Experimental Study on the Solvation Behavior in Aqueous Choline Chloride-based Deep Eutectic Solutions by Solvatochromic Dyes

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## ABSTRACT

The preferential solvation behavior of three solvatochromic indicators (4-Nitroaniline, *N, N*-dimethyl-4-nitroaniline, and 2,6-diphenyl-4-(2,4,6-tri phenyl pyridinium-1-yl)phenolate in some deep eutectic solvents (DESs) including choline chloride + glycerol (1:2), choline chloride + ethylene glycol (1:2) and choline chloride + lactic acid (1:2), and their mixtures with water was investigated at constant temperature 298.15±0.1 K by using UV–vis absorption measurements. The solvent exchange model was successfully utilized to analyze the spectral shifts of these dyes to make a description of the preferential solvation behavior of the solute in mixed solvents under study. It was found that the solvation shell of the dyes is mainly affected by the solvent-solvent and solvent-solute interactions, especially hydrogen bonding. The preferential solvation parameter shows that in all aqueous mixtures of DES, the order of preferential solvation for the solvatochromic dyes is as DES > (water-DES) complex > water. The contribution of water to the preferential solvation of dyes is low. This is probably due to the great affinity of water molecules for the self-association and the strong interaction between DES and the dyes.
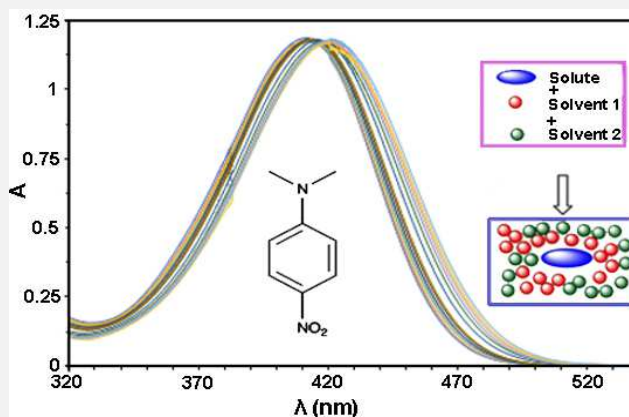
Keywords: Solvatochromic dyes, preferential solvation, solvent exchange model, local composition, aqueous DES systems

1. Introduction

To evaluate the behavior of a liquid as a solvent, understanding the solution interactions at a molecular level is necessary. In this direction, it is of interest to quantify its most relevant molecular-microscopic solvent properties, which determine how it will interact with potential solutes. An appropriate method to study solute-solvent interactions is the use of solvatochromic indicators that reflect the specific and nonspecific solute-solvent interactions on the UV-Vis spectral band shifts. The study of the solvent-solvent interactions using solvatochromic dyes is simple and effective because the transition energy of the dye depends on the solvating sphere composition and properties [1-4].

In a co-solvent mixture, the local composition around the solute molecules differs from the compositions of the bulk solvent. Because the solute interacts to a different extent with each component of solvents present in the mixture as well as due to solvent-solvent intermolecular interactions in the co-solvent system. This phenomenon is called preferential solvation. For obtaining information about the preferential solvation of selected solvatochromic indicators in co-solvent mixtures, the solvatochromism behavior, i.e. the spectral changes of solute induced by the solvent medium, can be exploited to analyze the local environment around the indicator molecules describing the local composition of its solvation sphere [5-7].

One of the most convenient and successful models for studying preferential solvation is the theoretical solvent exchange model [8]. This model extended the stepwise solvent exchange model of Skwierczynski and Connors [9] to derive equations that relate the electronic transition energy values of the solvatochromic dyes with the solvent

composition. The present equations propose preferential solvation parameters that consider the solvent–solvent as well as the solute-solvent interactions [10].

In recent years, a new type of solvent named Deep Eutectic Solvents (DESs) has been developed as green solvents that can be utilized for diverse applications [11]. DESs are a new group of room-temperature ionic liquids that have various properties such as low vapor pressure, low melting point, environmental compatibility, thermal and chemical stability, 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 [12,13]. 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 [14-16]. The hydrogen bonding interactions between HBA and the HBD groups typically lead to DESs. There are a few studies in the literature in which the solvation behavior of DES+molecular solvent mixtures has been examined [16-18].

Adding molecular solvents especially water to DESs is beneficial in some cases such as in biophysics and biochemistry [17]. Therefore, understanding the effect of different solvents and the preferred solvent is critical in binary mixtures. Therefore, in the present work, the preferential solvation behavior of three solvatochromic dyes (4-Nitroaniline, *N, N*-dimethyl-4-nitroaniline, and 2,6-diphenyl-4-(2,4,6-tri phenyl pyridinium-1-yl)phenolate or Betaine dye (30) was studied in the aqueous mixtures (in the whole compositional range) of choline chloride-based deep eutectic solvents to better and deeply understand the microscopic interactions between the solute and solvents in solvation sphere. The deep eutectic solvents were 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.

