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ARTICLE

A closer look into Deep Eutectic Solvents: exploring intermolecular interactions using solvatochromic probes

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Deep eutectic solvents (DESs) constitute a new class of ionic solvents that has been developing at a fast pace in recent years. Since these solvents are commonly suggested as green alternatives to organic solvents, it is important to understand their physical properties. In particular, polarity plays an important role in solvation phenomena. In this work, the polarity of different families of DESs was studied through solvatochromic responses of UV-vis absorption probes. Kamlet-Taft α , β , π^* and E_TN parameters were evaluated using different solvatochromic probes, as 2,6-Dichloro-4-(2,4,6-triphenyl-N-pyridino)-phenolate (Reichardt's betaine dye 33), 4-nitroaniline, and N,N-diethyl-4-nitroaniline for several families of DESs based on cholinium chloride, DL-Menthol and a quaternary ammonium salt ([N₄₄₄₄]Cl). In addition, a study to understand the difference in polarity properties between DESs and the corresponding ILs, namely ILs based on cholinium cation and carboxylic acids as anions ([Ch][Lev], [Ch][Gly] and [Ch][Mal]), was carried out. The chemical structure of the hydrogen bond acceptor (HBA) in a DES clearly controls the dipolarity/polarizability afforded by the DES. Moreover, Kamlet-Taft parameters do not vary much within the family, but they differ among families based on different HBA, either for DESs containing salts ([Ch]Cl or [N₄₄₄₄]Cl) or neutral compounds (DL-Menthol). A substitution of the HBD was also found to play an important role in solvatochromic probe behaviour for all the studied systems.

Introduction

Solvents are omnipresent in chemical processes and are also one of the major contributors to industrial waste streams. Solvents are used in nearly all industries, from cosmetics, pharmaceuticals and personal care to paints, semiconductors, from biotechnology-based industries to iron and steel production. Consequently, solvents represent a huge economical market, reaching the tenths to hundredths of million tons per year. The implementation of stricter regulations regarding solvent safety and health issues, are revolutionizing the solvents scenario. Today, green and sustainable solvents are becoming a corner stone of modern chemical engineering. In this context, Deep eutectic solvents (DESs) have been emerging since 2004 as a new generation of solvents with a great potential for a variety of applications.¹ DESs can be regarded as a new class of ionic solvents, typically composed of an organic salt and an at least one hydrogen bond donor, which presents a lower melting point than any of its individual components.² The formation of these liquid

compounds at room temperature is due to the formation of hydrogen bonds between an hydrogen bond donor (HBD), such as a carboxylic acid or an alcohol, and a hydrogen bond acceptor (HBA), which is usually the anion in an ammonium salt.³ Please note that in a salt, generally the cation acts as an HBD and the anion as HBA, and in the case of DES formation an extra HBD is added. DESs are currently attracting widespread scientific and technological interest as alternatives to ionic liquids (ILs).^{4, 5} Although these solvents are generally compared to ILs, mainly due to their equivalently negligible vapour pressures at room temperature, they have important advantages such as their straightforward and green synthesis, that does not need any solvent and does not require any further purification steps, their low toxicity and cost, since the compounds used are usually non-toxic, abundant and from renewable resources.^{6, 7} The first proposed DESs were based on cholinium chloride, an essential nutrient, as HBA and different HBD such as urea, glycerol and ethylene glycol, but several DESs based on ammonium and imidazolium salts as HBA have already been proposed.^{8, 9}

One of the most attractive aspects of these alternative solvents is the ability to carefully design their physical-chemical properties, including hydrogen bond donating/accepting ability and polarizability, through the easy manipulation of the chemical structures of the starting compounds. Although DESs are one of the most versatile and environmentally-benign alternative media, due to the huge number of HBD and HBA combinations available, there is a lack in the knowledge of some important solvent properties, such

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as polarity. Polarity is the key indicator of the solvent's solvation ability and thus most solvents are often classified based on their ability to dissolve polar and/or charged species. In molecular solvents, the exact meaning of "polarity" is complex (the sum of all possible interactions between a solvent and any potential solute¹⁰) as many different interactions can be involved, such as hydrogen bonding, π -interactions or van der Waals forces. In the case of ILs and DESs, polarity is still more complex, since both the cations and anions or HBAs and HBDs, can have their own distinct interactions. The polarity of a chemical entity can be measured through the use of solvatochromic probes, which change in the position, intensity and shape of its absorption band(s) due to the change of solvent's polarity.¹¹ Although solvatochromic shifts are commonly used as simple univocal indices to classify the environment, they reflect extremely complex phenomena involving many different intermolecular forces, including coupled dynamical processes of both the molecular probe and the solvent. Solvatochromism can be classified as positive or negative, depending on the occurrence of a bathochromic (red) shift or a hypsochromic (blue) shift with increasing solvent polarity, respectively.¹² In particular, Kamlet–Taft parameters have been extensively used to quantify the hydrogen-bond donating ability (α , acidity), the hydrogen bond accepting ability (β , basicity) and polarity/polarizability (π^*) of ILs and DESs.^{5, 13–15} It should be remarked that polarity is not an absolute property of the pure liquid and^{16, 17} hence, there is no single correct value when comparing polarity scales.^{15, 16} All polarity scales are relative and different scales give different polarities for the same solvent and even different relative polarities can arise for the many different measurement techniques that have been used.¹⁸ Nevertheless, polarity scales have been shown to be very useful to understand a wide range of phenomena such as rate constants, equilibrium constants, solubilities and spectral frequencies, based upon data acquired for a few solvents.^{19, 20, 21}

