Aggregation Behavior of Sodium Dioctyl Sulfosuccinate in Deep Eutectic Solvents and Their Mixtures with Water: An Account of Solvent’s Polarity, Cohesiveness, and Solvent Structure

Komal, Gagandeep Singh, Gurbir Singh, and Tejwant Singh Kang

Department of Chemistry, UGC Sponsored Centre for Advanced Studies-II, Guru Nanak Dev University, Amritsar 143005, India

Supporting Information

ABSTRACT: An anionic surfactant sodium dioctyl sulfosuccinate (AOT) aggregates in deep eutectic solvents (DESs) and their mixtures with water (up to 50% w/w) in a contrasting manner. Two DESs, a mixture of choline chloride + urea and choline chloride + ethylene glycol, commonly known as Reline and Ethaline, respectively, are used as solvents. Behavior of AOT at air–solution interface and aggregation in bulk is investigated using surface tension, conductivity, fluorescence, and dynamic light scattering measurements. The obtained results are correlated with structural aspects of solvent systems as well as with inherent properties of solvent such as Kamlet–Taft polarity parameters, degree of cohesiveness derived from Gordon parameter (G), and cohesive energy density. It is observed that the spontaneity of aggregation in neat DESs or DES–water mixtures follows a trend reflected by various solvent parameters. However, characteristic properties of aggregation in water does not fit into this trend, where critical aggregation concentration of AOT is found in between 30 and 50% (w/w) of respective DES–water mixtures. 1H NMR and 2D NOESY spectroscopy is employed to get insights into reason behind this anomalous behavior. It is observed that AOT forms self-assembled structures similar to that of other surfactants in neat DESs, whereas it undergoes nanosegregation in DESs–water mixtures. The present results are expected to be useful for colloidal aspects of DESs and their mixtures with water.

INTRODUCTION

Deep eutectic solvents (DESs) are mixtures of hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) groups mixed in an appropriate ratio and are liquid at room temperature.1 DESs are regarded as green solvents that can be utilized for diverse applications owing to their properties such as low volatility, wide liquidus range, wide electrochemical window, and bio-degradability, which places them at par with ionic liquids (ILs). However, low-cost, nontoxicity, and ease of preparation render DESs as better solvents or materials than many of the ILs. DESs were found to act as solvents for self-assembly of amphiphiles despite having low cohesive energy density (ced) as compared to water and other organic solvents. Their utility as a medium for self-assembly of amphiphiles can be further enhanced by employing mixtures of DESs with water, as physicochemical properties of DESs–water mixtures are unique and not present in either of the pure components. In this regard, variety of amphiphiles such as phospholipids, anionic, and cationic surfactants were shown to self-assemble in DESs or their mixtures with water. The solvophobic interactions between hydrophobic alkyl chains of surfactants and DESs along with H-bonding network of DESs seem to play an important role in self-assembly of amphiphiles.

It has been established that the water content in DESs plays an important role in modifying the structural properties of DESs depending on the nature of components comprising DESs. Water when present even in small amounts (∼6.5 wt %) has been found to alter the solvent structure of DES (Reline) comprising 1:2 choline chloride (ChCl) and urea (U). The interactions between components of DES were found to weaken nonlinearly with the increase in water content up to 40 wt %; however, the nanostructure of DES was substantially observed. Higher water content, that is, 51 wt % disrupts the nanostructure of DES, and the solvent system behaves like an aqueous solution of components of DES. A similar destructuring effect of water was observed for other DESs based on 1:2 ChCl–ethylene glycol (EG, Ethaline) as well as 1:2 ChCl–glycerol (Glyceline). Therefore, it seems important to investigate self-assembly behavior of amphiphiles in DESs differing in inherent structures controllable by choice of constituent components and addition of water.

Considering the above discussed points, herein, aggregation behavior of AOT in DESs prepared by mixing choline chloride and urea (Reline) as well as choline chloride and ethylene glycol (Ethaline) is studied. It is observed that AOT forms self-assembled structures similar to that of other surfactants in neat DESs, whereas it undergoes nanosegregation in DESs–water mixtures. The present results are expected to be useful for colloidal aspects of DESs and their mixtures with water.
Interfacial behavior of AOT in DESs and their mixtures with water (10, 30, and 50%, w/w of water) is investigated using tensiometry. Thus, obtained concentration profiles of surface tension, \( \gamma \), are shown in Figure 1A,B. In the absence of AOT, surface tension, \( \gamma_0 \), of DES—water mixtures is found to be higher as compared to that of neat DESs. Observed values of \( \gamma \) for neat DES are compared with the literature (Table 1). \( \gamma_0 \) increases with the increase in water content as can be seen from Table 1. The systems involving Ethaline exhibit lower values of \( \gamma_0 \) as compared to those having Reline in neat DESs or at any similar composition.

Using concentration profiles of \( \gamma \), critical aggregation concentration (cac) of AOT in DESs and their respective mixtures with water is obtained as a concentration of AOT corresponding to the onset of plateau in \( \gamma \) as shown in Figure 1. Various parameters such as surface tension at cac (\( \gamma_{ \text{cac}} \)), surface pressure at air—solution interface (\( \pi_{ \text{cac}} \)), Gibbs surface excess (\( \Gamma_{ \text{max}} \)), and minimum surface area per molecule (\( A_{ \text{min}} \)) are derived from profiles of \( \gamma \) using standard equations and are documented in Table 1. In brief, \( \pi_{ \text{cac}} \) is calculated as difference of surface tension of pure solvent (\( \gamma_0 \)) to that at cac (\( \gamma_{ \text{cac}} \)). \( \Gamma_{ \text{max}} \) and \( A_{ \text{min}} \) are deduced using the following equations:

\[
\Gamma_{\text{max}} = \frac{-1}{nRT} \frac{d\gamma}{d\ln C}
\]

\[
A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{max}}}
\]

where \( n = 2 \) for ionic surfactant, \( R \) and \( T \) have their usual meanings, and \( N_A \) is Avogadro’s number. It is assumed that AOT is fully dissociated in investigated solvents although there