2. Materials and methods
2.1. Chemicals and apparatus
All materials, except solvatochromic dyes, were supplied from Merck with high purity. The purity of choline chloride (ChCl), glycerol (Gly), and Lactic acid (LA) was ≥99%, ethylene glycol (EG) ≥99.5%, and solvent acetone ≥99.8%. The salt choline chloride was dried for 2 days at 333.15 K in a high-vacuum oven before use. The solvatochromic dyes including Betaine dye 30 (BD 30) (≥99%), 4-Nitroaniline (NA) (≥99%), and *N, N*-dimethyl-4-nitroaniline (DMNA) (≥98%) were obtained from Sigma-Aldrich. The solvatochromic dyes used in this work are represented in **Figure 1**. Double-distilled water was used to prepare the aqueous solutions under investigation. All the mass measurements were performed on a Kern electronic balance (ACJ 220-4) with uncertainty in the mass of ±0.0001 g. Absorbance spectra were recorded on a Perkin-Elmer (Lambda 25) UV-Vis spectrophotometer in conjunction with a LabTech LCB-R08 thermo-circulator.
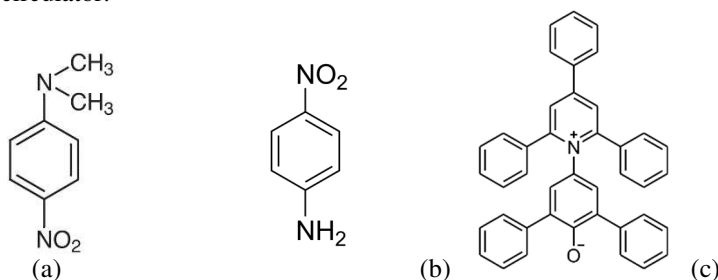

Figure 1. Solvatochromic dyes used: (**a**) *N, N*-dimethyl-4-nitroaniline, (**b**) 4-Nitroaniline, and (**c**) Betaine dye 30

2.2. Preparation of choline chloride-based DES
In this study, three deep eutectic solvents including 1:2 ChCl+Gly (DES1), 1:2 ChCl+EG (DES2), and 1:2 ChCl+LA (DES3) were prepared. For the preparation of each DES, the required amounts of dried choline chloride as HBA were added to each HBD (Gly, EG, and LA) in screw-capped glass vials. The mixtures were heated at a temperature of 353.15 K using a hot plate and stirred with constant stirring until a colorless liquid and uniform liquid without any precipitation was obtained even after cooling down to room temperature. The prepared DESs were then placed into a vacuum oven for further utilization.

2.3. Experimental measurements

UV−vis spectroscopic measurements were performed to analyze the shifts in the absorption band of the solvatochromic dyes in the different aqueous DES systems under study. To begin the measurements, first, a stock solution (10^{-2} M) of each solvatochromic dye was prepared in the solvent acetone and stored in a dark glass vial at 277.15 K. In every measurement, 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 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. Aqueous DES mixtures of each solvatochromic dye were carefully prepared by mass. In the next step, the UV-Vis spectrum of the dyes was recorded over the wavelength ranges of λ = 300-500 nm for NA, 350-600 nm for DMNA, and 400-700 nm for BD 30 at the lowest scanning rate and accuracy of 0.1 nm. Finally, the maxima on the UV−Vis spectra (λ_{max}) of each dye in different compositions of the mixed water/DES systems studied were recorded for the next calculations. For each dye, an average of three individual experiments was taken.

3. Preferential solvation model

To descript the solvation behavior of a solute in a solvent mixture the two-step solvent exchange model is a simple well-known approach, which is based on an exchange of two pure solvents S1 and S2 between the solvation sphere of the solute I (marked by parentheses) and the bulk area according to the following expressions [19,20].