Only four studies^{21–24} on the characterization of DESs polarities have been reported. The first study of determined the solvatochromic parameters for the most common and popular DESs, namely cholinium chloride: urea (1:2), cholinium chloride: glycerol (1:2) and cholinium chloride: ethylene glycol (1:2).¹⁵ Pandey et al. reported two publications on the use of solvatochromic probes to characterize DESs polarity.^{15, 21} In their work, the effect of temperature and addition of water on the three above mentioned DESs' polarity was studied. They concluded that an increase in temperature results in reduced H-bond donor acidity of the DESs, while no temperature effect was observed on the dipolarity/polarizability and H-bond accepting basicity. It was also shown that addition of water to DESs resulted in increased dipolarity/polarizability and a decrease in H-bond accepting basicity. Very recently, Teles et al.²⁴ published a more detailed study of solvatochromic parameters of DES formed by ammonium-based salts and carboxylic acids. It was showed that the high acidity of the studied DESs was mainly due to the organic acid present in the mixture, and that an increase of the alkyl side chain of both the HBA and the HBD species leads to a lower ability of the

solvent to donate protons. They concluded that DES composed of ammonium-based salts and carboxylic acids present a higher capacity to donate and accept protons when compared to most of the ionic liquids or organic molecular solvents.

In the present work, the aim is to evaluate and discuss the polarity of DESs, which have different chemical structures, using the solvatochromic shift of different probes in the visible absorbance spectrum. Recently, we have compared the densities and viscosities of hydrophilic cholinium-based DESs and corresponding ILs.⁴ We have also studied highly fluid hydrophobic DESs based on DL-Menthol²⁵ while other hydrophobic DESs based on quaternary ammonium salts have also been reported in literature.²⁶ Thus, it is important now to characterize all these different DESs from the point of view of polarity. In this way, a range of DESs, based on hydrophilic HBA (cholinium chloride) and a hydrophobic HBD (tetrabutylammonium chloride or DL-Menthol), combined with several different carboxylic acids, were studied in terms of normalised polarity (E_T) and the Kamlet–Taft parameters (α , β and π^*). Additionally, a comparison of the solvatochromic parameters obtained for hydrophilic DESs and their corresponding cholinium-based ILs is also presented.

Results and discussion

Betaine Dye scale

Due to the large shift in the lowest energy charge-transfer absorption band between polar and non-polar solvents, Reichardt's dye or betaine dye 30 (2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate) is one of the most widely used solvatochromic probes. However, its zwitterionic nature causes its solvatochromic behaviour to be strongly affected by the HBD character of the solvent: it is well known that hydrogen-bond donating solvents stabilize the ground state more than the excited state.²⁷ Since most of our DESs present strong acidic character ($\text{pH} \approx 1$), they extensively interfere with this dye solvatochromic behaviour. To circumvent this problem, a derivative of Reichardt's dye named Reichardt's betaine dye 33 (2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate) was used in this work. Molecular structures of the solvatochromic probes used are presented in Fig. 1.

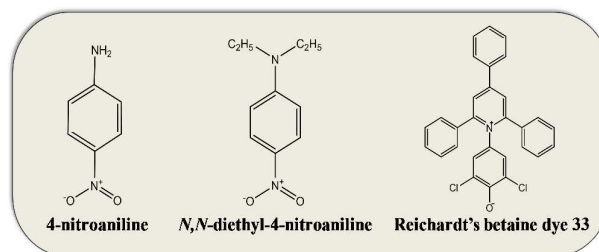


Fig. 1 Chemical structures of the solvatochromic probes used in this work.

The solvatochromic parameter $E_T(33)$ was determined from the lowest energy of charge-transfer absorption band of dye in

the solvent under study, and can be calculated the similarly for $E_T(30)$, using the following equation:

$$E_T(30 \text{ or } 33) = \frac{28591}{\lambda_{\max}} \quad (1)$$

where $E_T(33)$ is in kcal.mol^{-1} and $\lambda_{\max}$ (nm) is the wavelength corresponding to maximum of absorption of the probe in the solvent under study.²⁸

$E_T(33)$ is used as a measure of the solvent's overall polarity, dipolarity/polarizability and/or HBD ability, arising from interactions between the solvent and the dye.²⁹ E_TN is a normalized, thus dimensionless, polarity parameter and varies between 0 for TMS (extremely non-polar) and 1 for water (extremely polar). Thus, its use is recommended instead of $E_T(30)$. Chemical structures and respective acronyms of the ILs and DESs used in this work are presented in Fig. 2 and 3, respectively.

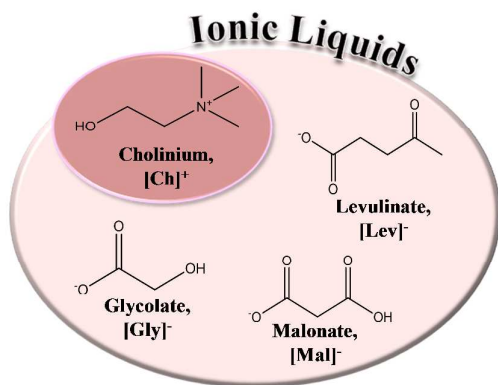


Fig. 2 Chemical structures and respective acronyms of the cholinium-based ionic liquids and deep eutectic solvents used in this work.

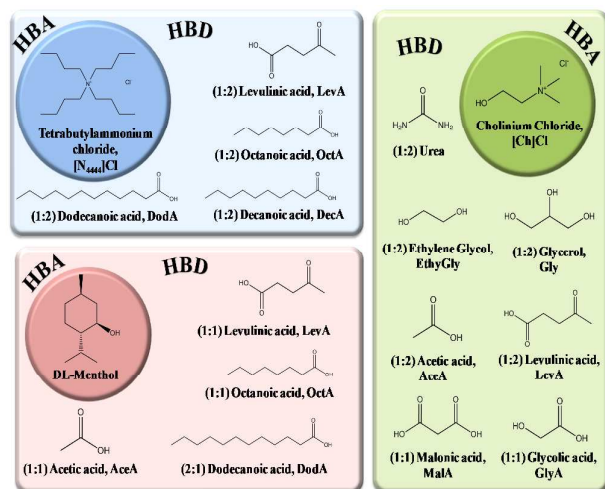


Fig. 3. Chemical structures and respective acronyms of the DESs, using cholinium chloride ([Ch]Cl), DL-Menthol and tetrabutylammonium chloride ([N₄₄₄₄]Cl) as hydrogen bond acceptors (HBA), studied in this work.