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Table 1. Experimentally Determined Surface Tension (\( \gamma_0 \)) of Investigated Solvents, Surface Tension at cac (\( \gamma_{ \text{cac}} \)), and Calculated Surface Pressure (\( \pi_{ \text{cac}} \)), Gibbs Surface Excess (\( \Gamma_{ \text{max}} \)), and Minimum Surface Area per Molecule (\( A_{ \text{min}} \)) of AOT in Reline and Ethaline along with Their Water Mixtures at 298.15 K

| system        | \( \gamma_0 \) (mN/m) | \( \gamma_{ \text{cac}} \) (mN/m) | \( \pi_{ \text{cac}} \) (mN/m) | \( \Gamma_{ \text{max}} \times 10^6 \) (mol/m²) | \( A_{ \text{min}} \) (Å²) |
|---------------|------------------------|-------------------------------|------------------|---------------------------------|----------------|
| Reline        | 53.1 ± 0.7             | 24.1 ± 0.7                    | 290 ± 1          | 1.2 ± 0.4                       | 139 ± 5       |
| 10% (w/w) water | 58.3 ± 0.5             | 26.1 ± 0.5                    | 32.2 ± 1         | 2.0 ± 0.2                       | 83 ± 9        |
| 30% (w/w) water | 66.0 ± 0.5             | 26.4 ± 0.5                    | 39.6 ± 0.7       | 3.0 ± 0.2                       | 55 ± 4        |
| 50% (w/w) water | 68.0 ± 0.5             | 24.3 ± 0.5                    | 43.7 ± 0.6       | 4.2 ± 0.4                       | 39 ± 5        |
| Ethaline      | 46.5 ± 1               | 24.1 ± 1                      | 22.4 ± 1         | 0.8 ± 0.04                      | 203 ± 11      |
| 10% (w/w) water | 49.5 ± 0.8             | 26.1 ± 0.7                    | 23.4 ± 0.8       | 0.9 ± 0.05                      | 185 ± 9       |
| 30% (w/w) water | 51.9 ± 0.4             | 27.9 ± 0.5                    | 24 ± 0.8         | 1.0 ± 0.07                      | 166 ± 11      |
| 50% (w/w) water | 53.5 ± 0.3             | 28.3 ± 0.4                    | 25.2 ± 0.6       | 1.4 ± 0.1                       | 118 ± 2       |
| water         | 71.9 ± 0.2             | 27.7 ± 0.2                    | 44.2 ± 0.4       | 2.6 ± 0.2                       | 64 ± 2        |

(Ethalone) in molar ratio of 1:2 and their mixtures with water (10, 30, and 50%, w/w of water) is investigated. The choice of AOT, which is an anionic double-chained surfactant, is derived by its wide applications in cosmetic industries, emulsion and biochemistry, and so forth.\(^2\) Till date, most commonly investigated surfactants in DES systems includes anionic sodium dodecyl sulfate (SDS) and cationic n-alkyltrimethylammonium bromides (C\(_n\)TAB).\(^3\)\(^-\)\(^1\)\(^1\)\(^5\) This could be due to their good solubility and well-established micellization behavior in the aqueous medium. On the other hand, AOT has never been tested for aggregation in DESs or their mixtures with water. AOT favors inverse micelle formation in oil systems\(^2\)\(^5\) although it does also micellize in water.\(^2\)\(^4\) A low solubility of AOT in water, above which it forms liquid crystalline phases,\(^2\)\(^5\) increases its likelihood to undergo microscopic phase separation or nanosegregation in already nanostructured DESs\(^19\) having a strong hydrogen bonding network. Therefore, it seems very important to understand the aggregation behavior of AOT in these novel nanostructured solvents for future applications.

The nature of forces governing aggregation are evaluated in terms of Kamlet—Taft polarity parameters (\( \pi^\alpha, \beta, \) and \( \alpha \)) and cohesiveness of solvents provided by Gordon parameter (\( G \)) and ced. These parameters are correlated with the ability of investigated solvent systems to promote self-assembly of amphiphile.\(^1\)\(^H\) NMR and \( ^1\)\(^H\)-\(^1\)\(^H\) 2D NOESY spectroscopy are employed to get a detailed picture of prevailing interactions in the investigated systems. This along with previous reports on solvent structure of DESs and their mixtures with water\(^19\)\(^-\)\(^21\) helped in understanding exceptional aggregation behavior of AOT in DES—water (30 or 50% w/w) as compared to that in water.

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Figure 1. Variation of surface tension, \( \gamma \), as a function of concentration of AOT in (A) Reline; and (B) Ethaline along with their mixtures with water at 298.15 K. Lines are just guide for eye.
might be a effect of strong cat-anionic interactions between AOT and weakly hydrated choline cations in DESs having higher water content. Thus obtained values of $\gamma_{\text{cac}}$ increases with the water content, till a water content of 30% (w/w), in respective DES−water mixtures. Beyond that, $\gamma_{\text{cac}}$ decreases marginally only in the case of Reline. Further, $\gamma_{\text{cac}}$ is found to be higher in the case of Ethaline−water mixtures as compared to that in Reline−water mixtures. $\pi_{\text{cac}}$ which gives efficiency of surfactant to reduce $\gamma$ of solvent, is found to increase with the increase in the content of water in respective DESs. On comparing both solvent systems in neat or at any composition with water, it is observed that $\pi_{\text{cac}}$ is higher in the case of Reline. $\Gamma_{\text{max}}$ increases with the increase in the content of water in the DES system, whereas for same (w/w)% of water in DESs, the order of $\Gamma_{\text{max}}$ is water > Reline > Ethaline. In bulk, aggregation of AOT is monitored by conductivity and fluorescence measurements. The value of cac is obtained from variation of conductivity as a break point corresponding to sharp change in conductivity profile (Figure 2). As can be seen from Figure 2, with the addition of a surfactant to neat DESs, conductivity increases with a greater slope which follows a relatively lower slope after cac.

