Micellization Behavior of Conventional Cationic Surfactants within Glycerol-Based Deep Eutectic Solvent

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1. INTRODUCTION

Deep eutectic solvents (DESs) are receiving increased attention from both academic and industrial research due to their immense application potential.1-4 DESs find various applications in the synthesis of polymers, organic catalysis, biotransformation, and materials chemistry, as sustainable solvent systems in dissolution and extraction processes.5-8 DESs are analogues of ionic liquids (ILs), which show tremendous promise as emerging green and tuneable solvents with low cost, less toxicity, high conductivity, nonflammability, environmentally friendliness, and biodegradability.9-15

Surfactants show the tendency of forming micelles and microemulsions and are of immense importance due to their extensive applications in various fields of colloidal science and technology.16-18 Surfactants are amphiphilic molecules that reduce the surface tension of water.19-21 Surfactants act as wetting agents that lower the interfacial tension between two liquids.22 These are the most common and versatile constitutive elements that are found in many topical wetting agents, dispersants, emulsifier, foaming agents, antiseptics, corrosion inhibitors, and shampoos.23 Interfacial phenomena in pharmacy and medicine are significant factors that affect the adsorption of drugs onto solid adjuncts in dosage forms, penetration of molecules through the biological membrane,
emulsion formation, stability, and the dispersion of insoluble particles in liquid media to form suspensions. The dual nature of the surfactant (i.e., hydrophobic and hydrophilic) gives rise to various extensive properties in the solution, like "self-assembly" also known as micelles and the concentration at which this phenomenon occurs is called critical micelle concentration (CMC). The hydrophobic alkyl chain of the surfactant is oriented away from the aqueous solvent media, forming the micellar core, and the head group of the surfactant is located toward the bulk aqueous media. The nature of the surfactant, additive, and temperature strongly influence the micellization behavior of the surfactant and hence the CMC and the shape of the micelles.

The aggregation of a surfactant plays important roles in many fields, including biology, materials science, chemical engineering, and petroleum recovery. The interactions responsible for the formation of micelles are van der Waals, hydrophobic, and electrostatic interactions, which contribute to the overall micellization process. Thermodynamic and interfacial properties of the binary system surfactant, DES, is extremely sensitive to the hydrophobic and hydrophilic interactions and also the electrostatic interaction. The molecular interaction of the surfactant with the DES system can help to improve an understanding of this in biological and pharmaceutical systems and their potential applications in different fields. The change of the micellar properties of surfactants within novel types of green solvent (DES) is currently a topic of immense importance.

Many research studies worldwide have been involved in the investigation of the physicochemical properties of surfactants and their interaction with DES, and the number of publications dedicated to the use of DESs for this purpose is rapidly increasing. Pandey et al. have investigated the interaction between sodium dodecyl sulfate (SDS) within rylene-based DESs by surface tension, dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), density and dynamic viscosity measurements, and fluorescence probe behavior of pyrene and 1,3-bis-(1-pyrenyl)propane to characterize these molecular aggregates. Ghosh et al. studied the micellization behavior of 1-butyl-3-methylimidazolium octylsulphate [Bmim][OS] within two synthesized choline-based DESs (ChCl–urea and ChCl–Gly) using different spectroscopy techniques such as fluorescence, UV–vis spectroscopy, dynamic light scattering, and Fourier transform infrared (FTIR). A significant decrease in the CMC and increase in the aggregation number (Nagg) are observed, and the interactions of [Bmim][OS] with DESs are highlighted from FTIR spectral responses. Bantala et al. also applied to study the micellar solution–drug binding of the promazine hydrochloride drug. Jackson et al. have studied the aggregation of alkyltrimethylammonium bromides within choline chloride/glycerol DES by means of surface tension, X-ray and neutron reflectivity, and small-angle neutron scattering.