Absorbance spectra of Reichardt's 33 were collected in several solvents (DESS and ILs) at room temperature, and the corresponding values of $E_T(33)$ converted into $E_T(30)$ values, through a linear regression analysis using the following equation (2)^{12, 15}:

$$E_T(30) = 0.9953(\pm 0.0287) \times E_T(33) - 8.1132(\pm 1.6546) \quad (2)$$

If Reichardt's dye is being used, the E_TN polarity parameter is easily obtained by measuring the wavelength corresponding to the maximum of absorption of the dye in the solvent under study, according to the following equations:

$$E_{TN} = \frac{[E_T(30)_{\text{solvent}} - E_T(30)_{TMS}]}{[E_T(30)_{\text{water}} - E_T(30)_{TMS}]} = \frac{E_T(30) - 30.7}{32.4} \quad (3)$$

where $E_T(30)$ is given by equation (1).

In Figure 4, the absorbance spectra of Reichardt's 33 dissolved in several ILs and DESS are presented.

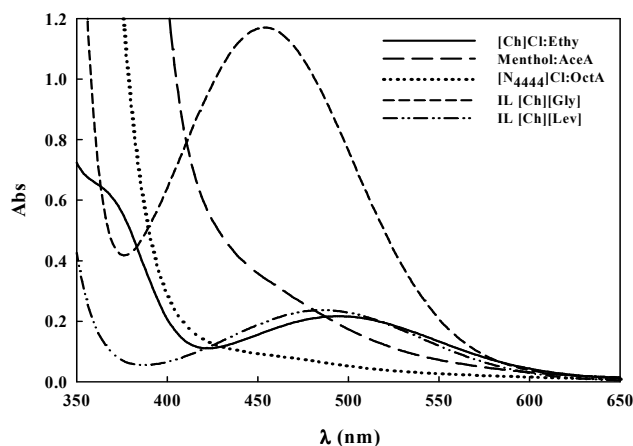


Fig. 4 Example of the lowest energy intramolecular charge-transfer absorption band of Reichardt's betaine dye 33 for some ILs and DESS studied in this work.

It can be observed that the peaks for DL-Menthol:AceA and [N₄₄₄₄]Cl:OctA in the region between 400 nm and 600 nm are difficult to detect. To overcome this issue, first derivatives of the spectra were used to determine the $\lambda_{\max}$. The $\lambda_{\max}$ value, as well as $E_T(33)$ and E_TN calculated using equations (1) and (3), are listed in Table 1 for all the ILs and DESS studied in this work.

Table 1 UV-Vis absorbance maxima (λ_{max}) of Reichardt's 33, $E_T(33)$ and E_TN for all DESs and corresponding ILs.

		λ_{max} of Reichardt's 33 (nm)	$E_T(33)$ (Kcal.mol ⁻¹)	E_TN
Ionic Liquids	[Ch][Lev]	485.07	58.94	0.61
	[Ch][Mal]	428.73	66.69	0.85
	[Ch][Gly]	453.17	63.09	0.74
	[Ch]Cl: LevA	568.89	50.26	0.35
	[Ch]Cl: MalA	442.53	64.61	0.79
	[Ch]Cl: GlyA	562.44	50.83	0.36
	[Ch]Cl: Urea	434.84	65.75	0.81
	[Ch]Cl: Ethy	433.82	65.91	0.83
	[Ch]Cl: Gly	429.99	66.49	0.84
	DL-Menthol:			
Deep	AceA	457.80	62.45	0.72
Eutectic Solvents	DL-Menthol:			
	LevA	456.56	62.62	0.73
	DL-Menthol:			
	OctA	453.12	63.10	0.74
	DL-Menthol:			
	DodA	454.52	62.90	0.73
	[N ₄₄₄₄]Cl: OctA	464.71	61.52	0.69
	[N ₄₄₄₄]Cl: DecA	474.72	60.23	0.65
	[N ₄₄₄₄]Cl: DodA	464.36	61.57	0.69

In order to validate our experimental method, the $E_T(33)$ values for [Ch]Cl:Urea, [Ch]Cl:Ethy and [Ch]Cl:Gly were also measured in this work and compared with those published in literature 65.4²¹, 65.7²¹ and 66.4²³ Kcal mol⁻¹, respectively. There is a good agreement between our results listed in Table 1 and those reported in literature, thus validating the methodology here used. High E_TN values were obtained for the two families of hydrophobic DESs studied in this work, DL-Menthol-based and [N₄₄₄₄]Cl-based, listed in Table 1, demonstrating that these solvents are hydrophobic and polar. For example, if one compares the values of DL-Menthol:OctA (0.74) or DL-Menthol:DodA (0.73) with those of the corresponding quaternary ammonium based DESs, [N₄₄₄₄]Cl:OctA (0.69) and [N₄₄₄₄]Cl:DodA (0.69), only small differences can be observed. Nevertheless, the E_TN values obtained for the DL-Menthol-based DESs are slightly higher than those obtained for [N₄₄₄₄]Cl-based DESs, indicating the important role of HBA in defining the polarity of hydrophobic DESs. Another observation is that E_TN values are almost constant within the same HBA family. For example, the same E_TN value (0.73) was obtained for DL-Menthol:LevA and DL-Menthol:DodA, despite the obvious chemical differences between the HBD of the two DESs. In the same way, similar E_TN values were obtained for [N₄₄₄₄]Cl-based DESs, despite the differences in the chain length of the HBDs used. These observations corroborate the conclusion that the HBA plays a

more important role in overall polarity than the HBD in hydrophobic DESs.

