

Spectroscopic Analysis of Solvatochromic Properties in Some Deep Eutectic Solvents and Their Aqueous Mixtures

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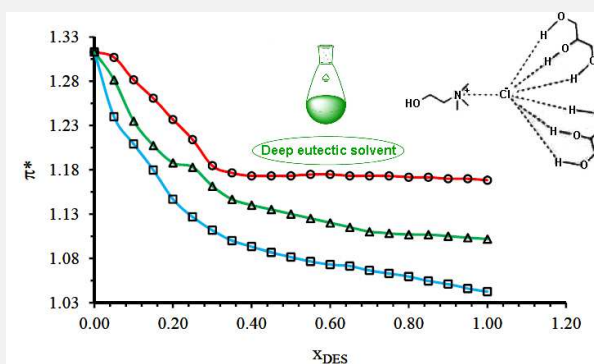


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ABSTRACT

To study the polarity scale of three deep eutectic solvents (DESs), *i.e.* choline chloride + glycerol (1:2), choline chloride + ethylene glycol (1:2), and choline chloride + lactic acid (1:2), and their mixtures with water (in the whole mole fraction range), Kamlet-Taft solvent parameters (α , β , and π^*), Dimroth-Reichardt's $E_T(30)$ parameter were experimentally measured at constant temperature 298.15 ± 0.1 K. These parameters were obtained based on UV-Vis absorbance of some solvatochromic probes. The spectral changes of these indicators were interpreted in terms of specific and nonspecific dye-solvent interactions. The parameter $E_T(30)$ was obtained from the electronic absorbance of the betaine dye within the mixtures. It was found that the polarity, polarizability, and acidity of the co-solvent mixtures decrease by increasing the mole fraction of DESs in the system, while the basicity of the media increases with the mole fraction of DESs.



Keywords: Deep eutectic solvents, solvatochromic properties, Kamlet-Taft parameters, Dimroth-Reichardt scale, aqueous DES mixtures

1. Introduction

Deep eutectic solvents (DESs) are a new group of room temperature ionic liquids that have various properties such as biodegradability, low vapor pressure, wide liquidus range, nonflammability, high solvability, and relatively unreactive with water. However, low toxicity, easy availability, and low-cost and facile synthesis make DESs better solvents or materials than many ionic liquids [1-2]. DESs are considered suitable candidates as green media or environment-friendly solvents that can be utilized for a variety of technological applications. In general, these liquids are a binary mixture in an appropriate molar ratio of a hydrogen bond acceptor (HBA) group, *e.g.*, a salt, and the other a hydrogen bond donor (HBD) group, such as polyols [3-5]. The hydrogen bonding interactions between HBA and the HBD groups, typically lead to DESs.

It has been reported in the literature that the addition of co-solvents, such as molecular solvents (water, alcohols, etc.) to DESs, can greatly vary their physicochemical properties of them [6]. Therefore, binary mixtures of DESs with co-solvents can show new physicochemical properties compared to pure DESs. The tunable nature of DESs opens up the feasibility of their application as a solvent in phase equilibria, catalysis, and chemical synthesis [7]. It is well-known that the intermolecular interactions in a mixture system play an essential role in changing the physicochemical properties of the system [8,9]. Thus, it is important and interesting to understand how the interactions between DES and co-solvents will affect the properties of their mixture.

The analysis of shifting UV-Vis absorbance spectra of a series of organic chromophores as solvatochromic indicators by varying the composition of the co-solvent mixture is one of the simplest ways to measure the possible interactions in solvent systems [10,11]. The one-parameter Dimroth-Reichardt $E_T(30)$ scale and Kamlet-Taft (K-T)