In the present work, we have studied the aggregation behavior of two structurally different cationic surfactants in aqueous solutions of Gly-based DES. A universal and widespread DES glycerine, composed of choline chloride and glycerol in a 1:2 mole ratio, was chosen as the solvent. Prototypical cationic surfactants, viz., cetyldimethylammonium bromide (CDMEAB) and cetyltributylphosphonium bromide (CTBPB) with different head groups, were used as the amphiphiles. The main focus of this work is to highlight the role of surfactant head groups (quaternary ammonium vs phosphonium) in the micellization process of the cationic surfactants within aqueous DES media and, more importantly, to present a detailed comparative investigation into their aggregation behavior within an aqueous DES solution as compared to that in water. Interestingly, it is observed that the aqueous DES medium facilitates the micellization of both cationic surfactants as compared to that of water, resulting in a decreased CMC and increased aggregation number of both CDMEAB and CTBPB. Different techniques, such as the surface tension, conductivity, fluorescence, DLS, FTIR, 1H NMR, and two-dimensional (2D) nuclear Overhauser effect spectroscopy (NOESY), have been used to gain insight into the self-aggregation behavior of the surfactants in glyceline (Gly) solution and to study the micellar properties. The effect of Gly on micellization behavior and surface properties, i.e., CMC, surface excess concentration (Γmax), the free energy at CMC (ΔGtrans), minimum area per molecule (Amin), packing parameter (P), the efficiency of adsorption (pC20), is evaluated by the surface tension method. The various thermodynamic parameters, i.e., the standard Gibbs free energy of micellization (ΔGmic), Gibbs energy of adsorption (ΔGads), Gibbs energy of transfer (ΔGtrans), the free energy at the air–water interface (ΔGtrans), and Gibbs energy of the air–water interface (ΔGads), have also been calculated. The CMC, aggregation number (Nagg), Stern–Volmer constant (Ksv) have been studied by a steady-state fluorescence method. Nuclear Overhauser effect spectroscopy (NOESY) is used to study the way by which cationic surfactants self-assemble within the DES solution. The results obtained from FTIR, NMR, and DLS spectroscopy techniques clearly suggest strong surfactant–DES interactions that result in the change in the micellar structure in the presence of the Gly DES.
Chemical structures of conventional surfactants, i.e., cetyltrimethyl ammonium bromide (CDMEAB), cetyltributylphosphonium bromide (CTBPB), glycerol, pyrene, 1-pyrene carboxyaldehyde, and cyclopentadienyl chloride, are represented in Scheme 1.

2. EXPERIMENTAL SECTION

2.1. Materials. Cetyltrimethyl ammonium bromide (≥99%), cetyltributylphosphonium bromide (≥99%), potassium bromide (FTIR grade ≥99% trace metal basis), potassium chloride (≥99%), choline chloride (≥99%), glycerol (≥99%), pyrene (≥99%), 1-pyrene carboxyaldehyde (≥99%), and cyclopentadienyl chloride (≥99%) were purchased from India. It was calibrated with aqueous KCl solution containing the probe pyrene (1.2 × 10−4 M) was added to the cuvette.

2.2. Methods. Surface tension measurements were obtained using a Jencon tensiometer. The specific conductance (κ) studies were carried using a digital conductivity meter (Systronics Type-306). Fluorescence experiments were carried out on an Agilent Technology spectrophotometer. FTIR spectra were recorded on a Nicolet iS10 spectrometer (Thermo Fisher) using KBr pellets. Dynamic light scattering was performed using a Malvern Nano zetasizer (Nano ZS90, U.K.). NMR was recorded by a Bruker 400 MHz spectrometer. Chemical shifts are given comparative to tetramethylsilane (TMS).

2.2.1. Surface Tension. Surface tension measurements were obtained using a Jencon tensiometer purchased from Kolkata, India. A platinum ring was used. The surface tension was calibrated, and the obtained surface tension value of water was found to be 71 ± 0.02 mN m−1. The values were measured in triplicate, and the mean value was taken. After each measurement, the ring was cleaned thoroughly with degassed double-distilled deionized water.

2.2.2. Conductometric Method. The measurements of specific conductance (κ) were carried out using a digital conductivity meter (Systronics Type-306). The conductivity cell having electrodes made up of platinum metal was purchased from India. It was calibrated with aqueous KCl solutions (0.01 and 0.1 M) before experimental measurements. Three readings were noted for every particular concentration, and finally, mean values were considered.