Focusing now on the hydrophilic [Ch]Cl-based DESs, a wider range of E_TN can be observed: [Ch]Cl:MalA (0.79) has the highest E_TN value, while very similar values were obtained for the other two DESs, [Ch]Cl:LevA (0.35) and [Ch]Cl:GlyA (0.36). This means that the DES with HBD based on the diacid (MalA) as HBD is more polar than those based on monoacids with different chemical groups, such as a ketone (in LevA) or an alcohol group (in Gly). In other words, the interactions between the probe and the referred DESs decrease as the groups change from acid to alcohol to ketone, as expected. Comparing the E_TN values obtained for hydrophilic and hydrophobic DESs for the same HBD, [Ch]Cl:LevA (0.35) and for DL-Menthol:LevA (0.73), it can be concluded that the latter is much more polar than the former. This is somehow surprising since the first DESs have an IL as HBA, while the second contains a neutral molecule. Again, and as it was mentioned before when two hydrophobic DESs with the same HBD were compared, this can be attributed to the differences in the HBA: the chloride anion establishes a more stable hydrogen bond with the LevA than that between DL-Menthol and LevA, decreasing the HBD ability of the former and thus its interaction with the probe.

The values here obtained for the three studied ILs are very similar to those found in literature for other common and well-studied ILs. In general, the E_TN values for ILs vary significantly depending upon the nature of cation and anion, ranging from 0.5 to 0.7,¹⁹ in agreement with the results here obtained: [Ch][Lev] (0.61), [Ch][Gly] (0.74), [Ch][Mal] (0.85). The explanation for this variation is essentially related to the length and the hydroxyl group functionalities of the alkyl chains of the anions and their ability to participate in hydrogen-bonding networks. Generally, for the same cation, the E_TN values of ILs decrease in the following order of anions: [HCO₂]⁻ > [NO₃]⁻ > [BF₄]⁻ > [NTf₂]⁻ > [PF₆]⁻, which is the order of decreasing basicity of the anions.³⁰ Regarding the available values of E_TN for common ILs, they are essentially dominated by the cations with the general trend [RNH₃]⁺ = [R₂NH₂]⁺ > [R_xR_yim]⁺ = [Rpy]⁺ > [R₄N]⁺ > [R₄P]⁺, according to the hydrogen bond donor capacity of these cations. It should be noted that the highest values of E_TN are similar to those of highly polar solvents such as water, and the lowest are similar to those of dipolar non-HBD solvents. Finally, comparing among the different ILs studied, where the anion is changed and the cation is kept constant, it can be observed that the E_TN scale is particularly sensitive to the HBD ability of the anion.

Comparing the DESs based on [Ch]Cl and acids with the corresponding ILs, ILs are generally much more polar than the corresponding DESs, since the E_TN for the ILs are generally higher than those of the corresponding DESs. This is in agreement with Pandey's observations, who studied DESs formed from choline chloride combined with 1,2-ethanediol, glycerol, and urea, in 1:2 molar ratios.^{15, 21} Another important observation is that the polarity order observed in the DESs and ILs is maintained, that is, from the most polar to the less polar the following order is attained: MalA > GlyA > LevA.

Kamlet-Taft scale

Hydrogen Bonding Acceptor Ability: β Parameter. The Kamlet-Taft HBA ability (β) is obtained by a solvatochromic comparison method, which compares solvent-induced shifts of the absorption bands of two probes. These probes are selected to be structurally very similar (i.e. homomorphic) except for their capacity as HBD, since one can act as HBD and the other cannot. Another characteristic of these probes is that they have a good correlation of both their spectra in non-HBA solvents, but with significant deviations in their spectra in hydrogen bond accepting solvents, so that the construction of a scale based upon these differences is possible.¹⁷ Kamlet and Taft²⁰ proposed two pairs of probes, 4-nitroaniline/*N,N*-diethyl-4-nitroaniline or 4-nitrophenol/ 4-nitroanisole, to construct the β scale. In this work, the 4-nitroaniline/*N,N*-diethyl-4-nitroaniline probe set was used, since they are the most commonly used pair for ionic liquids.³¹ The β values for the ILs and DESs under study are listed in Table 2 and were calculated using the following equations:

$$\beta = \frac{0.76 (\Delta\bar{\nu}_{\text{solvent}} - \Delta\bar{\nu}_{\text{cyclohexane}})}{\Delta\bar{\nu}_{\text{DMSO}} - \Delta\bar{\nu}_{\text{cyclohexane}}} \leftrightarrow$$

$$\beta = \frac{1.035 \bar{\nu}_{N,N\text{-diethyl-4-nitroaniline}} + 2.64 - \bar{\nu}_{4\text{-nitroaniline}}}{2.80} \quad (5)$$

where $\Delta\bar{\nu} = \bar{\nu}_{N,N\text{-diethyl-4-nitroaniline}} - \bar{\nu}_{4\text{-nitroaniline}}$

Table 2 Kamlet-Taft parameters, using the dye set: Reichardt's 33, *N,N*-diethyl-4-nitroaniline and 4-nitroaniline.