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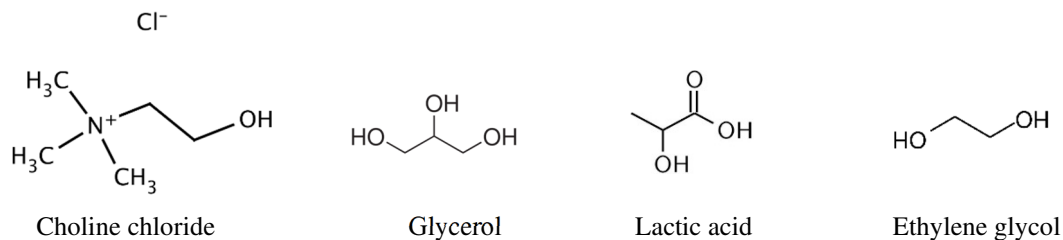
parameters are the most comprehensive and frequently used qualitative and quantitative solvatochromic indexes of solvent microscopic interactions, respectively. The $E_T(30)$ parameter is a simplistic polarity scale and the K-T parameters include α , β , and π^* , which quantify the ability of HBD (acidity) and HBA (basicity) and polarity/polarizability of the solvent system, respectively [12,13]. An increase in one or more of the K-T parameters in the mixture over the values of both pure solvents K-T parameters is referred to as “synergism”. Synergism in K-T parameters has been reported for many HBD-HBA solvent mixtures, due to the occurrence of HBD-HBA complex molecules that have either higher or lower polarity, higher or lower basicity, or higher or lower acidity than both of the pure solvent values [14].

A key aim of this work is to evaluate four solvatochromic parameters ($E_T(30)$, π^* , α , β) in green DESs prepared by mixing choline chloride and glycerol, choline chloride and ethylene glycol as well as choline chloride and lactic acid in a mole ratio of 1:2 and their mixtures with water (in the whole compositional range). Three solvatochromic indicators (4-Nitroaniline, *N,N*-dimethyl-4-nitroaniline, and 2,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate or betaine dye (30) were used to determine these four solvatochromic parameters.

2. Materials and methods

2.1. Chemicals

Choline chloride (ChCl) (>99%), was supplied from Merck and was dried for 2 days at 323 K in a high-vacuum oven before use. Lactic acid (LA) (>99%), ethylene glycol (EG) (>99.5%), and glycerol (Gly) (>99%) as spectrophotometric grades were obtained from Merck and were dried by a 3 Å molecular sieve. The structures of the selected chemicals for the preparation of DESs are presented in **Scheme 1**. The solvent acetone (>99.8%), was purchased from Merck. Betaine dye 30 (BD) (>99%), 4-nitroaniline (NA) (>99%), and *N,N*-dimethyl-4-nitroaniline (DMNA) (>98%) were obtained from Sigma-Aldrich and were used as received. Twice-distilled water with conductivity less than $0.8 \mu\Omega^{-1} \text{ cm}^{-1}$ at 298.15 K was used to prepare the aqueous DES mixtures under investigation. The binary mixtures were prepared by weighing with an electronic analytical balance (KERN model ACJ 220-4) with uncertainty in the mass of $\pm 10^{-7}$ kg.



Scheme 1. Molecular structure of DES components used in this work

2.2. DESs preparation

Choline chloride-based deep eutectic solvents used in this work include ChCl/Gly (1:2), ChCl/EG (1:2), and ChCl/LA (1:2). For the preparation of each DESs, the required amounts of dried choline chloride was added to each hydrogen-bond donor (Gly, EG, and LA) in screw-capped glass vials. The mixtures were heated at temperature 353.15 K in an oil bath and stirred for 3-4 h with constant stirring at around 500 rpm until a colorless liquid and homogenous liquid without any precipitation was obtained. The prepared DESs were cooled to room temperature and were then placed into a vacuum oven for 24 h to reduce the content of water/moisture.

2.3. Solvatochromic measurements

The solvatochromic measurements were carried out by a Perkin-Elmer (Lambda 25) UV-Vis spectrophotometer equipped with a PTP-1 Peltier temperature controller accessory, at 298.15 ± 0.1 K. To begin the measurements, first a stock solution (4.0 ml, 1×10^{-2} M) of each indicator dye was prepared in high purity acetone and then an appropriate aliquot of this solution was transferred to 10 mL glass volumetric tubes. After the evaporation of the solution by vacuum, the known volume of solvent water or DESs under study was pipetted into the tubes in order to obtain absorbance values in the range of 0.8-1.2 in absorption units. All indicator solutions prepared were kept in dark glass