2.2.3. Fluorescence. Steady-state fluorescence experiments were carried out using a Cary Eclipse Agilent technology spectrofluorimeter. An excitation wavelength of 334 nm and an emission wavelength varying from 340 to 600 nm were used. The excitation and emission slit widths were kept at 0.5 nm. The desired amount of freshly prepared surfactants/glyceline solution containing the probe pyrene (1.2 × 10−4 M)/PyCHO (1.2 × 10−4 M) was added to the cuvette.

2.2.4. Dynamic Light Scattering. The size of the aggregates of CDMEAB/CTBPB within Gly-based DES was obtained using the dynamic light scattering (DLS) technique. DLS measurements were performed using a zetasizer Nano ZS90 (Malvern Instruments, Japan) instrument.

2.2.5. Fourier Transform Infrared. FTIR spectra were measured using a Nicolet iS10 spectrometer (Thermo Fisher). Samples are prepared using potassium bromide pellets with 1 mg of components and 100 mg of dry KBr. FTIR measurements were performed in the scanning range of 4000–400 cm−1 at room temperature.

2.2.6. Nuclear Magnetic Resonance. 1H NMR and 2D NOESY spectra of mixtures of the cationic surfactants CDMEAB/CTBPB and ChCl–Gly DES in deuterium oxide (D2O) were recorded at 298 K using a Bruker 400 MHz spectrometer. Chemical shifts are given comparative to tetramethylsilane (TMS).

2.2.7. Preparation of ChCl–Gly DES. Glycerine-based DES was prepared by simple mixing between ChCl and glycerol at a 1:2 molar ratio of ChCl to glycerol in a sealed bottle. The mixture was stirred at 353 K for 2 h until a homogeneous and transparent DES liquid was produced. The DES liquid was left to cool slowly at normal temperature.

2.2.8. Preparation of CDMEAB/CTBPB/DES Solution. The desired amounts of CDMEAB/CTBPB and glycerine were mixed in a sealed bottle. Then, the mixture was stirred at normal temperature until a homogeneous solution was formed and characterization by FTIR and NMR techniques shown in Figures 1 and 2.

3. RESULTS AND DISCUSSION

3.1. Characterization of Choline-Chloride- and Glycerol-Based Deep Eutectic Solvents. The characterization of Gly-based DES was done using FTIR and 1H NMR spectroscopy.

3.1.1. FTIR Spectroscopy. It is important to learn the strength of H-bonding interactions involved in DES among a hydrogen bond acceptor (HBA), viz., ChCl, and a hydrogen bond donor (HBD), viz., glycerol. FTIR spectroscopy is regularly used to study the interactions among the groups to analyze the structure of a synthesized DES. It is effectively used to characterize the H-bond interactions taking place within a system.

In this present work, FTIR study is carried out to estimate the strength of H-bonding interactions between ChCl (HBA) and glycerol (HBD) and also to highlight the surfactant–DES interactions. As shown in Figure 1, peaks at 3320–3345 cm−1
of glycerol may be assigned to the stretching vibration of the O−H functional group. Peaks at about 3160−3210 cm\(^{-1}\) of DES could be recognized to the stretching vibration of the O−H functional group after the formation of the Gly-based DES. It has to be illustrous that the N−H stretching of ChCl is also observed to overlie through the O−H between 3150 and 3200 cm\(^{-1}\), asymmetrical −NH\(_2\) stretching at 3410 cm\(^{-1}\), C−H stretching at 2932 cm\(^{-1}\), C−O stretching at 2077 cm\(^{-1}\), N−H bending at 1730 cm\(^{-1}\), H-bending at 1424 cm\(^{-1}\), NH bending + CN bending at 1345 cm\(^{-1}\), and CH\(_2\) deformation at 1213 cm\(^{-1}\).