$$I(S2)_m + m\ S1 \rightleftharpoons I(S1)_m + m\ S2 \tag{1}$$

$$I(S2)_m + \frac{m}{2}\ S1 \rightleftharpoons I(S12)_m + \frac{m}{2}\ S2 \tag{2}$$

where S12 shows a new solvent species that is formed by the interaction between S1 and S2; the m is the number of solvent molecules whose exchange in the solvation sphere affects the solvatochromic properties of the solute. The two solvent-exchange processes can be defined by preferential solvation parameters, $f_{1/2}$ and $f_{12/2}$, which represent the relative affinity of solvents S1 and S12 for solvent S2 in the solvation microsphere of the solute as well as $f_{12/1}$, which corresponding to the relative affinity of solvent S12 for solvent S1 in solvation shell as follows:

$$f_{1/2} = \frac{x_1^L / x_2^L}{(x_1 / x_2)^m} \tag{3}$$

$$f_{12/2} = \frac{x_{12}^L / x_2^L}{\sqrt{(x_1 / x_2)^m}} \tag{4}$$

$$f_{12/1} = \frac{x_{12}^L / x_1^L}{\sqrt{(x_1 / x_2)^m}} = \frac{f_{12/2}}{f_{1/2}} \tag{5}$$

herein, x_i^L and x_i are the solvation sphere and bulk mole fractions of mixed solvent, respectively. $f_{i/j}$ higher than 1 shows that the solute is preferentially solvated by solvent i rather than by solvent j. Conversely, if $f_{i/j}$ < 1 says the solute is better solvated by solvent j. Finally, $f_{i/j}$ close to 1 corresponds to an ideal mixture with no preferential solvation. Since in the sphere of solvation, $x_1^L + x_2^L + x_{12}^L$ = 1, therefore using Eqs. 3-5, the mole fraction of solvents S1, S2, and S12 in the solvation microsphere of the solute can be expressed as:

$$x_1^L = \frac{f_{1/2}(x_1)^m}{f_{1/2}(x_1)^m + (x_2)^m + f_{12/2}(x_1 x_2)^{m/2}} \tag{6}$$

$$x_2^L = \frac{(x_2)^m}{f_{1/2}(x_1)^m + (x_2)^m + f_{12/2}(x_1 x_2)^{m/2}} \tag{7}$$

$$x_{12}^L = \frac{f_{12/2}(x_1 x_2)^{m/2}}{f_{1/2}(x_1)^m + (x_2)^m + f_{12/2}(x_1 x_2)^{m/2}} \tag{8}$$

The solvatochromic property Z for a solvent mixture is calculated as an average of the Z values of solvents S1, S2, and S12 in the solvation sphere of the solute [21]:

$$Z = x_1^L Z_1 + x_2^L Z_2 + x_{12}^L Z_{12} \tag{9}$$

Replacing Eqs. 6-8 into Eq. 9, a general equation that relates the Z property of a binary solvent mixture to the Z property of the solvents S1, S2, and S12, the preferential solvation parameters, $f_{1/2}$ and $f_{12/2}$, and the solvent bulk composition can be obtained as follows:

$$Z = \frac{Z_2(x_2)^m + f_{1/2}Z_1(x_1)^m + f_{12/2}Z_{12}(x_1 x_2)^{m/2}}{(x_2)^m + f_{1/2}(x_1)^m + f_{12/2}(x_1 x_2)^{m/2}} \tag{10}$$

In the above equation, Z_{12}, $f_{1/2}$, and $f_{12/2}$ are unknown and can be readily determined from experimental solvatochromic data, Z, gathered over the whole mole fraction range by using a nonlinear least-squares fitting to Eq. 10.

4. Results and discussion

Solvation refers to the encircling of a dissolved molecule or ion by a shell of solvent molecules. This is because of the intermolecular interaction between the solute and the solvent molecule. In binary mixtures, a solute can bind itself preferentially to one type of solvent rather than the other. This will again depend upon the nature of the solute and the solvent. The wavelength values of the maximum absorption band for the solvatochromic dyes were recorded in aqueous mixtures of DES solvents (DES1 [ChCl+Gly], DES2 [ChCl+EG], and DES3 [ChCl+LA]). These data were used in the study of the preferential solvation of the dye, in terms of both solute-solvent and solvent–solvent interactions. **Figure 2** shows solvatochromic UV–Vis shifts of dye N, N-dimethyl-4-nitroaniline at 298.15 K by adding water to the solution of the dye in DES2. As seen in **Figure 2**, by increasing the water content in the mixture the maximum band of dye shifts to higher wavelengths. Solvation shells of dye as the important reason for turning UV−Vis spectra were discussed.
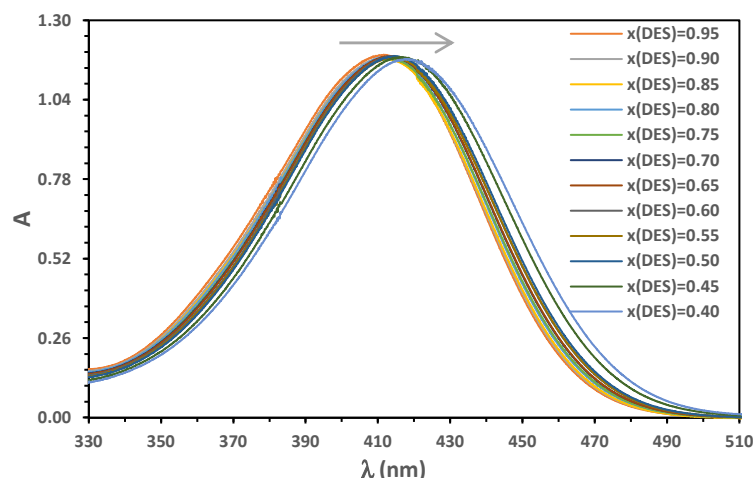