vials in the refrigerator. In the next step, the spectrophotometric measurements were carried out as two series titrations: in the first series, for each binary water/DES system, a 1.2 ml solution of the dye prepared in solvent water (solution 1) was placed in 1 cm quartz cuvette and then weighed (the weight of empty cuvette has been previously measured). After recording the electronic absorption spectrum, a 0.2 ml solution of the same dye prepared in DES solvents mentioned above (solution 2) was added and the cuvette was weighed. Then the solution was vigorously stirred so that a steady-state solution was prepared and the spectrum of the new solution was recorded. The procedure was repeated for further additions of solution 2 until the final cuvette volume reached 3.4 ml. The second series of titration was done starting with solution 2 (1.6 ml) and adding volumes of solution 1 (0.03 ml) until the final cuvette volume reached 3.3 ml. The UV-Vis spectrum of the indicator dyes was recorded over the wavelength ranges of $\lambda = 300\text{-}500$ nm for NA, 350-600 nm for DMNA, and 400-700 nm for BD. Finally, the wavelength of maximum absorption of each of the indicator dyes in different compositions of the mixed water/DES solvents studied was recorded for the next calculations. For each dye, three individual solvatochromic measurements were repeated, and the average value was reported.

2.4. Solvatochromic parameters calculation

The values of solvatochromic parameters $E_T(30)$, α , β and π^* were calculated from the maximum wavelength (λ_{\max} in nm) obtained for dyes BD, NA, and DMNA as a function of mole fraction in binary mixtures of ChCl/Gly, ChCl/EG, and ChCl/LA with water by means of the following equations [11,15-18]

$$E_T(30) = 28590.5 / \lambda_{BD} \quad (1)$$

$$\alpha = \frac{(13180 / \lambda_{DMNA}) + (10^4 / \lambda_{BD}) - 47.7}{5.47} \quad (2)$$

$$\beta = \frac{(9841 / \lambda_{DMNA}) - (10^4 / \lambda_{NA}) + 3.49}{2.759} \quad (3)$$

$$\pi^* = \frac{28.18 - (10^4 / \lambda_{DMNA})}{3.52} \quad (4)$$

According to the above equations, the polarity scale $E_T(30)$ is the molar transition energy of dye BD [15]. The α scale can be determined from the solvatochromic comparisons of dyes BD and DMNA [16]. In a similar method, the comparison between a solvatochromic shift of dyes DMNA and NA was used to construct β α scales [17]. The scale π^* is based on the solvatochromic shift of dye DMNA [18]. All the calculations were performed in Excel (Microsoft Office 2016).

3. Results and discussion

3.1. Reichardt's polarity scale

The experimental wavelengths corresponding to the absorption maxima obtained for dyes BD, NA, and DMNA as a function of mole fraction of both water and DESs (ChCl+Gly, ChCl+EG, and ChCl+LA) at 298.15 K are listed in Tables 1-3. Based on these data, the values of Reichardt polarity parameter $E_T(30)$ were determined by means of Eq. (1) and are summarized in **Tables 1-3** and then depicted in **Figure 1**.

As shown in **Figure 1**, the polarity scale E_T decreases non-linearly with the addition of DES to water over the full compositions in all mixtures. It should be noted that E_T could not be determined in a mixture of water with ChCl+LA, because of the protonation of BD. With the addition of DES to water, the polarity declines sharply up to near $x_{DES} = 0.25$ and 0.35 in a water mixture with ChCl+Gly and ChCl+EG, respectively. A decrease in the polarity goes on up to pure DES but with a mild slope. A comparison between two DESs indicates that ChCl+Gly is more polar than ChCl+EG. In addition, no significant synergistic effect was observed in **Figure 1**. Synergism takes place in mixtures showing high hydrogen-bonding association such that the polarity of the mixture is out of the range of polarity of pure solvents [13,19,20].

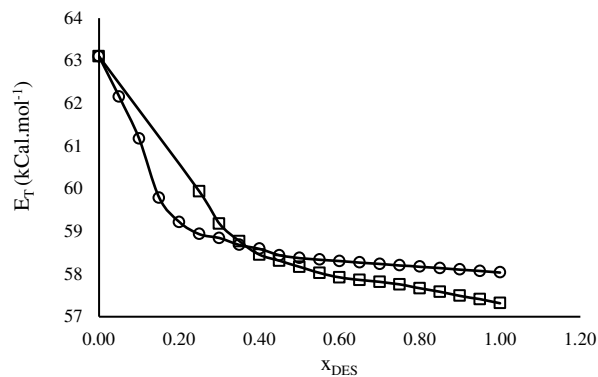


Figure 1. The property E_T of solvent as a function of mole fraction of DESs in aqueous mixtures of ChCl+Gly (\circ) and ChCl+EG (\square) at 298.15 K.