As can be seen in Figure 1, the FTIR absorption peaks of the stretching vibration of O−H functional group of glycerol as HBD change to lower wavenumber and show an obvious red shift after the formation of Gly-based DES, signifying that the O−H functional group of HBD takes part in the formation of the H-bonding interaction among anions of ChCl. Moreover, the red-shifting degree of FTIR absorption peaks of the O−H functional group of glycerol as HBD is conflicting, which appears to propose that the strength of H-bonding interaction among ChCl and the O−H functional group of HBD is dissimilar. Figure 1 shows the FTIR spectra of the synthesized glycline-based DES, and the following bands are changed due to the formation of Gly-based DES, i.e., asymmetrical −NH\(_2\) stretching at 3339 cm\(^{-1}\), C−H stretching at 2965 cm\(^{-1}\), C−O stretching at 2080 cm\(^{-1}\), N−H bending at 1750 cm\(^{-1}\), H-bending at 1455 cm\(^{-1}\), NH bending + CN bending at 1335 cm\(^{-1}\), CH\(_2\) deformation at 1218 cm\(^{-1}\), C−C stretching + other vibrations at 1057 cm\(^{-1}\), and N−C−C bending at 956 cm\(^{-1}\).

Zhang et al. have investigated the aggregation behavior of 1-alkyl-3-methylimidazolium chloride with DESs (choline chloride and glycerol in a 1:2 molar ratio) by different techniques including fluorescence probe response, small-angle X-ray scattering (SAXS), and FTIR spectroscopy.\(^{52}\) Kumar and group studied the 15 diﬀerent types of amine- and glycol-based deep eutectic solvents synthesized, characterized them by FTIR, and investigated them for CO2 absorption. The absorption band of ethylene glycol at 3275 cm\(^{-1}\), which is attributed to the stretching of the −OH group moved toward the higher wavenumber region of 3345 cm\(^{-1}\). Besides, CO2 solubility data were correlated with Henry’s law, and Henry’s constant was calculated for all DESs. The kinetic modeling of CO2 absorption in DESs was also studied and rate constants were evaluated.\(^{53}\)

3.1.2. \(^1\)H NMR. ChCl−Gly was characterized via \(^1\)H NMR spectral results to verify its chemical structure.\(^{54}\) Literature information has recommended that, depending on the NMR spectral behavior, the effectiveness of the DES synthesis method could be analyzed as is finished in the case of our ChCl- and glycerol-based DESs. The \(^1\)H NMR spectra obtained for Gly-based DES system are specified in Figure 2. The characteristic signals of both ChCl and Gly protons in ChCl−Gly were downfield-shifted as compared to those obtained for ChCl and Gly individual components in the D\(_2\)O solution (Figure 2). As results show, the downfield chemical shifts are due to the formation of an ion−hydrogen bond donor complex that characterizes the formation of DES.\(^{55}\)

\(^1\)H NMR results for DES (in the D\(_2\)O solution) are included. In this part, we have used the following abbreviations: aliphatic hydrogens of choline, Ch\(^i\); −OH hydrogens of Ch, OH−Ch\(^i\); aliphatic −H of the HBD compound, Gly; hydrogens of the HBD compound, such as hydroxyl, OH−Gly, water, W; and partly deuterated water, HDO. In addition, in the whole part, a finicky note will be used for each entity hydrogen or carbon. We have selected ChCl/glycerol/water as a model for a more complete study, owing to the higher number of −OH and aliphatic −H. In the present study, in the \(^1\)H NMR spectrum (Figure 2), the signals of the −CH\(_3\) group bonded to the choline nitrogen, CH\(_3\)−N+ (c), and those of two hydroxymethylene of glycerol (f) are overlapping; the rest are perfectly separated: δ = 5.08 (t, J = 4.7 Hz, 1H, Ha), 4.82 (d, J = 4.8 Hz, 2H, Hb), 4.73 (t, J = 5.0 Hz, 4H, He), 4.26 (s, 2.0H, Hf), 3.76–3.85 (m, 2H, Hg), 3.44–3.53 (m, 2H, Hh), 3.33–3.43 (m, 6H, Hf', Hc), 3.23–3.33 (m, 4H, Hf), 3.04 (s, 9H, Hd).