Figure 2. UV-Vis absorption spectra of the dye DMNA in aqueous mixtures of DES2 [ChCl+EG] at 298.15 K (x(DES) show the mole fraction of DES).

As a solvatochromic property, the electronic transition energy (E_T) defined as the excitation energy of any solvatochromic dye, can be calculated from the maximum wavelength (λ_{max}) of the absorption band as E_T(kcal mol^{-1}) = 28591/λ_{max}(nm) [3]. The experimental values of E_T were fitted to Eq. 10 by using a nonlinear regression procedure to obtain the preferential solvation parameters $f_{1/2}$ and $f_{12/2}$. The quality of fits can be checked according to the squared correlation coefficient (R^2).

After obtaining the preferential solvation parameters, according to Eqs. 6-8, the local mole fractions of S1, S2, and S12 were calculated as a function of the initial mole fraction of DES solvents. The solvatochromic parameters of three dyes in aqueous mixtures of co-solvents DES1, DES2, and DES3 at 298.15 K are listed in **Table 1**.

Table 1. Preferential solvation parameters of dyes BD 30, DMNA, and NA in binary mixtures of DESs (S1) with water (S2) at 298.15 K.

Solvent mixture	dye	E_{T1} (kcal mol^{-1})	E_{T2} (kcal mol^{-1})	E_{T12} (kcal mol^{-1})	$f_{1/2}$	$f_{12/2}$	$f_{12/1}$	m	R^2
water/(DES2)	BD 30	57.32	63.1	58.50	7.16	5.60	0.78	2.16	0.990
water/(DES1)		58.04	63.1	58.37	7.50	54.74	7.29	3.80	0.990
water/(DES2)		70.11	67.4	67.81	12.93	1.78	0.14	1.22	0.999
water/(DES1)	DMNA	68.81	67.4	68.77	68.51	9.70	0.14	3.55	0.999
water/(DES3)		69.48	67.4	68.74	64.55	34.01	0.53	3.15	0.999
water/(DES2)		74.83	75.3	74.31	556.84	132.58	0.24	3.22	0.998
water/(DES1)	NA	74.38	75.3	74.29	27.402	40.798	1.98	4.27	0.998
water/(DES3)		75.44	75.3	74.60	95.188	73.555	0.29	2.03	0.998

The solvation exchange model, **Table 1**, indicates that for dye BD 30 the parameters $f_{1/2}$ and $f_{12/2}$ are higher than unity in all aqueous mixtures. As clear in Figure 1, BD 30 is a hydrogen-bond acceptor dye because of its phenolate group. Therefore, BD 30 was more surrounded by DES via hydrogen bonding and electrostatic interactions between the oxygen atom on the phenolate group of the dye and the ChCl component of the DES solvent. This finding is by previous studies [17,22]. In water/DESs mixtures, BD 30 is mainly solvated by DES (S1) and (water-DES) solvent complex (S12) resulting from solvent–solvent interactions, for water (S2). The strong interaction of Gly with water in an aqueous DES1 solution to form the solvent complex (S12) causes $f_{12/2}$ to be higher compared with an aqueous DES2 solution. In addition, the E_T values obtained for BD 30 in these two aqueous DES mixtures are very close, which is probably due to the structural similarity of the solvents EG and Gly.

For the dye DMNA, the preferential solvation model gives a similar result; $f_{1/2}$ and $f_{12/2}$ are higher than unity (**Table1**). The greater solvation of DMNA by DES is mainly attributed to the polar-polar solute-solvent interactions because DMNA is a dye very sensitive to the polarity of the solvent, and is not capable to make effectively specific interactions with the solvent. Moreover, $f_{1/2}$ is very higher than $f_{12/2}$; indicating that S1 has a greater affinity to surround DMNA for water. In other words, the order of preferential solvation is S1>S12>S2 in the case of DMNA. The $f_{12/1}$ value lower than unity in all aqueous mixtures indicates that DMNA is preferentially solvated by the (water-DES) solvent complex for water. In addition, $E_{T12} \approx E_{T1}$ indicates that S12 is more similar to S1.