3.2. Kamlet-Taft ($K-T$) parameters

Kamlet-Taft parameters were determined from the wavelength of maximum absorption of the dyes BD, NA, and DMNA by using Eqs. (2)-(4) and the obtained values for π^* , α , and β are presented as a function of mixture composition in Tables 1, 2, 3, and Figures 2, 3, and 4.

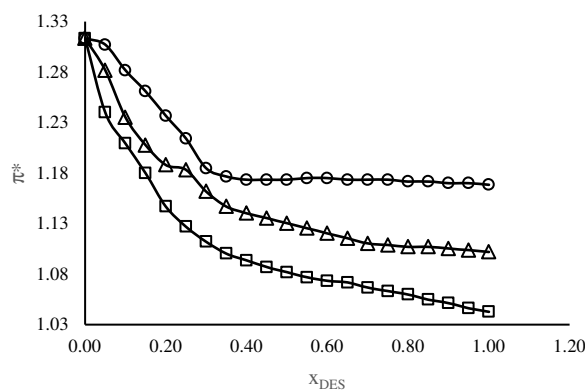


Figure 2. The π^* value of solvent as a function of mole fraction of DESs in aqueous mixtures of ChCl+Gly (\circ), ChCl+EG (\square), and ChCl+LA (Δ) at 298.15 K.

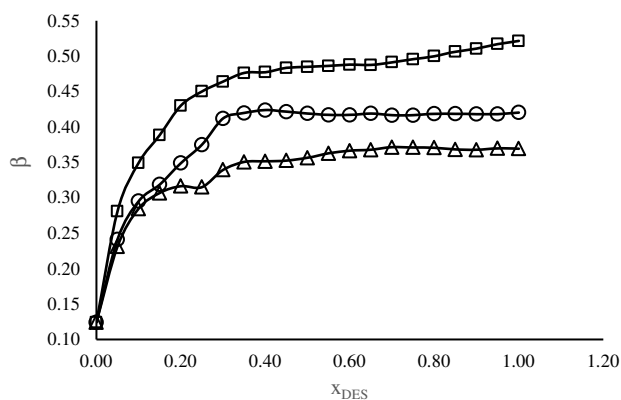


Figure 3. The β value of solvent as a function of mole fraction of DESs in aqueous mixtures of ChCl+Gly (\circ), ChCl+EG (\square), and ChCl+LA (Δ) at 298.15 K.

The plot for dipolarity-polarizability π^* in **Figure 2** shows a downward curve over the mole fraction of DES. The π^* decrease sharply up to near $x_{DES}=0.30$ in all mixtures, and then slowly decreases up to pure DES. Therefore, the polarity of mixtures decreases with the addition of DES to water in all binary mixtures. Comparison between DESs indicate that the order of polarity is ChCl+Gly > ChCl+LA > ChCl+EG. Similar to **Figure 1**, no significant synergistic effect was observed for dipolarity-polarizability π^* plot in all binary mixtures.

Table 1. The maximum wavelength of DPNA, NA, and BD, and solvatochromic parameters in binary mixtures of (ChCl+Gly) with water at 298.15 K.

x_{DES}	x_{water}	λ_{DMNA}	λ_{NA}	λ_{BD}	α	β	π^*	$E_T(30)$
1.00	0.00	415.5	384.4	492.6	0.79	0.42	1.17	58.04
0.95	0.05	415.6	384.4	492.3	0.79	0.42	1.17	58.07
0.90	0.10	415.6	384.4	492.0	0.79	0.42	1.17	58.11
0.85	0.15	415.7	384.5	491.8	0.79	0.42	1.17	58.14
0.80	0.20	415.7	384.5	491.5	0.80	0.42	1.17	58.17
0.75	0.25	415.8	384.5	491.2	0.80	0.42	1.17	58.21
0.70	0.30	415.8	384.5	490.9	0.80	0.42	1.17	58.24
0.65	0.35	415.8	384.6	490.6	0.80	0.42	1.17	58.27
0.60	0.40	415.9	384.6	490.4	0.80	0.42	1.17	58.31
0.55	0.45	415.9	384.6	490.1	0.80	0.42	1.17	58.34
0.50	0.50	415.8	384.6	489.8	0.81	0.42	1.17	58.38
0.45	0.55	415.8	384.7	489.2	0.81	0.42	1.17	58.44
0.40	0.60	415.8	384.8	488.0	0.82	0.42	1.17	58.59
0.35	0.65	416.0	384.8	487.2	0.82	0.42	1.18	58.69
0.30	0.70	416.5	384.9	485.9	0.83	0.41	1.18	58.84
0.25	0.75	418.3	384.9	485.1	0.81	0.38	1.21	58.94
0.20	0.80	419.7	385.0	482.8	0.81	0.35	1.24	59.22
0.15	0.85	421.2	385.0	478.2	0.82	0.32	1.26	59.79
0.10	0.90	422.5	385.1	467.3	0.89	0.30	1.28	61.18
0.05	0.95	424.1	384.2	460.0	0.94	0.24	1.31	62.16
0.00	1.00	424.5	379.8	453.1	0.99	0.12	1.31	63.10