		α	β	π^*
Ionic Liquids ^a	[Ch][Lev]	1.07	1.03	1.00
	[Ch][Mal]	1.55	0.62	1.04
	[Ch][Gly]	1.29	0.79	1.08
Deep Eutectic Solvents	[Ch]Cl: AceA	b	0.53	1.10
	[Ch]Cl: LevA	0.51	0.57	1.00
	[Ch]Cl: Mala	1.39	0.42	1.08
	[Ch]Cl: GlyA	0.49	0.50	1.08
	[Ch]Cl: Urea	1.42	0.50	1.14
	[Ch]Cl: Ethy	1.47	0.57	1.07
	[Ch]Cl: Gly	1.49	0.52	1.11
	DL-Menthol: AceA	1.64	0.60	0.53
	DL-Menthol: LevA	1.56	0.58	0.66
	DL-Menthol: OctA	1.77	0.50	0.41
	DL-Menthol: DodA	1.79	0.57	0.37
	[N ₄₄₄₄]Cl: LevA	b	0.82	1.06
	[N ₄₄₄₄]Cl: OctA	1.41	0.99	0.76
	[N ₄₄₄₄]Cl: DecA	1.36	0.97	0.73
	[N ₄₄₄₄]Cl: DodA	1.45	1.04	0.71

^aOther ILs were synthesized in order to provide direct comparison between ILs and DESs, but solvatochromic probes measurements were not possible due their solid physical state.

^bNo peak could be detected using the same probe for direct comparison.

In Figs. 5 to 8, the obtained Kamlet-Taft parameters are organized by families of hydrogen bond acceptors, [Ch]Cl-, DL-Menthol- and [N₄₄₄₄]Cl-based DESs and finally a comparison for cholinium-based ILs and the corresponding DESs is presented.

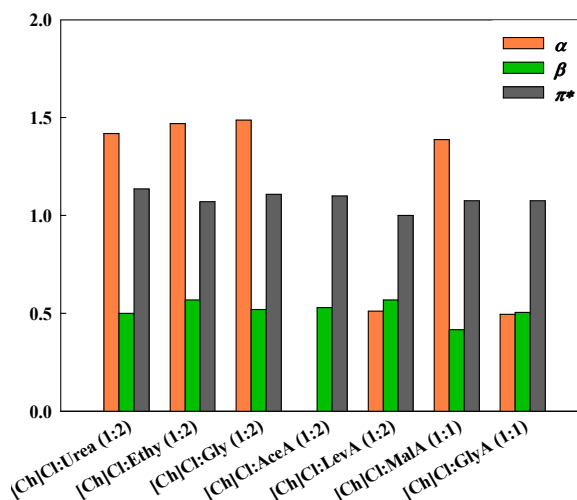


Fig. 5 Kamlet-Taft parameters obtained for a range of cholinium-based DESs.

The β values obtained for [Ch]Cl:Urea, [Ch]Cl:Ethy and [Ch]Cl:Gly are in agreement with those reported in the literature by Pandey et al.,²¹ where [Ch]Cl:Urea has the lowest β value, followed by [Ch]Cl:Gly and [Ch]Cl:Ethy. This can be attributed to the basicity of the HBD, since urea is by far the most basic compound, followed by glycerol and ethylene glycol, with pKa values of 0.10, 14.15 and 14.22, respectively. Regarding the β values obtained for [Ch]Cl: Urea, it is interesting to observe that the presence of the C=O group in urea does not increase the β value. In the case of [Ch]Cl: LevA, the effect of the C=O group in levulinic acid is still there, but the effect is smaller than for the IL analogue. Nevertheless, note that levulinic acid does have a carbonyl group which can act as a HBA.

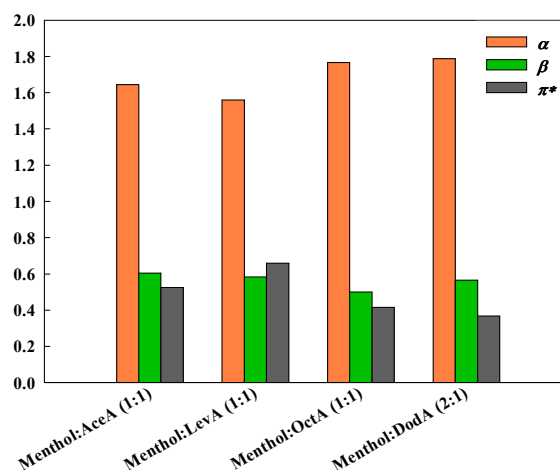


Fig. 6 Kamlet-Taft parameters obtained for a range of DL-Menthol-based deep eutectic solvents.

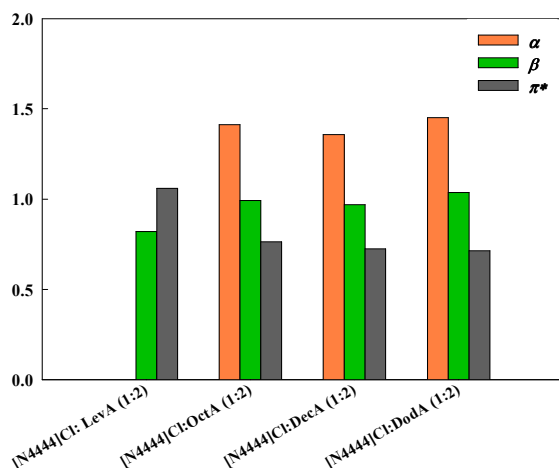


Fig. 7 Kamlet-Taft parameters obtained for a range of [N₄₄₄₄]Cl-based DESs studied in this work.

It can be seen that the values for the [Ch]Cl-based and the DL-Menthol-based DESs are moderate and similar to each other, while those for [N₄₄₄₄]Cl-based DESs are much higher. For example, the β value of [Ch]Cl:LevA (0.58) is similar to that of DL-Menthol:LevA (0.58) leading us to think that the influence of the HBA is negligible. However, comparing β values obtained for DL-Menthol-based DESs with those for [N₄₄₄₄]Cl-based DESs for the same HBD, a large difference can be observed. For example, the β value for DL-Menthol:OctA (0.50) is almost half of that of [N₄₄₄₄]Cl:OctA (0.97). This fact indicates that the nature of the HBA, or more precisely the interaction between the HBD and HBA which limits those with the probe, is of crucial importance in modulating the β results.