The analysis of the fitting parameters for the dye NA (**Table 1**) reveals that $f_{1/2} > f_{12/2} \gg 1$ in all aqueous mixtures excluding water/DES1. As can be seen in Figure 1, NA has different sides to have hydrogen bonding interactions with the surrounding molecules. The amine group of NA prefers to be solvated by the HBA component of DES via hydrogen bonding interactions between the hydrogen atoms of the amine group of the dye and oxygen atoms of DES solvent. Moreover, the nitro group of the dye can interact with the ChCl component of DES via hydrogen bonding. However, in a mixture of water/DES1, NA is preferentially solvated by the (water-DES) solvent complex. This is supported by the higher values of $f_{12/2}$ than $f_{12/1}$, which suggests the nature of the complex is closer to that of the DES molecules.

Values of the experimental and calculated E_T of three dyes NA, BD 30, and DMNA as well as the calculated local mole fractions of S1, S2, and S12 as a function of the initial mole fraction of the solvents in aqueous mixtures of DES at 298.15 K are given in **Tables 2-4**.

According to **Tables 2-4**, the calculated E_T values of the solvatochromic dyes used for pure solvents and binary mixtures of DESs and water are in satisfactory agreement with the experimental values. Therefore, the quality of fits was judged to be excellent for obtaining the preferential solvation parameters. In addition, the changes in E_T values

with the composition of solvents used reveal that the solute-solvent interactions between the dye and the solvent molecules affect the solvation behavior of the dye.

The local composition of solvent species around BD 30 is shown as a function of the bulk mole fraction of DESs in **Table 2**. It is clear that the contribution of S1 (DES) to the solvation shell composition of BD 30 (x_1^L) reaches maxima when the bulk composition approaches the DES-rich area. This phenomenon performs through hydrogen bonding interactions between the phenolate group of BD 30 and the hydroxyl group of DESs. The local composition of S12 (x_{12}^L) reaches a maximum of around $x_{water}=0.80$ for the water/DES2 mixture, $x_{water}=0.90$ for the water/DES1 mixture. Results indicate clearly that the solvation shell of BD 30 is most likely occupied by DES and complex formed by water-DES interactions. The contribution of water (S2) in the solvation shell of this dye is less in the whole composition (mole fraction) range because BD 30 is a non-polar compound.

Table 2. Experimental and calculated E_T values (kcal mol^{-1}) and the mole fractions of S1, S2, and S12 in the solvation shell of BD 30 in binary mixtures of DESs (S1) with water (S2) at 298.15 K.

x_{DES}	x_{water}	$E_T^{(EXP)}$	$E_T^{(CAL)}$	x_1^L	x_2^L	x_{12}^L
		(DES2)/water				
1.00	0.00	57.32	57.32	1.00	0.00	0.00
0.95	0.05	57.41	57.36	0.97	0.00	0.03
0.90	0.10	57.49	57.41	0.93	0.00	0.07
0.85	0.15	57.59	57.46	0.89	0.00	0.11
0.80	0.20	57.67	57.53	0.85	0.01	0.15
0.75	0.25	57.76	57.61	0.80	0.01	0.19
0.70	0.30	57.82	57.69	0.75	0.02	0.23
0.65	0.35	57.87	57.80	0.70	0.03	0.28
0.60	0.40	57.92	57.92	0.64	0.04	0.32
0.55	0.45	58.03	58.06	0.58	0.05	0.37
0.50	0.50	58.17	58.22	0.52	0.07	0.41
0.45	0.55	58.31	58.42	0.46	0.10	0.44
0.40	0.60	58.46	58.65	0.39	0.13	0.48
0.35	0.65	58.77	58.92	0.33	0.17	0.50
0.30	0.70	59.18	59.25	0.26	0.23	0.51
0.25	0.75	59.94	59.64	0.20	0.30	0.51
0.00	1.00	63.10	63.10	0.00	1.00	0.00
		(DES1)/water				
1.00	0.00	58.04	58.04	1.00	0.00	0.00
0.95	0.05	58.07	58.05	0.97	0.00	0.03
0.90	0.10	58.11	58.07	0.90	0.00	0.10
0.85	0.15	58.14	58.11	0.79	0.00	0.21
0.80	0.20	58.17	58.16	0.66	0.00	0.34
0.75	0.25	58.21	58.21	0.52	0.00	0.47
0.70	0.30	58.24	58.25	0.41	0.00	0.59
0.65	0.35	58.27	58.29	0.31	0.00	0.69
0.60	0.40	58.31	58.33	0.23	0.01	0.77
0.55	0.45	58.34	58.37	0.17	0.01	0.82
0.50	0.50	58.38	58.41	0.12	0.02	0.87
0.45	0.55	58.44	58.46	0.08	0.02	0.89
0.40	0.60	58.59	58.53	0.06	0.04	0.91
0.35	0.65	58.69	58.62	0.04	0.05	0.91
0.30	0.70	58.84	58.75	0.02	0.08	0.89
0.25	0.75	58.94	58.97	0.01	0.13	0.86
0.20	0.80	59.22	59.32	0.01	0.20	0.79
0.15	0.85	59.79	59.93	0.00	0.33	0.67
0.10	0.90	61.18	60.94	0.00	0.54	0.46
0.05	0.95	62.16	62.30	0.00	0.83	0.17
0.00	1.00	63.10	63.10	0.00	1.00	0.00