Mantle et al. have investigated the self-diffusion coefficients of the liquid mixtures in a noninvasive way at the equilibrium, which is measured by the pulsed field gradient (PFG) NMR method and observed the inter/intradipolar interactions taking place within the mixture and an enhance effect on the line shapes of the NMR spectra.\(^{56}\) Furthermore, D’Agostino et al. have studied the self-diffusion of molecular and ionic species in aqueous solutions of choline chloride (ChCl)-based DESs using the pulsed field gradient (PFG) NMR method. NMR spectra of aqueous ChCl−Gly in 13 wt % water revealed that the NMR peak positions are (in ppm): a = 2.40, b = 2.81, c = 3.13, d = 4.50, e,f = 2.67, g = 4.17, h = 4.25, i = 3.68; and for ChCl−urea DES in 1 wt % water content, the NMR peak positions are (in ppm): a = 2.43, b = 2.75, c = 3.18, d = 4.59, e = 5.38, f = 3.69. It is worth noting that in aqueous ChCl−urea DES, the amine species of Ch+ and HBD show stronger interaction with water when water is added to the system. However, in the case of ChCl−Gly DES, water has little effect on hydroxyl proton diffusion of both Ch+ and HBD.\(^{57}\) Zaid et al. synthesized ChCl−Gly-based DES and characterized it using proton NMR spectroscopy. The distinguished NMR signals of ChCl and glycerol protons in ChCl−Gly were observed to be downfield-shifted in the MeOD-d\(_4\) solution. Downfield chemical shift results suggest the formation of an ion−hydrogen bond donor supramolecular complex that characterizes the formation of DES, and accompanying NMR results verify the structure of the synthesized ChCl−Gly.\(^{58}\)

3.2. Micellization Behavior of Cationic Surfactants within Deep Eutectic Solvents. The critical micelle concentration (CMC) is a significant characteristic of a surfactant. Before reaching the CMC, the surface tension changes strongly with the concentration of the surfactants. After reaching the CMC, the surface tension remains relatively constant or changes with a slope.\(^{59}\) The value of the CMC for a given dispersant in a given medium depends on the temperature, pressure, concentration, and electrolytes. Micelles only form above the critical micelle temperature.\(^{52−54}\) When the concentration of a surfactant is increased, adsorption takes place on the surface until it is totally overlaid, which corresponds to the minimum value of surface tension.\(^{39}\) A lower CMC indicates that less surfactant is required to saturate interfaces and form micelles; CMC values offer valuable guidelines for comparison of surfactant detergency.

3.3. Impact of Deep Eutectic Solvents on Micellization. Micellar properties of conventional cationic surfactants, i.e., CDMEAB and CTBPB, are significantly influenced in the presence of Gly-based DES. The aggregation and surface properties of the surfactant solution depend on the type and amount of DES used. The CMC values of the both cationic surfactants in the presence of Gly-based DES were measured.
by three significant parameters, i.e., conductivity, surface tension, and fluorescence measurements, as shown in Table 1.

3.3.1. Surface Tension Measurements. CMC values of both cationic surfactants, i.e., CDMEAB and CTBPB, have been determined by surface tension measurements in the presence and absence of Gly-based DES. The CMC values were evaluated from the breakpoints of the surface tension (γ) vs [surfactant] as observed for a wide range of concentrations of surfactants within the Gly-based DES solution, as shown in Figure 3A. The pure aqueous solution of CTBPB/CDMEAB showed the expected behavior of a rapid difference of slope at CMC, as represented in Figure 3A. A linear decrease in the surface tension was observed with an increase in concentrations of CDMEAB and CTBPB (M) above the CMC value, after which no considerable change was observed. In the surface tension curves of pure surfactants, no dip (minimum) is noticed near the breakpoint, which certified that the prepared surfactants are highly pure. The CMC values of pure CTBPB and CDMEAB are 0.82 and 0.91 mM, respectively, even though the surface tension summary shows an unexpected behavior for CDMEAB–Gly, CTBPB, and CTBPB–Gly systems. Furthermore, we found breakpoints before CMC at concentrations in the surface tension curve corresponding to CTBPB/CDMEAB that establish uniting with Gly-based DES, CMC and critical saturation concentration. The exterior of these breaks in the surface tension plots is due to the formation of different types of complexes at different states of interaction. Further addition of CTBPB/CDMEAB causes a rapid decrease in the surface tension value up to minima of the CTBPB/CDMEAB concentration. It is worth noting that the addition of DES to the surfactant solution results in a decrease in the CMC value for both CTBPB and CDMEAB, thus favouring the micellization process. The CMC values of surfactant systems in the presence and absence of 5 wt % Gly-based DES obtained by the surface tensiometer method are listed in Table 1 (vide supra). Surface tension (interfacial parameter) discussions are given in SI 1 and Table S1.