Regarding only the hydrophobic DESs studied in this work, it can be concluded that although very different values were obtained for the two families, DL-Menthol- and [N₄₄₄₄]Cl-based DES, no large differences were obtained among the members of the same family, indicating the small effect of the HBDs on the acidity of the DESs. In particular, increasing alkyl chain of the HBD has very little effect on this descriptor in both families. Furthermore, the extra tunability of DES polarity by the easy introduction of different HBD/HBA ratios needs to be highlighted.

The β values for the studied cholinium-based ILs are consistently higher than those of the corresponding DESs. This is due to the fact that the IL anion is the deprotonated form of the acid while the DES contains the protonated form acid, and thus the deprotonated form should be less hydrogen bonding acceptor than the protonated form. To be highlighted the very high value of β for [Ch][Lev], with a value of 1.03, while the value found for [Ch]Cl:LevA is 0.58, similar to the other cholinium-based DESs. Moreover, [Ch]Cl:LevA is also composed of two moles of levulinic acid as opposed to the IL, where only 1 mole is present.

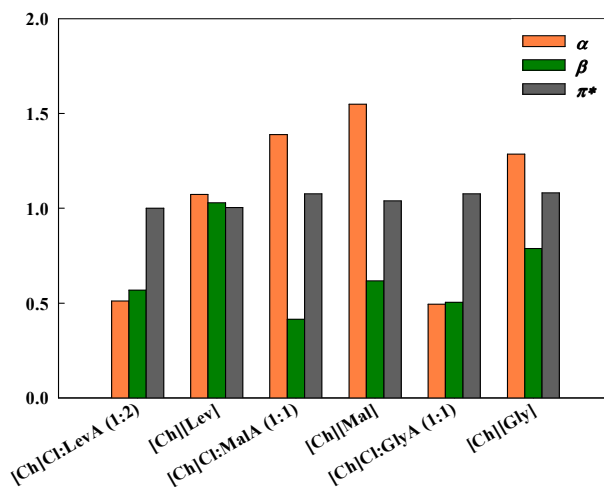


Fig. 8 Kamlet-Taft parameters obtained for a range of cholinium-based ILs and corresponding DESs.

As mentioned before the large β for [Ch][Lev] can be possibly explained due to the fact that levulinic acid anion can only act as HBA, while malonic and glycolic acid anions still have one acid group and one alcohol group, respectively and thus are able to act as HBA and HBD.

The higher values of β for the studied ILs, when compared to those of the corresponding DES, lead to the conclusion that the formation of DES, through establishment of hydrogen bonds, decreases the capacity of the DES to engage in further hydrogen bonds network as HBD. It has been demonstrated that for ILs the β value is dominated by the anion while the cation just plays a secondary effect.³²

Hydrogen Bonding Donor Ability: α Parameter. The Kamlet-Taft parameter α provides a measure of a solvent's hydrogen-bond donating acidity (HBD) and is calculated using Reichardt's dye $E_T(33)$ parameter and the π^* parameter using the following equation:

$$\alpha = 0.0649E_T(33) - 2.03 - 0.72\pi^* \quad (6)$$

where $E_T(33)$ and π^* were calculated using equations (1) and (7), respectively.

For the vast majority of the studied DESs and ILs, the α values obtained are higher than unity and thus higher than the values found for other common and well-studied ILs in the literature. In the literature, there are only a few cases of ILs composed of the imidazolium cation that display similar α values, such as 1-hydroxyethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide with an α value of 1.14 and 1-glyceryl-3-methylimidazolium chloride with an α value of 1.12.¹⁷ However, minor effects can be highlighted. For example, in the family of ILs it can be seen that [Ch][Lev] has

the lowest value (1.07), which is probably justified by the levulinic acid anion has no HBD functional group. In the [Ch][Mal] IL, the value of 1.55 can be related to the acid group in malonic acid anion that can act as a HBD. Finally, for [Ch][Gly], α value of 1.29 may be due to the OH group on glycolic acid anion that can act as a HBD, but not as strong as the acid group on malonic acid anion. Regarding the family of alcohol-based DESs, it is important to refer that there is also a small effect on α values (1.42 to 1.49) essentially due to the –OH group present on the ethyleneglycol and glycerol compounds. Concerning the family of cholinium-based DESs composed of carboxylic acids, the effect of the two acid groups in the malonic acid is translated in high value of α (1.39). However, in the case of glycolic acid the presence of the –OH group has little effect, leading to a lower α value (0.49).

Comparing the α values for the tetrabutylammonium-based ILs found in the literature¹⁷ with the corresponding [N₄₄₄₄]Cl-based DES obtained in this work, it can be concluded that α values for the ILs are much lower than those here obtained for the DES. For example, the α value for tetrabutylammonium 2-(cyclohexylamino)ethanesulfonate is 0.56, for tetrabutylammonium 2-[bis(2hydroxyethyl)amino]ethanesulfonate it is 0.31 and for tetrabutylammonium 2-hydroxy-4-morpholinepropanesulfate it is 0.28, which means the DES α values are 2 to 5 times higher than those observed in ILs. As already reported, and in line with the present study, there seems to be competition between the HBD and probe dye solute for the proton. The α values of the studied compounds are controlled by the ability of the compounds to act as a HBD moderated by its HBA ability.