According to the results of **Table 3**, for the dye DMNA, in the water-rich region, water solvates this dye initially, and then by the addition of DES, the solvent complex S12 form by hydrogen bonding interactions that is responsible for the selective solvation of DMNA. The local mole fraction of S12 increases in the solvation layer and reaches a maximum of around x_{water}=0.80 for the water/DES3 mixture. In the DES-rich region, DMNA is solvated by DES. The solvent S1 contributes mainly to the preferential solvation of DMNA over the large composition of DES/water mixtures. In water/DES2 and water/DES1 mixtures, around x_{water}=0.95, the local composition of S12 and S2 in the solvation layer of DMNA is equal. It should be here noted that S12 is not a real solvent species and should be considered a solvent structure. The real structure of S12 may be a complex of different species their stoichiometry depends on the mixture composition. The exchange solvent model defines S12 to explain the cooperative solvation of solute by two solvents in the interpretation of the solvatochromism in an aqueous mixture. Therefore, the physical and chemical nature of the system should be taken into account in order to reach a more reliable conclusion.

Table 3. Experimental and calculated E_T values (kcal mol^{-1}) for DMNA and the mole fractions of S1, S2 and S12 in solvation shell in binary mixtures of DESs (S1) with water (S2) at 298.15 K.

X_{DES}	X_{water}	$E_T^{(EXP)}$	$E_T^{(CAL)}$	X1	X2	X12
DES2/water						
1.00	0.00	70.08	70.11	1.00	0.00	0.00
0.95	0.05	70.04	70.05	0.98	0.00	0.02
0.90	0.10	69.99	70.02	0.96	0.01	0.03
0.85	0.15	69.96	69.98	0.95	0.01	0.04
0.80	0.20	69.91	69.95	0.93	0.01	0.05
0.75	0.25	69.87	69.91	0.92	0.02	0.06
0.70	0.30	69.84	69.87	0.90	0.02	0.07
0.65	0.35	69.79	69.83	0.88	0.03	0.08
0.60	0.40	69.77	69.78	0.87	0.04	0.09
0.55	0.45	69.74	69.73	0.85	0.05	0.10
0.50	0.50	69.68	69.67	0.82	0.06	0.11
0.45	0.55	69.63	69.61	0.80	0.08	0.12
0.40	0.60	69.57	69.53	0.77	0.10	0.14
0.35	0.65	69.50	69.44	0.73	0.12	0.15
0.30	0.70	69.38	69.33	0.69	0.15	0.16
0.25	0.75	69.23	69.19	0.64	0.19	0.17
0.20	0.80	69.03	69.02	0.57	0.24	0.18
0.15	0.85	68.70	68.79	0.49	0.32	0.19
0.10	0.90	68.40	68.48	0.38	0.43	0.20
0.05	0.95	68.09	68.02	0.21	0.61	0.18
0.00	1.00	67.35	67.35	0.00	1.00	0.00
DES1/water						
1.00	0.00	68.81	68.81	1.00	0.00	0.00
0.95	0.05	68.80	68.81	1.00	0.00	0.00
0.90	0.10	68.80	68.81	1.00	0.00	0.00
0.85	0.15	68.78	68.81	0.99	0.00	0.01
0.80	0.20	68.78	68.81	0.99	0.00	0.01
0.75	0.25	68.76	68.81	0.98	0.00	0.02
0.70	0.30	68.76	68.81	0.97	0.00	0.03
0.65	0.35	68.76	68.81	0.95	0.00	0.05
0.60	0.40	68.75	68.80	0.93	0.00	0.06
0.55	0.45	68.75	68.80	0.90	0.01	0.09
0.50	0.50	68.76	68.79	0.86	0.01	0.12
0.45	0.55	68.76	68.77	0.81	0.02	0.16
0.40	0.60	68.76	68.73	0.74	0.05	0.21
0.35	0.65	68.73	68.68	0.64	0.08	0.27
0.30	0.70	68.65	68.57	0.52	0.15	0.33
0.25	0.75	68.35	68.41	0.37	0.26	0.37
0.20	0.80	68.12	68.17	0.22	0.43	0.36

