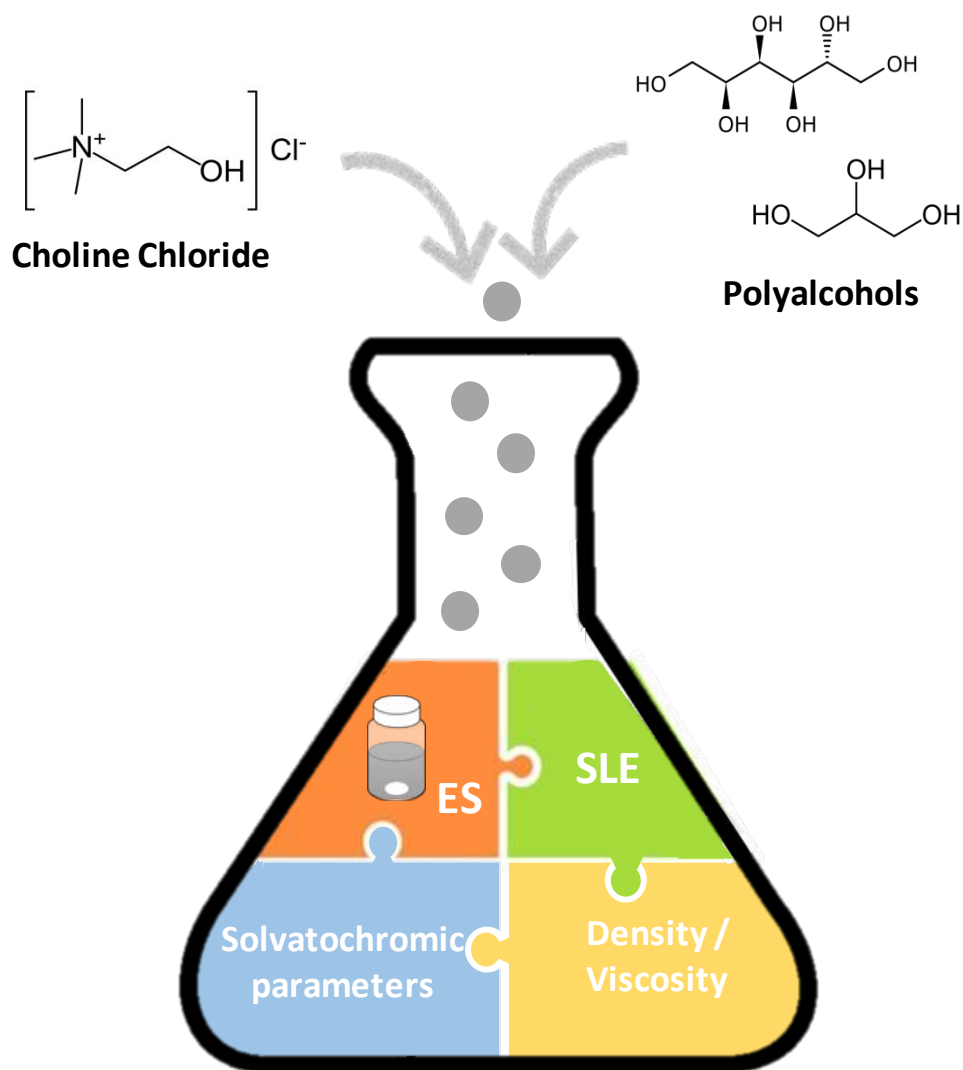
- 1
2
3 Solid Precursors of Deep Eutectic Solvents: The Example of Cholinium Chloride.
4 *Phys. Chem. Chem. Phys.* **2019**, *21*, 15046–15061.
5 <https://doi.org/10.1039/c9cp02548k>.
6
7
8
9 (30) Bagh, F. S. G.; Shahbaz, K.; Mjalli, F. S.; AlNashef, I. M.; Hashim, M. A. Electrical
10 Conductivity of Ammonium and Phosphonium Based Deep Eutectic Solvents:
11 Measurements and Artificial Intelligence-Based Prediction. *Fluid Phase Equilib.* **2013**,
12 *356*, 30–37. <https://doi.org/10.1016/j.fluid.2013.07.012>.
13
14
15
16 (31) Collin, R. L. Polymorphism and Radiation Decomposition of Choline Chloride. *J. Am.*
17 *Chem. Soc.* **1957**, *79*, 6086.
18
19
20 (32) Shanley, P.; Collin, R. L. The Crystal Structure of the High Temperature Form of
21 Choline Chloride. *Acta Crystallogr.* **1961**, *14*, 79–80.
22
23
24 (33) Meng, X.; Ballerat-Busserolles, K.; Husson, P.; Andanson, J. M. Impact of Water on
25 the Melting Temperature of Urea + Choline Chloride Deep Eutectic Solvent. *New J.*
26 *Chem.* **2016**, *40*, 4492–4499. <https://doi.org/10.1039/c5nj02677f>.