Figure 2. Variation of specific conductance, $\kappa$, as a function of concentration of AOT at 298.15 K in (A−C) Reline, 10% (w/w) water mixture, 30% (w/w) water mixture, respectively; (D−F) Ethaline, 10% (w/w) water mixture, 30% (w/w) water mixture, respectively.

Figure 3. (A) Representative emission spectra of pyrene in Reline solution of AOT at different concentration of amphiphile at 298.15 K. Variation of $I_1/I_3$ as a function of concentration of AOT in (B) Reline along with their water mixtures; (C) Ethaline and Ethaline−water (10%, w/w) mixture; and (D) Ethaline−water (30 and 50%, w/w) mixture at 298.15 K. Arrows represent their respective cac values.
Table 2. Critical Aggregation Concentration of the AOT in Reline, Ethaline, and Their Mixtures with Water Obtained Using Different Techniques along with $I_1/I_3$ Values of the Investigated Systems at 298.15 K

| System          | $C_{ac}^f$/mmol L$^{-1}$ | $C_{ac}^p$/mmol L$^{-1}$ | $C_{ac}^c$/mmol L$^{-1}$ | Average cac/mmol L$^{-1}$ | $I_1/I_3$ |
|-----------------|--------------------------|--------------------------|--------------------------|---------------------------|-----------|
| DES             | 0.91 ± 0.02              | 0.30 ± 0.02              | 10.1 ± 1                 | 8.9 ± 0.9                 | 2.26      |
| 10% (w/w) water | 0.68 ± 0.02              | 0.11 ± 0.02              | 6.2 ± 0.8                | 6.6 ± 0.8                 | 2.20      |
| 30% (w/w) water | 0.27 ± 0.01              | 0.036 ± 0.001            | 2.3 ± 0.5                | 2.5 ± 0.5                 | 2.08      |
| 50% (w/w) water | 0.12 ± 0.01              | 0.033 ± 0.001            | 0.9 ± 0.2                | 0.9 ± 0.2                 | 2.00      |
| Water           | 2.3 ± 0.4                | 2.3 ± 0.4                | 2.2 ± 0.4                | 2.2 ± 0.4                 | 1.70      |

“Surface tension. 2Steady-state fluorescence. 3Conductivity method. Average cac is average of cac obtained from fluorescence and conductivity measurements.

Figure 4. Variation of Kamlet-Taft parameters, $\pi^*, \beta, \alpha$ as a function of water (w/w) % in (A) Reline; and (B) Ethaline at 298.15 K. Values in parentheses denote their respective average cac values obtained from fluorescence and conductivity measurements.

However, in the presence of water, conductivity either decreases with a lower slope or remains almost unchanged on the addition of a surfactant till cac is reached, after which it decreases with a greater slope (Figure 2). A decrease in conductivity with addition of AOT is similar to that reported in literature for aggregation of SDS in a mixed solvent system of calcium nitrate tetrahydrate + acetamide melts. It is well known that the ratio of first ($I_1$) to third ($I_3$) vibronic bands ($I_1/I_3$) of pyrene fluorescence is very sensitive toward solvent polarity of cybotactic region and is generally used to determine micropolarity of solvent along with cac of surfactants. Figure 3A shows a decrease in intensity of vibronic bands of pyrene with increase in concentration of AOT. The variation of $I_1/I_3$ as a function of concentration of AOT in DESs and their mixtures with water is shown in Figure 3B–D.

With an increase in the content of water in DESs, the value of $I_1/I_3$ decreases in the absence of AOT (Table 2). For the investigated DESs and DES–water mixtures, variation of $I_1/I_3$ as a function of concentration of AOT follows a sigmoidal pattern as generally observed for self-assembling surfactant systems.32 The midpoint of transition is marked as cac of AOT, and obtained values of cac are listed in Table 2 along with those obtained from conductivity measurements. The value of cac of AOT in neat DESs (Reline 10.06 mM and Ethaline 15.52 mM) is relatively higher as compared to their mixtures with water and decreases with the increase in the content of water. On the other hand, in neat Ethaline and its mixtures with water, AOT exhibits a higher value of cac as compared to systems involving Reline. Interestingly, AOT is found to aggregate at much lower concentrations in DES systems involving Reline. Interestingly, AOT is found to aggregate at much lower concentrations in DES systems involving Reline. A further increase in water content up to 50% (w/w) in Reline and Ethaline decreases cac values to 0.94 and 1.36 mM, respectively. Different characteristic parameters of solvent such as polarity, Gordon parameter ($G$), and ced have been reported to affect the aggregation behavior of surfactants.32–35 Therefore, these parameters are explored in this study to have insight into the specific forces governing aggregation of AOT in DESs or their mixtures with water. At first, polarity parameter ($I_1/I_3$) using pyrene fluorescence has been measured, a lower value of which, signifies higher hydrophobicity of the cybotactic region around fluorophore (Table 2). Polarity of solvent systems under investigation is also probed by evaluating Kamlet-Taft parameters, which involves $\pi^*$ (polarizability), $\beta$ (H-bond acceptor ability, HBA), and $\alpha$ (H-bond donor ability, HBD) using 4-nitroanisole, 4-nitroaniline, and 4-carbomethoxy-1-ethylpyridinium iodide as probes, respectively, and correlated with the observed values of cac. The shifts in $\lambda_{max}$ of the probes in different solvents (as provided in Figure S1 and S2, Supporting Information) is used to determine the parameters by using following equations36

\[
\pi^* = 14.57 - 4270/\lambda_{max,OMe}
\]