Table 2. The maximum wavelength of DPNA, NA and BD, and solvatochromic parameters in binary mixtures of (ChCl+EG) with water at 298.15 K.

x_{DES}	x_{water}	λ_{DMNA}	λ_{NA}	λ_{BD}	α	β	π^*	$E_T(30)$
1.00	0.00	408.0	382.1	498.8	0.85	0.52	1.04	57.32
0.95	0.05	408.2	382.1	498.0	0.85	0.52	1.05	57.41
0.90	0.10	408.5	382.1	497.3	0.85	0.51	1.05	57.49
0.85	0.15	408.7	382.1	496.5	0.86	0.51	1.05	57.59
0.80	0.20	409.0	382.1	495.8	0.86	0.50	1.06	57.67
0.75	0.25	409.2	382.1	495.0	0.86	0.50	1.06	57.76
0.70	0.30	409.4	382.1	494.5	0.86	0.49	1.07	57.82
0.65	0.35	409.7	382.2	494.1	0.86	0.49	1.07	57.87
0.60	0.40	409.8	382.3	493.6	0.86	0.49	1.07	57.92
0.55	0.45	410.0	382.4	492.7	0.87	0.49	1.08	58.03
0.50	0.50	410.3	382.6	491.5	0.87	0.48	1.08	58.17
0.45	0.55	410.6	382.8	490.3	0.88	0.48	1.09	58.31
0.40	0.60	411.0	382.9	489.1	0.88	0.48	1.09	58.46
0.35	0.65	411.4	383.2	486.5	0.89	0.48	1.10	58.77
0.30	0.70	412.1	383.3	483.1	0.91	0.46	1.11	59.18
0.25	0.75	413.0	383.5	477.0	0.95	0.45	1.13	59.94
0.20	0.80	414.2	383.7	-	-	0.43	1.15	-
0.15	0.85	416.2	383.7	-	-	0.39	1.18	-
0.10	0.90	418.0	383.6	-	-	0.35	1.21	-
0.05	0.95	419.9	382.4	-	-	0.28	1.24	-
0.00	1.00	424.5	379.8	453.1	0.99	0.12	1.31	63.10

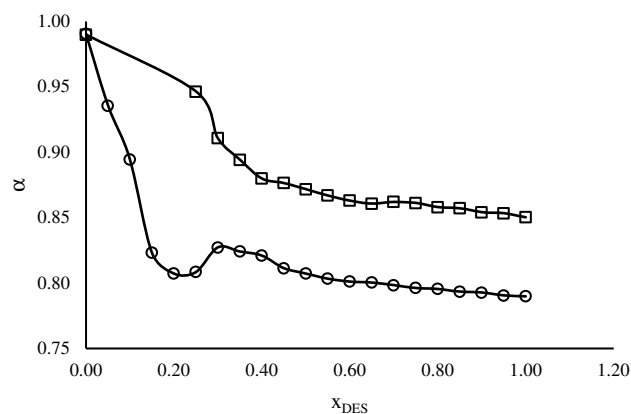
**Figure 4.** The α value of solvent as a function of mole fraction of DESs in aqueous mixtures of ChCl+Gly (\circ) and ChCl+EG (\square) at 298.15 K.