27
28
29 (34) Silva, L. P.; Fernandez, L.; Conceição, J. H. F.; Martins, M. A. R.; Sosa, A.; Ortega, J.;
30 Pinho, S. P.; Coutinho, J. A. P. Design and Characterization of Sugar-Based Deep
31 Eutectic Solvents Using Conductor-like Screening Model for Real Solvents. *ACS*
32 *Sustain. Chem. Eng.* **2018**, *6*, 10724–10734.
33 <https://doi.org/10.1021/acssuschemeng.8b02042>.
34
35
36
37 (35) Zhang, Q.; De Oliveira Vigier, K.; Royer, S.; Jérôme, F. Deep Eutectic Solvents:
38 Syntheses, Properties and Applications. *Chem. Soc. Rev.* **2012**, *41*, 7108–7146.
39 <https://doi.org/10.1039/c2cs35178a>.
40
41
42
43 (36) García, G.; Aparicio, S.; Ullah, R.; Atilhan, M. Deep Eutectic Solvents:
44 Physicochemical Properties and Gas Separation Applications. *Energy & Fuels* **2015**,
45 *29* (4), 2616–2644. <https://doi.org/10.1021/ef5028873>.
46
47
48
49 (37) López-Porfiri, P.; Brennecke, J. F.; Gonzalez-Miquel, M. Excess Molar Enthalpies of
50 Deep Eutectic Solvents (DESS) Composed of Quaternary Ammonium Salts and
51 Glycerol or Ethylene Glycol. *J. Chem. Eng. Data* **2016**, *61*, 4245–4251.
52 <https://doi.org/10.1021/acs.jced.6b00608>.
53
54
55
56 (38) Francisco M, van den Bruinhorst A, K. M. Low-Transition-Temperature Mixtures
57 (LTTMs): A New Generation of Designer Solvents. *Angew. Chemie Int. Ed.* **2013**, *52*,
58
59
60

- 3074–3085.
- (39) Marták, J.; Schlosser, Š. Density, Viscosity, and Structure of Equilibrium Solvent Phases in Butyric Acid Extraction by Phosphonium Ionic Liquid. *J. Chem. Eng. Data* **2017**, *62*, 3025–3035. <https://doi.org/10.1021/acs.jced.7b00039>.
- (40) Leron, R. B.; Wong, D. S. H.; Li, M. H. Densities of a Deep Eutectic Solvent Based on Choline Chloride and Glycerol and Its Aqueous Mixtures at Elevated Pressures. *Fluid Phase Equilib.* **2012**, *335*, 32–38. <https://doi.org/10.1016/j.fluid.2012.08.016>.
- (41) Abbott, A. P. Application of Hole Theory to the Viscosity of Ionic and Molecular Liquids. *ChemPhysChem* **2004**, *5*, 1242–1246. <https://doi.org/10.1002/cphc.200400190>.
- (42) Crespo, E. A.; Silva, L. P.; Martins, M. A. R.; Bülow, M.; Ferreira, O.; Sadowski, G.; Held, C.; Pinho, S. P.; Coutinho, J. A. P. The Role of Polyfunctionality in the Formation of [Ch]Cl-Carboxylic Acid-Based Deep Eutectic Solvents. *Ind. Eng. Chem. Res.* **2018**, *57*, 11195–11209. <https://doi.org/10.1021/acs.iecr.8b01249>.
- (43) Martins, M. A. R.; Crespo, E. A.; Pontes, P. V. A.; Silva, L. P.; Bülow, M.; Maximo, G. J.; Batista, E. A. C.; Held, C.; Pinho, S. P.; Coutinho, J. A. P. Tunable Hydrophobic Eutectic Solvents Based on Terpenes and Monocarboxylic Acids. *ACS Sustain. Chem. Eng.* **2018**, *6*, 8836–8846. <https://doi.org/10.1021/acssuschemeng.8b01203>.
- (44) D’Agostino, C.; Harris, R. C.; Abbott, A. P.; Gladden, L. F.; Mantle, M. D. Molecular Motion and Ion Diffusion in Choline Chloride Based Deep Eutectic Solvents Studied by ¹H Pulsed Field Gradient NMR Spectroscopy. *Phys. Chem. Chem. Phys.* **2011**, *13*, 21383–21391. <https://doi.org/10.1039/c1cp22554e>.
- (45) Harifi-Mood, A. R.; Buchner, R. Density, Viscosity, and Conductivity of Choline Chloride + Ethylene Glycol as a Deep Eutectic Solvent and Its Binary Mixtures with Dimethyl Sulfoxide. *J. Mol. Liq.* **2017**, *225*, 689–695. <https://doi.org/10.1016/j.molliq.2016.10.115>.
- (46) Crespo, E. A.; Costa, J. M. L.; Palma, A. M.; Soares, B.; Martín, M. C.; Segovia, J. J.; Carvalho, P. J.; Coutinho, J. A. P. Thermodynamic Characterization of Deep Eutectic Solvents at High Pressures. *Fluid Phase Equilib.* **2019**, *500*, 112249–112252. <https://doi.org/10.1016/j.fluid.2019.112249>.