3.3.2. Conductivity Measurements. Electrical conductance measurement is a widely used method as it not only evaluates the values of CMC but also provides basic information regarding the aggregation and thermodynamic behavior of solutes within a solution. The specific conductivity (κ) vs CTBPB/CDMEAB concentration (M) plots with varying surfactant concentrations in the presence and absence of 5 wt % Gly-based DES at the 298 K temperature are shown in Figure 3B. Figure 3B shows the difference of CMC of CTBPB/CDMEAB at 298 K in the presence of 5 wt % Gly-based DES. All plots enclose two linear curves having diverse slopes. The difference of slopes establishes the beginning of the micellization process, and the intersection of the two linear subdivisions is due to the formation of micelles and hence gives the CMC value. The addition of a surfactant in an aqueous solution causes an increase in the number of charge carriers and, consequently, an increase in the conductivity above the CMC; a further addition of the surfactant increases the micelle concentration, while the monomer concentration remains approximately constant (at the CMC level). The CMC is a measure of the concentration of a solution component that represents a critical value above which that component forces the formation of micelles.57 Graph plots of conductivity versus concentration of surfactants, that result in a break at the CMC, are shown in Figure 3B. Conductivity (thermodynamic parameter) discussions are in SI 2 and Table S2.

3.3.3. Fluorescence Spectral Response. We employed another technique, i.e., fluorescence spectroscopy, using 1-pyrene carboxyaldehyde (PyCHO) as a probe to study the micelle behavior of the surfactant.58 A fluorescence probe with distinctive structural differences, that has found usefulness in studies of solution and interfacial polarity, is PyCHO. PyCHO has two types of excited singlet states (n−π* and π−n*), both of which show emission in fluid solutions.59 In a nonpolar solvent, the emission from PyCHO is highly structured and weak arising from the n−π* state.

Changing to a polar from a nonpolar medium, the π−n* state is brought below the n−π* state via solvent relaxation to become an emitting state.58–62 This is manifested by a broad, reasonably intense emission that shows red shifts with increasing solvent dielectric constants. Figure S1 represents the PyCHO fluorescence intensity as a function of CDMEAB concentration in aqueous media. As expected, the fluorescence intensity decreases significantly upon micelle formation as the probe molecules reside in the micellar phase where they counter an enhanced hydrophobic interaction. The CMC value for CDMEAB was obtained as 0.9 mM. The CMC values are determined from the intensity vs concentration of surfactants graph. Figure 4 shows the variation of fluorescence emission intensity as a function of the CDMEAB concentration (M).

Table 1. Critical Micelle Concentration (CMC) of Aqueous Cationic Surfactants, i.e., CDMEAB and CTBPB, in the Presence of 5 wt % Gly