Table 3. The maximum wavelength of indicators DPNA and NA, and some solvatochromic parameters in binary mixtures of (ChCl+LA) with water at 298.15 K.

x_{DES}	x_{water}	λ_{DMNA}	λ_{NA}	β	π^*
1.00	0.00	411.5	379.0	0.37	1.10
0.95	0.05	411.6	379.1	0.37	1.10
0.90	0.10	411.7	379.1	0.37	1.11
0.85	0.15	411.8	379.2	0.37	1.11
0.80	0.20	411.8	379.3	0.37	1.11
0.75	0.25	411.9	379.4	0.37	1.11
0.70	0.30	412.0	379.5	0.37	1.11
0.65	0.35	412.3	379.6	0.37	1.12
0.60	0.40	412.6	379.8	0.37	1.12
0.55	0.45	412.9	379.9	0.36	1.13
0.50	0.50	413.2	379.9	0.36	1.13
0.45	0.55	413.5	380.0	0.35	1.14
0.40	0.60	413.8	380.2	0.35	1.14
0.35	0.65	414.2	380.5	0.35	1.15
0.30	0.70	415.1	380.8	0.34	1.16
0.25	0.75	416.4	380.9	0.32	1.18
0.20	0.80	416.7	381.2	0.32	1.19
0.15	0.85	417.9	381.8	0.31	1.21
0.10	0.90	419.6	382.3	0.28	1.24
0.05	0.95	422.5	382.5	0.23	1.28
0.00	1.00	424.5	379.8	0.12	1.31

Figure 3 shows that the hydrogen bond basicity β of the mixture increases upward with increasing mole fraction of DES in all binary mixtures. Trend as the mole fraction of water and ethyl acetate increases in binary mixtures. The rate of increase is high up to near $x_{DES}=0.25-0.35$ in all mixtures and then increases slowly up to pure DES. The change β is more remarkable in the water mixture with ChCl+EG. Comparing β values for DESs indicates that the hydrogen bonding basicity of DES has the order of ChCl+EG > ChCl+Gly > ChCl+LA. As expected, the β value for water is the lowest. None of the water + DES mixtures show the synergistic effect in their hydrogen bond basicity curve.

In an opposite trend, the plot for hydrogen bond acidity in Figure 4 indicates that the value α decreases in all water + DES mixtures with increasing the mole fraction of DES. A mixture of water with ChCl+LA, α could not be determined since BD became protonated in these mixtures and did not show its characteristic peak. In pure solvents, the order of hydrogen bond acidity is as water > ChCl+EG > ChCl+Gly. No synergistic effect on α a property is observed in mixed solvents studied here.

It is worth noting that the polarity scale based on E_T has main contributions from dipolarity-polarizability and hydrogen bonding acidity as discussed by Marcus [22]. Therefore, relationship between E_T (30) with π^* , β and α was examined. Eqs. (5) and (6) show the obtained linear relationship for mixtures of water with ChCl/Gly and ChCl/EG, respectively.

$$E_T(30) = 30.58 + 12.78\pi^* + 15.90\alpha \quad R^2=0.99 \quad (5)$$

$$E_T(30) = 30.66 + 14.30\pi^* + 13.83\alpha \quad R^2=0.99 \quad (6)$$

It is obvious that in good agreement with Marcus, the E_T polarity scale mainly quantifies the ability of solvent for non-specific dipolarity-polarizability and specific solute-solvent interactions where solvent acts as a hydrogen bond donor.

4. Conclusions

The influences of the addition of molecular co-solvent water on the solvatochromic properties of mixing of ChCl/Gly, ChCl/EG, and ChCl/LA as green DES solvents in the whole mole fraction range were analyzed systematically. Each of the four empirical solvatochromic properties, $E_T(30)$, α , β and π^* within water/DES mixtures are observed which show deviation from ideal additive behavior. Results indicate that $E_T(30)$, α , and π^* of the mixture decrease with increasing the mole fraction of DES in all binary mixtures. In the opposite trend, the hydrogen bond basicity of mixtures increases from pure water by increasing the mole fraction of DES in mixtures. In all mixtures, the rate of change is high in the water-rich region up to near $x_{DES} = 0.25-0.35$. In a higher mole fraction of DES, the rate of change becomes slower up to pure DES.

Authors' contributions

All authors contributed to data analysis, drafting and revising of the paper and agreed to be responsible for all the aspects of this work.

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Declaration of competing interest

The authors declare no competing interest.

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Data availability

Data will be made available on request.

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