- (47) Yadav, A.; Trivedi, S.; Rai, R.; Pandey, S. Densities and Dynamic Viscosities of

- (Choline Chloride+glycerol) Deep Eutectic Solvent and Its Aqueous Mixtures in the Temperature Range (283.15-363.15)K. *Fluid Phase Equilib.* **2014**, *367*, 135–142. <https://doi.org/10.1016/j.fluid.2014.01.028>.
- (48) Florindo, C.; Oliveira, F. S.; Rebelo, L. P. N.; Fernandes, A. M.; Marrucho, I. M. Insights into the Synthesis and Properties of Deep Eutectic Solvents Based on Cholinium Chloride and Carboxylic Acids. *ACS Sustain. Chem. Eng.* **2014**, *2*, 2416–2425. <https://doi.org/10.1021/sc500439w>.
- (49) Alomar, M. K.; Hayyan, M.; Alsaadi, M. A.; Akib, S.; Hayyan, A.; Hashim, M. A. Glycerol-Based Deep Eutectic Solvents: Physical Properties. *J. Mol. Liq.* **2016**, *215*, 98–103. <https://doi.org/10.1016/j.molliq.2015.11.032>.
- (50) Siongco, K. R.; Leron, R. B.; Li, M. H. Densities, Refractive Indices, and Viscosities of N,N-Diethylethanol Ammonium Chloride-Glycerol or -Ethylene Glycol Deep Eutectic Solvents and Their Aqueous Solutions. *J. Chem. Thermodyn.* **2013**, *65*, 65–72. <https://doi.org/10.1016/j.jct.2013.05.041>.
- (51) Sarmad, S.; Xie, Y.; Mikkola, J. P.; Ji, X. Screening of Deep Eutectic Solvents (DESs) as Green CO₂ Sorbents: From Solubility to Viscosity. *New J. Chem.* **2016**, *41*, 290–301. <https://doi.org/10.1039/c6nj03140d>.
- (52) Gabriele, F.; Chiarini, M.; Germani, R.; Tiecco, M.; Spreti, N. Effect of Water Addition on Choline Chloride/Glycol Deep Eutectic Solvents: Characterization of Their Structural and Physicochemical Properties. *J. Mol. Liq.* **2019**, *291*, 111301. <https://doi.org/10.1016/j.molliq.2019.111301>.
- (53) Hammond, O. S.; Bowron, D. T.; Edler, K. J. The Effect of Water upon Deep Eutectic Solvent Nanostructure: An Unusual Transition from Ionic Mixture to Aqueous Solution. *Angew. Chemie* **2017**, *129*, 9914–9917. <https://doi.org/10.1002/ange.201702486>.
- (54) Ma, C.; Laaksonen, A.; Liu, C.; Lu, X.; Ji, X. The Peculiar Effect of Water on Ionic Liquids and Deep Eutectic Solvents. *Chem. Soc. Rev.* **2018**, *47*, 8685–8720. <https://doi.org/10.1039/c8cs00325d>.
- (55) Martins, M. A. R.; Silva, L. P.; Schaeffer, N.; Abranches, D. O.; Maximo, G. J.; Pinho, S. P.; Coutinho, J. A. P. Greener Terpene-Terpene Eutectic Mixtures as Hydrophobic Solvents. *ACS Sustain. Chem. Eng.* **2019**, *7*, 17414–17423. <https://doi.org/10.1021/acssuschemeng.9b04614>.

- 1
2
3 (56) Jessop, P. G.; Jessop, D. A.; Fu, D.; Phan, L. Solvatochromic Parameters for Solvents
4 of Interest in Green Chemistry. *Green Chem.* **2012**, *14*, 1245–1259.
5
6 <https://doi.org/10.1039/c2gc16670d>.
7
8
9 (57) Pandey, A.; Pandey, S. Solvatochromic Probe Behavior within Choline Chloride-
10 Based Deep Eutectic Solvents: Effect of Temperature and Water. *J. Phys. Chem. B*
11 **2014**, *118*, 14652–14661. <https://doi.org/10.1021/jp510420h>.
12
13
14 (58) Florindo, C.; McIntosh, A. J. S.; Welton, T.; Branco, L. C.; Marrucho, I. M. A Closer
15 Look into Deep Eutectic Solvents: Exploring Intermolecular Interactions Using
16 Solvatochromic Probes. *Phys. Chem. Chem. Phys.* **2017**, *20*, 206–213.
17
18 <https://doi.org/10.1039/c7cp06471c>.
19
20
21 (59) Teles, A. R. R.; Capela, E. V.; Carmo, R. S.; Coutinho, J. A. P.; Silvestre, A. J. D.;
22 Freire, M. G. Solvatochromic Parameters of Deep Eutectic Solvents Formed by
23 Ammonium-Based Salts and Carboxylic Acids. *Fluid Phase Equilib.* **2017**, *448*, 15–
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
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Synopsis

Design and characterization of sustainable eutectic solvents formed by choline chloride and polyalcohols.