X_{DES}	X_{water}	$E_T^{(EXP)}$	$E_T^{(CAL)}$	X_1	X_2	X_{12}
0.15	0.85	67.88	67.88	0.09	0.63	0.28
0.10	0.90	67.67	67.61	0.02	0.82	0.16
0.05	0.95	67.42	67.42	0.00	0.95	0.05
0.00	1.00	67.35	67.35	0.00	1.00	0.00

Table 3. Continued

X_{DES}	X_{water}	$E_T^{(EXP)}$	$E_T^{(CAL)}$	X_1	X_2	X_{12}
DES3/water						
1.00	0.00	69.48	69.48	1.00	0.00	0.00
0.95	0.05	69.46	69.48	0.99	0.00	0.01
0.90	0.10	69.45	69.47	0.98	0.00	0.02
0.85	0.15	69.43	69.46	0.97	0.00	0.03
0.80	0.20	69.43	69.44	0.94	0.00	0.06
0.75	0.25	69.41	69.42	0.91	0.00	0.09
0.70	0.30	69.40	69.39	0.88	0.00	0.12
0.65	0.35	69.35	69.35	0.83	0.00	0.17
0.60	0.40	69.30	69.31	0.78	0.00	0.22
0.55	0.45	69.25	69.26	0.72	0.01	0.28
0.50	0.50	69.20	69.21	0.65	0.01	0.34
0.45	0.55	69.15	69.14	0.57	0.02	0.41
0.40	0.60	69.09	69.06	0.49	0.03	0.49
0.35	0.65	69.03	68.98	0.40	0.04	0.56
0.30	0.70	68.88	68.87	0.31	0.07	0.62
0.25	0.75	68.66	68.75	0.22	0.11	0.67
0.20	0.80	68.61	68.60	0.15	0.18	0.68
0.15	0.85	68.42	68.40	0.08	0.29	0.64
0.10	0.90	68.14	68.11	0.03	0.47	0.50
0.05	0.95	67.67	67.70	0.00	0.75	0.25
0.00	1.00	67.35	67.35	0.00	1.00	0.00

The local composition of solvents in the solvation shell of NA is listed in **Table 4**. With an exception of the water/DES2 mixture, when DES is added to pure water up to DES-rich regions, the solvation shell of NA mainly involves S12, because NA has a great affinity to be solvated through hydrogen bond interaction of its amine group with DES components. The local composition of S12 reaches a maximum of around $x_{water}=0.90$. Results indicate clearly that the solvation shell of NA is most likely occupied by DES (S1) and the complex formed (S12) by water-DES interactions. In water/DES1 and water/DES3 mixtures, the contribution of water for preferential solvation of NA over the large composition of DES/water mixtures is almost zero. This is probably due to the great affinity of water molecules for self-association and the strong interaction between DESs and the dye.

5. Conclusions

The knowledge of preferential solvation is of critical importance in the description of the solute behavior in mixed solvents. The analysis of solvatochromic shifts as a function of solvent composition was used in this work to obtain the preferential solvation parameters. The addition of (ChCl+Gly), (ChCl+EG), and (ChCl+LA) as green DES co-solvents to aqueous solutions of the solvatochromic dyes causes UV-Vis spectrum shifts which analysis of these shifts shows solvation behavior in the whole mole fraction range. In binary solvent mixtures, by determining the electronic transition energy, E_T, the effect of solvent-solvent interaction was evaluated by the solvent exchange model. Results indicated that the solvent-solvent interactions are the main factor controlling the nonlinearity of solvatochromism behavior. Approximately for all solvatochromic dyes, $f_{1/2}> f_{12/2}>>1$ in all aqueous mixtures that show the dyes are preferentially surrounded by DES solvents rather than by water. It shows that solvent-solvent interactions indirectly govern the solute-solvent interactions and the extent of preferential solvation. In most of the mole fractions of water/DES mixtures under study, the dyes prefer to be solvated in the order of components: S1> S12>>S2.