(3)

\[
\beta = 11.134 - 3580/\lambda_{max,NH_2} - 1.125\pi^*
\]

(4)

\[
\alpha = 0.0485Z - 2.75 - 0.46\pi^*
\]

(5)

where $Z$ (kcal mol$^{-1}$) = 28.591/$\pi^*$

(6)

The obtained values of $\pi^*$, $\beta$, and $\alpha$ in DESs and their mixtures with water are provided in Table S1 (Supporting Information). Kamlet-Taft values are quite consistent with the literature reports,37 and slight inconsistency is assigned to use of different probes. Figure 4 shows the variation of $\pi^*$, $\beta$, and $\alpha$ as a function of water (w/w) % in DESs.

Further, cohesiveness of solvent is considered to probe the aggregation behavior as high cohesiveness is generally related with aggregation promoting capacity of given solvent.32–35 The cohesion in a solvent involves various interactions such as
dispersion, dipole interactions, repulsion interactions, and so forth, between like molecules and is given by Gordon parameter \((G)\), which is calculated using following equation\(^{32-34}\)

\[
G = \frac{\gamma}{V_m^{1/3}}
\]

where \(\gamma\) is surface tension and \(V_m\) is molar volume of solvent. The value of densities employed to derive \(V_m\) values of \(V_m\) and

Figure 5. Variation of Gordon parameter, \(G\), as a function of water (w/w) % in (A) Reline and (B) Ethaline. Values in parentheses denote their respective average cac values obtained from fluorescence and conductivity measurements. Lines are just a guide for eye.

Figure 6. Expanded \(^1\)H NMR spectra of various protons of DESs along with their mixtures in (A) Reline and (B) Ethaline at 298.15 K.

Figure 7. \(^1\)H–\(^1\)H 2D NOESY spectra of (A) Reline; (B) 50% (w/w) Reline–water mixture; (C) Ethaline; and (D) 50% (w/w) Ethaline–water mixture.
Figure 8. Number weighted size distribution of aggregates formed in (A) Reline and (B) Ethaline along with their water mixtures at 298.15 K obtained from DLS measurements. Variation of $D_h$ as a function of concentration of amphiphile in (C) Reline and (D) Ethaline.

$G$ are provided in Table S2 (Supporting Information). Value of $G$ for neat Ethaline is found to be consistent with the literature report, but inconsistency with the literature is observed in the case of Reline. A discrepancy in the obtained values of $G$ in the case of Reline as compared to that reported in literature stems out from different values of surface tension used to calculate $G$ (discussed later). Similarly, ced, which is the energy required to remove unit volume of molecules from their neighbors to infinite separation by disrupting interactions between same molecules present in solution phase is calculated for solvent systems under investigation. Even a small expansion in volume has a significant effect on these interactions; therefore, enthalpy of vaporization ($\Delta H^\circ_m$) is considered as a good measure of ced, which can be determined using surface tension, $\gamma$, and molar volume, $V_m$, of the solvent employing following expressions

$$\Delta H^\circ_m = A(yV_m^{2/3}N_A^{1/3}) + B$$

$$\text{ced} = \frac{\Delta H^\circ_m - RT}{V_m}$$

where $N_A$ is Avogadro’s number and $A$ and $B$ are constants with values of 0.01121 and 2.4 kJ mol$^{-1}$ at 298.15 K, respectively. This equation has been successfully tested to evaluate $\Delta H^\circ_m$ and ced of the ILs with very satisfactory results. The obtained values of ced are provided in Table S3 (Supporting Information). Variation of $G$ as a function of water content (w/w) % in DESs is shown in Figure 5.

$^1$H NMR and $^1$H–$^1$H 2D NOESY spectroscopy has been employed to investigate changes in the solvent structure, which is correlated with variation in characteristic properties of aggregation. The obtained spectra are shown in Figures 6 and 7.

A change in chemical shift of different protons of DESs as a function of the water content in DESs reflects a change in the environment of components of DES. In the case of Reline, all four protons of urea appeared as a singlet in $^1$H NMR spectra and show a continuous up-field shift along with peak broadening while moving from neat DES to DES–water (50% w/w) mixture (Figure 6A). An up-field shift, varying in magnitude, is also observed for all protons of cholinium ion present in Reline. As compared to other protons ($-$CH$_2$ group protons at position (1) exhibit maximum up-field shift in Reline–water (50% w/w) mixture as compared to neat Reline. Further, 2D $^1$H–$^1$H NOESY measurements shows that correlation peaks originating from the interaction of protons of water and urea becomes more and more stronger with increasing water content in Reline (Figures 7 and S5, Supporting Information).

In the case of Ethaline, protons of EG at position (2) and that of cholinium ion at position (4) experience marginal downfield shift with addition of water (Figure 6B). On the other hand, protons at positions (1) and (3) of cholinium ion shifts up-field while going from Ethaline to Ethaline–water (50% w/w) mixture (Figure 6B). However, the change in the chemical shift for all protons of cholinium ion in Ethaline is nearly half to that observed in the case of Reline.

Further, to have insight into the size of formed aggregates and the presence of dimers or trimmers below cac, dynamic light scattering (DLS) measurements were performed at different concentrations of AOT in DESs and their mixtures with water (Figure 8A–D).