Polarisability/Dipolarity π^* Parameter. The π^* parameter provides a measure of a solvent's dipolarity and polarizability. In the Kamlet–Taft methodology, the π^* value is the most open to interpretation and the hardest to definitively determine as a reproducible value, and consequently presents the largest deviation. To avoid these problems, the Kamlet–Taft π^* scale was first created using seven primary solvatochromic dyes with strong and symmetric solvatochromic absorption spectra. The variability in reported values for other systems, such as ILs, arises due to the number of specific dyes being used to determine π^* . As the solvent-dye interaction is unique, this resulted in the calculated value of π^* being unique to each dye.

The original π^* values were an average of the values for all of the solvatochromic dyes used, with a normalisation between 0 (cyclohexane) and 1 (dimethylsulfoxide). Since in this work, we used the three most commonly used Kamlet–Taft dyes, *N,N*-diethyl-4-nitroaniline, 4-nitroaniline and Reichardt's dye, the π^* parameter was calculated from spectroscopic data of the *N,N*-diethyl-4-nitroaniline probe in our solvents using the following equations:

$$\pi^* = \frac{\bar{\nu}_{\text{solvent}} - \bar{\nu}_{\text{cyclohexane}}}{\bar{\nu}_{\text{DMSO}} - \bar{\nu}_{\text{cyclohexane}}} \quad (7)$$

$$\pi^* = 0.314(27.52 - \bar{\nu}_{N,N\text{-diethyl-4-nitroaniline}}) \quad (8)$$

where $\bar{\nu} (cm^{-1}) = 10^7 / \lambda_{\text{max}} (nm)$. The obtained π^* values for the solvents under study are shown in Table 2. The π^* values obtained for the ILs and cholinium-based DESs are high in comparison with those of conventional organic solvents and ILs, which can be as high as 0.9.³³ π^* values can be affected by both the cation and anion,³⁴ and tend to be higher in ILs than most organic solvents due to the degree of delocalisation of the charge between the ions.

Major differences between the cholinium-based hydrophilic DESs and the hydrophobic DESs (either composed by DL-Menthol or [N₄₄₄₄]Cl) were found. Both cholinium-based ILs and DESs studied in this work present similar π^* values, around the unity, meaning that for these compounds the π^* values are largely determined by the cholinium cation (HBA), and that chemical nature of the anion/does not greatly affect the dipolarity/polarizability. On the other hand, no significant differences were observed for the π^* values of cholinium-based DESs containing acids and the corresponding ILs, meaning that no difference in terms of dipolarity/polarizability is found between ILs and the corresponding hydrophilic DESs. As for the hydrophobic DESs, it can be seen that both the DL-Menthol-based and the [N₄₄₄₄]Cl-based families have lower π^* values than the [Ch]Cl-based hydrophilic DESs, indicating that the former are less dipolar and/or polarisable than the latter. For example, for the π^* value for [Ch]Cl:LevA (1.00) is much higher than that for DL-Menthol:LevA (0.66). Comparing the two families of hydrophobic DESs, DL-Menthol-based DESs have lower values of π^* than the [N₄₄₄₄]Cl-based DESs. This can be particularly appreciated when the HBD is maintained, such as in the case of DL-Menthol:OctA (0.41) and [N₄₄₄₄]Cl:OctA (0.76). Thus, it can be concluded that the HBA plays the dominant role for this descriptor since the studied compounds can be organized according to the following π^* trend: Cholinium-based ILs $\approx$ Cholinium-based DESs > [N₄₄₄₄]Cl-based DESs > DL-Menthol-based DESs, where the latter is the family with the lowest values of π^* . This trend can be explained by the fact that the ILs and cholinium based DES are constituted by charged moieties with polar groups, thus are more polar than the [N₄₄₄₄]Cl-based DESs, which are constituted by charged moieties with apolar alkyl chains, which are more polar than the DL-Menthol-based DESs, which are constituted by non-charged compounds. The HBD role in the π^* parameter within each one of the families can also be clearly seen. The π^* value decreases with the increase of the alkyl chain of the HBD, as expected. The π^* values of DL-Menthol-based DESs decrease as follows: DL-Menthol:AceA > DL-Menthol:OctA > DL-Menthol:DodA, and the same trend is observed for the [N₄₄₄₄]Cl-based DESs. Thus, it can be concluded that the increase of the non-polar part of the HBD decreases the overall polarizability of the DESs, as expected.

Experimental

Materials

2,6-Dichloro-4-(2,4,6-triphenyl-N-pyridino)-phenolate (Reichardt's betaine dye 33), 4-nitroaniline, and N,N-diethyl-4-nitroaniline were purchased from Fluka ($\geq 97\%$ mass fraction purity), Sigma Aldrich ($\geq 99\%$ mass fraction purity) and Frinton Laboratories, respectively, and were used as received. For the synthesis of the ILs the following reagents were used: Cholinium bicarbonate solution (80% mass fraction purity in H_2O), malonic acid (99% mass fraction purity), glycolic acid (99% mass fraction purity) were purchased from Sigma Aldrich and Levulinic acid (98% mass fraction purity) was supplied by Acros Organics ($> 98\%$ mass fraction purity). Methanol and diethyl ether were purchased as AnalaR NORMAPUR (VWR chemicals) and dichloromethane was purchased as GPR Rectapur (VWR chemicals), and were used as received. For the synthesis of the deep eutectic solvents the following reagents were used: cholinium chloride ($[\text{Ch}]\text{Cl}$) ($\geq 98\%$ mass fraction purity) and tetrabutylammonium chloride ($[\text{N}_{4444}]\text{Cl}$) ($> 97\%$ mass fraction purity) were purchased from Sigma-Aldrich and were dried under vacuum prior to use. Urea, ethylene glycol, glycerol, levulinic acid, glycolic acid, malonic acid, acetic acid, octanoic acid, decanoic acid and dodecanoic acid (all $\geq 99\%$ mass fraction purity) were purchased from Sigma-Aldrich and used as supplied.