Table 4. Experimental and calculated E_T values (kcal mol^{-1}) for NA and the mole fractions of S1, S2, and S12 in solvation shell in binary mixtures of DESs (S1) with water (S2) at 298.15 K.

x_{DES}	x_{water}	$E_T^{(EXP)}$	$E_T^{(CAL)}$	x_1	x_2	x_{12}
DES2/water						
1.00	0.00	74.83	74.83	1.00	0.00	0.00
0.95	0.05	74.83	74.83	1.00	0.00	0.00
0.90	0.10	74.83	74.83	0.99	0.00	0.01
0.85	0.15	74.83	74.82	0.99	0.00	0.01
0.80	0.20	74.83	74.82	0.98	0.00	0.02
0.75	0.25	74.83	74.81	0.96	0.00	0.04
0.70	0.30	74.83	74.80	0.94	0.00	0.06
0.65	0.35	74.81	74.79	0.92	0.00	0.08
0.60	0.40	74.79	74.77	0.89	0.00	0.11
0.55	0.45	74.77	74.76	0.85	0.00	0.15
0.50	0.50	74.73	74.73	0.81	0.00	0.19
0.45	0.55	74.69	74.71	0.75	0.00	0.25
0.40	0.60	74.67	74.67	0.68	0.00	0.31
0.35	0.65	74.61	74.63	0.60	0.01	0.39
0.30	0.70	74.59	74.59	0.51	0.01	0.48
0.25	0.75	74.55	74.55	0.41	0.03	0.57
0.20	0.80	74.52	74.52	0.30	0.05	0.66
0.15	0.85	74.52	74.50	0.19	0.09	0.72
0.10	0.90	74.53	74.55	0.09	0.19	0.72
0.05	0.95	74.77	74.77	0.02	0.46	0.53
0.00	1.00	75.28	75.28	0.00	1.00	0.00
DES1/water						
1.00	0.00	74.38	74.38	1.00	0.00	0.00
0.95	0.05	74.38	74.38	1.00	0.00	0.00
0.90	0.10	74.38	74.38	0.98	0.00	0.02
0.85	0.15	74.36	74.38	0.95	0.00	0.05
0.80	0.20	74.36	74.37	0.91	0.00	0.09
0.75	0.25	74.36	74.37	0.84	0.00	0.16
0.70	0.30	74.36	74.36	0.76	0.00	0.24
0.65	0.35	74.34	74.35	0.65	0.00	0.35
0.60	0.40	74.34	74.34	0.55	0.00	0.45
0.55	0.45	74.34	74.33	0.44	0.00	0.56
0.50	0.50	74.34	74.32	0.34	0.00	0.66
0.45	0.55	74.32	74.31	0.25	0.00	0.75
0.40	0.60	74.30	74.31	0.17	0.00	0.83
0.35	0.65	74.30	74.30	0.12	0.00	0.88
0.30	0.70	74.28	74.30	0.08	0.00	0.92
0.25	0.75	74.28	74.30	0.05	0.00	0.95
0.20	0.80	74.26	74.30	0.03	0.00	0.97
0.15	0.85	74.26	74.29	0.01	0.00	0.99
0.10	0.90	74.24	74.29	0.00	0.00	1.00
0.05	0.95	74.42	74.29	0.00	0.00	1.00
0.00	1.00	75.28	75.28	0.00	1.00	0.00

Table 4. Continued

X$_{DES}$	X$_{water}$	$E_T^{(EXP)}$	$E_T^{(CAL)}$	X$_1$	X$_2$	X$_{12}$
DES3/water						
1.00	0.00	75.44	75.44	1.00	0.00	0.00
0.95	0.05	75.42	75.43	0.99	0.00	0.01
0.90	0.10	75.42	75.41	0.97	0.00	0.03
0.85	0.15	75.40	75.40	0.95	0.00	0.05
0.80	0.20	75.38	75.38	0.93	0.00	0.07
0.75	0.25	75.36	75.37	0.91	0.00	0.09
0.70	0.30	75.34	75.35	0.89	0.00	0.11
0.65	0.35	75.32	75.33	0.86	0.00	0.14
0.60	0.40	75.28	75.30	0.84	0.00	0.16
0.55	0.45	75.26	75.28	0.81	0.00	0.19
0.50	0.50	75.26	75.25	0.77	0.00	0.23
0.45	0.55	75.24	75.22	0.73	0.00	0.27
0.40	0.60	75.20	75.18	0.69	0.00	0.31
0.35	0.65	75.14	75.14	0.64	0.00	0.36
0.30	0.70	75.08	75.10	0.59	0.00	0.41
0.25	0.75	75.06	75.04	0.53	0.00	0.47
0.20	0.80	75.00	74.98	0.45	0.00	0.55
0.15	0.85	74.89	74.91	0.37	0.00	0.63
0.10	0.90	74.79	74.83	0.27	0.00	0.73
0.05	0.95	74.75	74.72	0.15	0.00	0.85
0.00	1.00	75.28	75.28	0.00	1.00	0.00

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.

Acknowledgments

Declaration of competing interest

The authors declare no competing interest.

Funding

Data availability

Data will be made available on request.

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