There are various assumptions that must be followed for highly reliable DLS measurements. These include non-absorption of light by the particles, reduced multiple scattering, dilute solutions, exact values of viscosity, and refractive index of the solutions. The present systems comply most of these assumptions as the investigated systems do not have any chromophore, which could absorb light at the wavelength of photon (535 nm) used. The effect of multiple scattering is reduced by using a quartz cuvette of small volume (75 $\mu$L) and samples were measured at very low concentration of surfactant. The values of required parameters such as viscosity and refractive index of solution were measured and used for calculations by software. Two different types of data fitting, that is, cummulant and distribution fit were tested to extract
the size. Only the size corresponding to the best fit is reported. The observed profiles of the hydrodynamic diameter ($D_h$) are shown in Figure 8A,B. It is observed that formed aggregates of AOT in neat DESs are relatively small ($D_h \approx 50 \text{ nm}$ in Reline and $\sim 34 \text{ nm}$ in the case of Ethaline) as compared to that in water ($D_h \approx 120 \text{ nm}$). In the case of Reline, $D_h$ of aggregates of AOT decreases with the addition of water till 10% (w/w) of water to $\approx 35 \text{ nm}$, after which it increases marginally to $\approx 50 \text{ nm}$ at water content of 50% (w/w). On the other hand, in the case of Ethaline, $D_h$ remains almost constant with change in composition of the DES–water mixture. Further, to check the effect of concentration of AOT on the size of aggregate, DLS experiments have been performed at 3 and 6 times of cac.

**DISCUSSIONS**

The $\gamma$ for Reline comes out to be 53.1 mN/m, which is consistent with literature reports\textsuperscript{26–28} however is much lower than at least one instance reported in the literature.\textsuperscript{13} The varying sensitivity of method used in the present work (du Noiyy ring) and that reported in the literature (drop shape method) could be a reason for the same. No doubt our results are reproducible; however, it is important to mention that drop shape method is better for measurements of surface tension of such viscous solvents as viscosity do not affect the shape of the drop. On the other hand, viscous forces could affect weight of the liquid film immediately beneath the ring as well as shape of meniscus during detachment of ring when $\gamma$ is measured using du Noiyy ring method. $\gamma$ for Reline and Reline–water mixtures is found to be higher than Ethaline and Ethaline–water mixtures because of dominance of donor–donor H-bonding interactions in Ethaline over Reline. A larger value of $\gamma$ in the case of DES–water mixtures as compared to neat DESs is ascribed to high surface tension of water. However, it seems that the interactional phenomenon between DESs and water is complex\textsuperscript{16} which affects $\gamma$. Small amounts of water when added to DESs (ChCl/urea/water = 1:2:1.44 or ChCl/EG/water = 1:2:1.46) increases $\gamma$, whereas $\gamma$ decreases when water was added to ChCl/MalAc in a molar ratio of 1:1:2 or 1:1:5.\textsuperscript{16}

A decrease in $\gamma$ with a relatively steeper slope with addition of AOT in the case of DESs can be assigned to interaction of the AOT chains with the cholium cation. The $\gamma_{\text{cac}}$ is more in the case of systems having Ethaline and is affected by (i) surface pressure, $\pi$, and (ii) the adsorption of surfactant and its orientation at air–solution interface. An increase in surface pressure generally results in the decrease in $\gamma$ of solution, which is contrary to the obtained results. In the present case, an increase in $\pi$ with the addition of water is due to increased values of $\gamma_0$ and hence cannot be correlated with $\gamma_{\text{cac}}$. Further, the role of orientation of AOT at air–solution interface is ruled out based on decreasing values of $A_{\text{min}}$ with increase in the water content. The marginal increase in values of $\gamma_{\text{cac}}$ with the increase in water content in both DES–water systems indicate relatively lesser change in surface structure of solvents in the presence of water. Further, a higher value of $\pi_{\text{cac}}$ in the case of Reline as compared to Ethaline at any investigated composition is attributed to higher surface tension of Reline. An increase in $I_{\text{max}}$ with the increase in the content of water signifies increased compactness at the air–solution interface, which is more in the case of Reline as compared to Ethaline. This could be due to the more perpendicular alignment of the amphiphile at air–solution interface in the presence of water in mixed solvents. It is quite probable that the increased content of water weakens the interactions between different compo-
viscous solvents similar to that reported earlier for other surfactants in DESs systems.\textsuperscript{2,4} Therefore, the concentration of AOT corresponding to surface saturation is denoted as C\textsubscript{S}. Further the absence of any sort of structured assemblies around C\textsubscript{S} is confirmed from DLS measurements (Figure 8). In highly viscous systems that is, pure DES and DES–water (10 w/w\%) system, there is some difference in values of cac obtained from conductivity and fluorescence measurements. This might be due to reduced mobility of amphiphile ions in nano-segregated domains formed by AOT complexed with water and components of DESs. The viscous nature of investigated solvents may also affect the partition of pyrene into aggregates in fluorescence measurements.