Methods

Synthesis of ILs. The ILs used in this work, namely the cholinium levulinate ($[\text{Ch}][\text{Lev}]$), cholinium malonate ($[\text{Ch}][\text{Mal}]$) and cholinium glycolate ($[\text{Ch}][\text{Gly}]$), were prepared by dropwise addition of the corresponding acid (1:1) to aqueous cholinium bicarbonate, following an established procedure.³⁵ The mixtures were stirred at ambient temperature and pressure for 12 h. The resulting products were washed with diethyl ether to remove any unreacted acid. Excess water and traces of other volatile substances were removed first by rotary evaporation, and then by stirring and heating under vacuum. The chemical structures and the purities of the synthesized cholinium-based ILs were confirmed by ^1H and ^{13}C NMR. All the IL samples were dried prior to their use by stirring and heating under vacuum at moderate temperature (40 $^\circ\text{C}$, > 48 h, ca. 0.01 mbar). Their water contents were determined by Karl Fischer titration (831 KF Coulometer, Metrohm) and considered in all experiments.

Synthesis of DESs. All DESs were prepared by mixing the HBA, cholinium chloride, DL-Menthol or tetrabutylammonium chloride, with the respective HBD, in a certain mole ratio. The resulting mixtures were then ground in a mortar with a pestle at room temperature until a homogeneous, colourless liquid had been formed. The water content was determined by Karl Fisher titration (model Metrohm 831 Karl Fisher coulometer).

Solvatochromic probes. Stock solutions of all probes were prepared by dissolution in dichloromethane in pre-cleaned amber glass vials. The required amount of each probe was weighed using a Sartorius CPA Analytical Balance CPA224S with a precision of 0.1 mg. An appropriate amount of the probe solution was transferred from the stock to the 1 mm

light path quartz cuvette. The dichloromethane was evaporated using a gentle stream of high purity nitrogen gas. A pre-calculated amount of DES was directly added to the cuvette and the solution thoroughly mixed. A Perkin-Elmer Lambda 25 double beam spectrophotometer was used for acquisition of the UV-Vis molecular absorbance data. All spectroscopic measurements were performed in triplicate starting from the sample preparation.

Conclusions

Owing to the very large gap in understanding solvent-solute interaction in DESs, and considering that DESs and their corresponding ILs present a significant opportunity for a wide array of fields, the knowledge and understanding of their polarity in terms of their chemical structure is vital for their confident design for specific applications. To that end, solvatochromic data, polarity (E_T and E_T^N) and Kamlet-Taft parameters (α , β , π^*) were obtained two different families of DES: those based on salts, such as cholinium chloride and tetrabutylammonium chloride, and those based on neutral compound, DL-Menthol. The polarity properties of the cholinium-based DESs were studied and compared for the first time with the corresponding ILs. A structural study on the influence of the HBD or the HBA, as well as increasing the alkyl chain length in a DES on polarity and on Kamlet-Taft parameters at room temperature was carried out. It was found that all the DES investigated display high values of hydrogen bonding acidity, probably due to the organic acids presented in all systems. On the other hand, the hydrogen bonding basicity in these compounds does not vary much within the same HBA family, but substantially differs from $[\text{Ch}]\text{Cl}$ family to $[\text{N}_{4444}]\text{Cl}$ family and DL-Menthol family.

It is also important to note that while one of the general characteristics of ILs is the dipolarity/polarizability parameter uniformly high irrespective of the chemical structures of the cations and anions, the same is not observed for DESs. In a DES the molecular structure of the hydrogen bond acceptor (HBA) clearly controls the dipolarity/polarizability afforded by the DES. Moreover, the Kamlet-Taft and polarity parameters of several families of DESs based on different acceptors, namely salts (cholinium chloride and $[\text{N}_{4444}]\text{Cl}$) and a neutral compound (DL-Menthol) here reported demonstrate that DES displays a high capacity to donate and accept protons when compared to common solvents and also ILs. In summary, DESs polarity can be easily designed by the convenient choice of their components.

Conflicts of interest

There are no conflicts to declare.

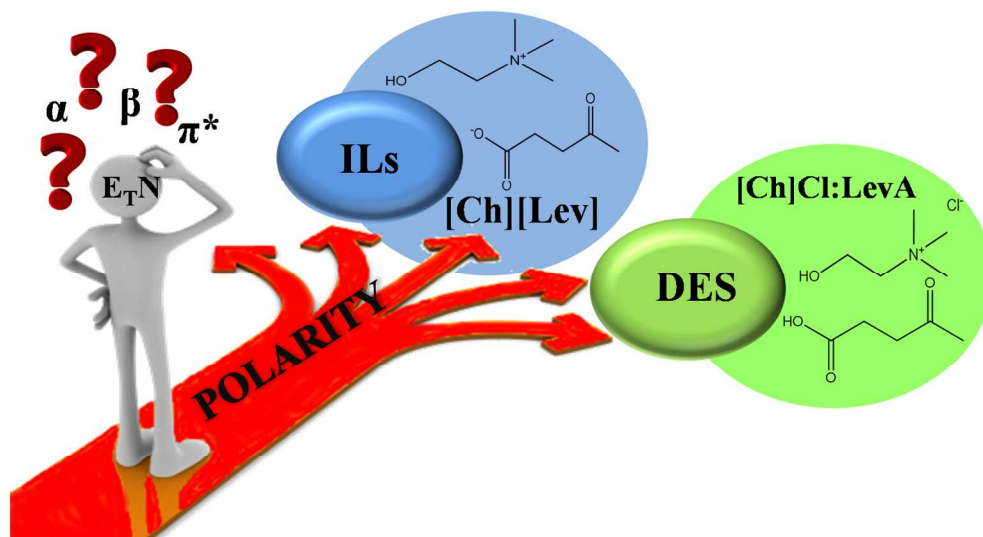
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