A higher value of cac in neat DESs as compared to that observed in their mixtures with water is consistent with literature reports that aggregation behavior is less favorable in a nonaqueous medium or cosolvent such as EG, dimethyl sulfoxide, and methanol-modified water systems.\textsuperscript{32,43} The presence of enhanced hydrophobic interactions with nano-structured domains of neat DESs, the content of which decreases with addition of water, could delay cac. Greater solvophobicity offered by H-bonded EG, which preserves its structure in Ethaline–water mixtures, to hydrophobic AOT having less solubility in polar solvents, leads to delay in cac as compared to that observed in Reline at every composition of DES–water mixtures. A lower value of I\textsubscript{1}/I\textsubscript{3} in the case of the Reline system supports our assumption. The role of van der Waals interactions between alkyl chain of AOT and –CH\textsubscript{2} groups present in EG and choline chloride cannot be ruled out. With the increase in the content of water, electrostatic interactions between the cholinium cation and AOT head group enhances at the cost of decreased interactions between cholinum and EG/urea as observed from NMR measurements (discussed later). This results in screening of electrostatic repulsions between AOT head groups, leading to decrease in cac. This situation is similar to the formation of mixed micellar systems where negatively charged amphiphile and positively charged choline behaves as a cat-anionic surfactant system.\textsuperscript{11–47} Both DESs exhibit relatively higher value of I\textsubscript{1}/I\textsubscript{3} (Reline \(\approx 2.26\), Ethaline \(\approx 1.96\)) as compared to that of water \((\sim 1.7)\), which indicates relatively higher polarity of neat DESs as sensed by the fluorescence probe. This is in contrast with the higher value of cac in neat DESs as compared to that observed in water and suggests that the cac is mainly affected by inherent structure of DESs. Further, with the addition of water, I\textsubscript{1}/I\textsubscript{3} decreases from 2.25 (Reline) to 2.01 (Reline–water, 50% w/w), whereas it changes marginally \((1.96–1.93)\) in the case of the Ethaline–water system but still remains more as compared to that of water \((\sim 1.7)\). It has been established that medium with higher polarity favors self-assembly; therefore, cac of AOT should be lower in the case of DESs or their mixtures with water as compared to that in water. However, this is not the case at least from polarity point of view as AOT has limited solubility in water\textsuperscript{27} and it favors to undergo micellization in the nonpolar medium.\textsuperscript{23} Therefore, AOT is not expected to form micelles in DES–water systems with high polarity, which supports our claim of nano-segregation of AOT in DES–water mixtures.

In continuation, Kamlet–Taft Parameters were calculated for all investigated DES systems. \(\pi^*\), \(\beta\), and \(\alpha\) values for neat DESs are more in the case of Reline as compared to Ethaline. Higher value of \(\pi^*\) suggests higher ionic character of Reline as compared to Ethaline, which is ascribed to the polar nature of urea present in Reline. Similarly, Reline exhibits higher H-bond donor and acceptor capacity as compared to Ethaline as indicated by higher value of \(\alpha\) and \(\beta\), respectively. This is in line with the fact that the H-bonding structure of hydroxyl donors such EG and glycerol dominates the structural network of DES formed with choline chloride.\textsuperscript{31,42} Therefore, the lower value of cac in Reline is in line with the reported literature where higher values of \(\pi^*\), \(\beta\), and \(\alpha\) supports self-assembly of amphiphiles.\textsuperscript{11} Further, it can be seen from Figure 2A that \(\pi^*\), which is a measure of the ionic character of solvent, increases with the increase in the water content in DESs. It has been established that the presence of water decreases H-bonding interactions between constituents of DESs at the cost of enhanced H-bonding interactions between water and components of DESs.\textsuperscript{19} This reduces the viscosity and stabilizes the ionic character of the solvent. A decrease in interactions between constituent ions of DESs in the presence of water is supported by increased conductivity with the increased content of water in the absence of AOT (Figure 2). On the other hand, \(\alpha\) and \(\beta\) decrease with the increase in the water content in respective DES–water mixtures, which signifies a decrease in H-bonding capability of the solvent\textsuperscript{11,36} and is due to establishment of stronger interactions between water and components of DESs. This increases the solvophobic effect leading to lowering of cac with the increase in the content of water. However as discussed earlier, cac for water does not follow the pattern followed by \(\pi^*\), \(\alpha\), and \(\beta\) in DESs–water mixtures. It remains somewhere close to cac observed for DES–water (30–50%) mixtures, as can be seen from Figure 4.

A lower value of cac in Reline or Reline–water mixtures at all compositions as compared to Ethaline is also justified by the higher value of \(G\) in the former case. With the addition of water, \(G\) increases for both the systems under investigation, which is reflected by the decrease in cac with the increase in the water content. As can be seen from Figure S3 and Table S3 (Supporting Information), similar to \(G\), ced increases with the increase in the water content. This supports the decrease in cac with the increase in the content of water in both the investigated systems.\textsuperscript{48} On comparing \(G\) and ced of Ethaline and Reline, it is observed that both exhibit comparable or even better \(G\) and ced as compared to organic solvents or ILs tested so far as medium for self-assembly (Tables S2 and S3, Supporting Information).\textsuperscript{49–55} Therefore, it is expected that Reline and Ethaline could be considered as better self-assembly media as compared to organic solvents or even ILs.

Interestingly, water exhibits a higher value of \(G\) and ced as compared to DESs and their mixtures with water. However, cac of AOT in water lies somewhere closer to that observed in the case of DES–water (30 and 50% w/w) mixtures, which otherwise should be lowest. Similar observations have been made from various polarity parameters where cac of AOT in water does not fall in line with the observed value of these parameters. It is obvious that polarity as well as cohesiveness of investigated solvents governs aggregation, as cac decreases with the change in solvent parameters as expected. However, cac lower than that observed in the case of water, in the case of DES–water (50% w/w), suggests that some additional forces are promoting aggregation in DES–water mixtures having higher content of water. The DESs–water mixture (50 w/w %) behaves like a solution of components of DES in water\textsuperscript{19} wherein constituent ions (cholinium cation, Cl anion) or compounds (EG, urea) could interact with AOT and thus
affect the cac. Therefore, enhanced ionic interactions between AOT anion and cholinium cation in DES—water (50 w/w %) mixtures seems to assist in nanosegregation of AOT at much lower concentrations, which is further probed using NMR measurements.

A change in the chemical shift of different protons of DESs as a function of concentration of water in DESs is observed from $^1$H NMR spectroscopy (Figure 6 and S4, Supporting Information). This change occurs because of intrusion of water molecules into the existing molecular arrangements in neat DESs through differential hydration of various species comprising DESs. An up-field shift of protons observed in the case of Reline with the addition of water could be due to increasing H-bonding interactions of urea with the water molecules. This results in confinement of urea in H-bonded urea—water network (Figure 6A). Such confinement leads to a decrease in spin–lattice relaxation time and leads to peak broadening. An up-field shift can also be correlated to increased importance of van der Waals interactions between weakly hydrated nanostructured domains of cholinium ions. The absence of cross peaks between protons of cholinium ion with either urea or water in Reline—water mixtures supports the above assumption (Figures 7 and S5, Supporting Information). In the case of Ethaline, increased H-bonding interaction of OH groups of EG and cholinium ion with added water molecules results in marginal down-field shift of protons of EG at position (2) and that of cholinium ion at position (4), although EG is expected to preserves its structuring network. On the other hand, decreased extent of interactions between EG and cholinium ion at the cost of enhanced H-bonding interactions between EG and water as well as cholinium ion and water results in up-field shift of protons at positions (1) and (3) on moving from neat Ethaline to 50% (w/w) Ethaline—water mixtures.

The above inference is further supported by 2D $^1$H-–$^1$H NOESY spectroscopy where the intensity of cross peaks for interaction of cholinium ion protons with that of EG continuously decreases with the increase the water content in Ethaline. At the same time, new cross peaks originates signifying interactions between water and EG as well as between water and cholinium ion protons. Moreover, the change in chemical shift for all protons of cholinium ion in Ethaline is nearly half of that observed in the case of Reline. This indicates relatively less disruption in the solvent structure of Ethaline as compared to Reline with the addition of water (Figure S5, Supporting Information). In addition, interactions of water with urea in Reline are much stronger than those with EG in Ethaline as depicted by the 2D $^1$H–$^1$H NOESY spectra of two systems (Figures 7 and S5, Supporting Information).

From the above discussion, it is inferred that cholinium ion remain less hydrated in the case of Reline where water specifically bounds to urea resulting in formation of weakly hydrated nanostructured domains of cholinium ions. On the other hand, the presence of water does not disturb internal structure of Ethaline to greater extent, where water does not differentially hydrate cholinium ion and EG. Therefore, cholinium ion remains more available to interact with oppositely charged AOT in the case of Reline.

It is clear that Reline—water (50 w/w %) behaves more like a solvent system rich in electrolyte (segregated cholinium ion) and urea, where the electrolyte is more free to interact with AOT. Such interactions assist in nanosegregation via charge neutralization and brings cac of AOT in Reline—water (50% w/w) mixtures to a value even smaller than that observed in water. Similar phenomena happen in the case of Ethaline but to a relatively smaller extent as compared to that in Reline owing to lesser change in the solvent structure by addition of water. It can be seen that $D_h$ of aggregates of AOT (Figure 8A) in neat DESs is relatively less than that in water (≈120 nm). In Reline ($≈56$ nm), $D_h$ of aggregates are about 2.4 times less than water, whereas in Ethaline ($≈40$ nm), $D_h$ is 3 times less than that observed in water. $D_h$ of AOT aggregates decreases with the decrease in the content of water in DES—water mixtures. This is in line with variation of values of $c_e$ and $G$, suggesting that the solvent cohesion forces are governing the aggregation of AOT. While considering polarity parameters of solvent, a change in $β$ with addition of water in DESs (Table S1, Supporting Information) is also in line with the change in $D_h$ of AOT aggregates. This suggests that not only solvent cohesion but HBA ability of the solvents also affects the size of formed aggregates. Further, the dimensions of nanosegregates of AOT are larger than that observed for a normal micelle, which could be due to complexation of AOT with different components of DES depending on the nature of the component as discussed earlier. Therefore, it is established that not only polarity and cohesiveness of DESs or their mixtures with water govern self-assembly of amphiphiles but other factors such as change in the solvent structure also play an important role.

Further, AOT does not self-assemble in the form of smaller aggregates such as premicelles as observed from DLS measurements performed at concentrations much below cac (Figure 8). As can be seen from Figure 8C,D, there is a marginal increase in $D_h$ with the increase in the concentration of AOT. The increase in $D_h$ could reflect both growth of aggregates in size and effects of interaggregate hydrodynamic interactions. It is observed that $D_h$ increases relatively more in the case of water rich DES—water mixtures, which suggests the growth of nanosegregates.

**CONCLUSION**

Present work along with earlier reported work on self-assembly of surfactants in DES provides ample evidence of aggregation of AOT in two commonly used DESs namely Reline and Ethaline as well as their mixtures with water. AOT is found to self-assemble in a contrasting manner in neat DESs and their mixtures with water, where AOT forms micelle-like aggregates in neat DESs and undergoes nanosegregation in DES—water mixtures. The different extent of perturbation of the inherent structure of DES by water in two DESs led to varying characteristic properties of aggregation that include cac and types of self-assembled structures. Various polarity parameters and cohesion forces in different systems are found to directly correlate with observed cac values.

The only exception is the observance of much lower cac value in DES—water (50%, w/w) mixtures as compared to that with water. It is established that DESs—water mixtures at higher water content (30 and 50% w/w) behave similar to concentrated aqueous solution of components of DESs, where weakly hydrated cholinium ion remains more available to interact with AOT resulting in relatively hydrophobic nanosegregates at much lower concentrations. The observed behavior of the complex DES—water mixture as simple concentrated aqueous solution of DES components at higher water content resulting in the formation of nanosegregated domains of marginally hydrophilic surfactant would offer a new platform to investigate such systems from the view point of...
basic understanding and their applications. Therefore, it is expected that the present work would not only provide new insights into the field of colloid and interface science but also find a place for various applications related to controlled photophysical properties, catalysis, and nanoscience owing to presence of differentially hydrated segregates in DES–water mixtures.

**EXPERIMENTAL SECTION**

**Materials and Methods.** Choline chloride (≥99%), urea (≥99%), AOT (≥99%), 4-nitroaniline (≥99%), 4-carbomethoxy-1-ethylpyridinium iodide (97%), and pyrene (≥98%) were purchased from Sigma-Aldrich; 4-nitroanisole (98%) was purchased from TCI chemicals, India. EG (99%) was purchased from Loba Chemie, India, and used as received.

Before performing physicochemical measurements, DESs under investigation, that is, Reline and Ethaline were prepared by mixing choline chloride and urea as well as choline chloride and EG in the molar ratio of 1:2 under stirring for 4–5 h at 70 °C until clear and homogenous mixtures were obtained. Thus prepared DESs were then cooled to room temperature and dried under vacuum for 48 h to remove moisture. The water content in synthesized DESs, as indicated by Karl Fischer analysis, was found to be less than 2000 ppm in both DESs. Synthesized DESs were characterized by ¹H NMR spectroscopy using a Bruker Ascend 500 spectrometer (AVANCE III HD console) employing a sealed-glass capillary placed inside a 5 mm NMR tube containing D₂O for lock purposes. Scheme 1 shows molecular structures of components of DESs and AOT.

Scheme 1. Molecular Structure of Components of Investigated DESs and AOT

Double-distilled deionized water having resistivity ≥18 MΩ cm at 298.15 K obtained from Millipore water purification systems was used for experiments. Appropriate amount of water was added to make DES–water mixtures having water content of 10, 30, and 50% (w/w). All measurements were made by adding concentrated solution of AOT prepared in DESs or DES–water mixtures to respective DESs or DES–water mixtures by the titration method at 298.15 K, if not mentioned otherwise. After addition, the solutions were stirred for 3–4 min for homogeneous mixing and equilibrated for another 3–4 min before measurements. Surface tension (γ) was measured using a Krüss easy dynes tensiometer equipped with a thermostat with a temperature control of ±0.1 K using the ring method. The accuracy for the measurement was 0.1 mN/m for water as the solvent and 0.25 mN/m for other solvent systems. Conductivity analysis (κ) was measured using a digital conductivity meter (Systronics 308) employing a cell of unit cell constant. The temperature of the conductivity cell was controlled by using Julabo water thermostat within ±0.1 K. Measurements were made in triplicate with an uncertainty of 0.7%. Prior to the measurements, the conductivity cell was calibrated using aqueous solutions of KCl of different concentrations. Steady-state fluorescence measurements were performed using a PerkinElmer luminescence spectrometer LS-55 in a quartz cell of path length 1 cm. Pyrene was used as an external fluorescent probe at a concentration of 2 × 10⁻⁶ M to prevent the formation of excimer. Measurements were performed using an excitation wavelength of 334 nm, employing an excitation and emission slit width of 2.5 nm, each in wavelength range of 350–450 nm. The data were collected in duplicate with an uncertainty of less than 0.5%. Temperature during measurement was controlled using a built-in temperature controller within ±0.1 K. DLS measurements were performed on a light scattering apparatus (Zetasizer, Nano ZS) from Malvern Instruments using a quartz cuvette of path length 1 cm at a scattering angle of 173°. Temperature during measurement was controlled using an built-in temperature controller with an accuracy of ±0.1 K. An average of 10 measurements, each consisting of 20 runs, was considered as an experimental data. Data were analyzed using standard algorithms with an uncertainty of less than 8%. DLS measurements were performed on solutions of AOT at different concentrations ranging from below average value of cac, to higher than cac obtained from literature. Density (ρ) of solutions was measured using a vibrating-tube digital densimeter (model: DMA 60/602, Anton Paar, Austria) with uncertainty 3 × 10⁻³ kg m⁻³. Kamlet–Taft parameters (π*, β, and α) for DESs and their mixtures with water were determined by using 4-nitroanisole, 4-nitroaniline, and 4-carbomethoxy-1-ethylpyridinium iodide, respectively. For this purpose, UV–vis measurements were performed using a UV–vis spectrophotometer (UV-1800 SHIMADZU) in wavelength range 200–800 nm using a quartz cuvette of path length 1 cm. Stock solutions of used probes (2 × 10⁻⁴ M) were prepared in ethanol. An appropriate amount of stock solution was added to the cuvette and ethanol was evaporated by purging nitrogen gas before the addition of the solvent. This was followed by vigorous stirring to achieve complete solubilization of probes in solvents. Final concentration of probes in solvents was 5 × 10⁻⁶ M. The ¹H→¹H 2D NOESY experiment was recorded on a Bruker Ascend 500 spectrometer (AVANCE III HD console) in pure D₂O in the case of 10% (w/w) water systems, whereas for DES–water (30 and 50 w/w %) mixtures 35 and 20% (w/w) D₂O–water systems were used, respectively.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01637.

UV–vis plots of 4-nitroanisole, 4-nitroaniline, and 4-carbomethoxy-1-ethylpyridinium iodide in DESs and their water mixtures; plots showing the variation of ced as a function of water (w/w) % in DESs; variation of change in chemical shift value for different protons of DESs; ¹H→¹H 2D NOESY spectra of 10 and 30% (w/w) water mixtures with DESs; and values of Kamlet–Taft solvent parameters, Gordon parameter G, and ced (PDF)
The authors are thankful to CSIR, Govt. of India, for financial assistance wide project scheme no. 01(2774)/14/EMR-II. K. and G.S. are thankful to UGC and CSIR, respectively, for award of SRF. We are thankful to UGC, India, for their UGC-CAS program awarded to the Department of Chemistry, Guru Nanak Dev University, Amritsar. The infrastructure facility utilized for carrying out this work under the UPE grant is highly acknowledged. Authors are also thankful to Prof. A. P. Abbott for valuable discussion.

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