| surfactants | water | DES (ChCl–Gly) | surfactants | water | DES (ChCl–Gly) | surfactants | water | DES (ChCl–Gly) |
|-------------|-------|----------------|-------------|-------|----------------|-------------|-------|----------------|
| CDMEAB      | 0.909 ± 0.002 | 0.525 ± 0.003 | conductivity | 0.87 ± 0.05 | 0.50 ± 0.03 | fluorescence | 0.92 ± 0.03 | 0.62 ± 0.02 |
| CTBPB       | 0.825 ± 0.002 | 0.566 ± 0.005 |             | 0.79 ± 0.04 | 0.43 ± 0.05 |             | 0.82 ± 0.02 | 0.45 ± 0.05 |
The curve shows a sharp decrease when micelles are formed at CMC. The calculated CMC values for the both surfactant systems are observed to be higher in water compared to those for the 5 wt % Gly-based DES aqueous solution. The DES shows a significant impact on the CDMEAB system compared to CTBPB because of the presence of the −OH group in the hydrophilic part of CDMEAB, and this is responsible for strong surfactant−DES interactions, i.e., H-bonding, electrostatic, and hydrophobic, etc., as shown in Scheme 2. The calculated fluorescence data are in good agreement with those obtained by surface tension and conductivity measurements. It is worth mentioning that the presence of DES favors the micellization process for both the surfactants significantly; the extent is more for CDMEAB than CTBPB.

3.4. Micellar Aggregation Number Measurements. The micellar aggregation number ($N_{agg}$) is determined from steady-state fluorescence quenching of pyrene by the cetylpyridinium chloride (CPC) quencher according to eq 1

$$\ln \frac{I_0}{I_Q} = \frac{[\text{CPC}]_{\text{micelle}}}{[\text{micelle}]_{\text{surfactant}}}$$

$$= \frac{N_{agg}}{[\text{surfactant}] - \text{cmc}_{\text{DES}}}$$

(1)

where $I_0$ and $I_Q$ are the intensities of fluorescence (at 384 nm) of pyrene in the absence and presence of CPC, respectively. $[\text{CPC}]_{\text{micelle}}$ and $[\text{surfactant}]$ are the concentrations of the quencher and surfactant, respectively. Plots of $\ln(I_0/I_Q)$ vs the concentration of quencher $[\text{CPC}]$ (mM) in the presence of Gly DES in CDMEAB/CTBPB are represented in Figure 5. These plots in Figure 5 clearly show the ideal linear correlations ($R = 0.99$) for CDMEAB−Gly/CTBPB−Gly. As a result, the values of $N_{agg}$ achieved from eq (1) for CDMEAB−Gly/CTBPB−Gly were calculated and are listed in Figure 4.

![Figure 4. Fluorescence intensity vs logarithm of [surfactant] concentration (M), i.e., CDMEAB, CDMEAB−Gly, CTBPB, and CTBPB−Gly-based DES aqueous solution.](image)

Scheme 2. Schematic Representation of Hydrogen Bonding for ChCl−Gly with Surfactants in the Micellar Solution: (A) CDMEAB and (B) CTBPB
in the presence of Gly. It is well established that these constants were calculated using eq 2.

$$\ln(\frac{I_0}{I_Q}) = 1 + K_{SV}[Q]$$

The Stern–Volmer quenching constant ($K_{SV}$) can be feasible from the slope values of the plots of $\ln(\frac{I_0}{I_Q})$ vs [CPC]. The obtained $K_{SV}$ values are illustrated in Table 2. $K_{SV}$ clarifies the hydrophobicity of micellar solutions, and it is used to decrease the fluorophore. Table 2 clearly shows that the $K_{SV}$ value of pure surfactants are lower compared to those of mixtures of surfactant–DES (CDMEAB–Gly > CTBPB–Gly). The result shows that the broad behavior of the micellar aggregation of surfactants in Gly is comparable to that in water, i.e., the micellization of surfactants in Gly is mainly determined by the solvophobic effect, similar to the micellization of surfactant molecules in water caused by the hydrophobic effect.

Ghosh et al.⁵ have investigated the micellar properties of ionic liquid 1-butyl-3-methylimidazolium octyl sulfate within the urea/Gly-based DES solvent by different techniques, i.e., fluorescence, UV–vis, DLS, and FTIR. They observed that [Bmim][OS] directly interacts with Gly-based DES and the $K_{SV}$ value of pure IL is smaller as compared to those of [Bmim][OS]–DES mixtures (ChCl–urea > ChCl–Gly).

### 3.5. Dynamic Light Scattering

DLS gives the size distribution of amphiphile molecules, which is an important property. These contain nonabsorption of light by the particles in dilute/concentrated solutions, multiple scattering takes place that depends on the exact values of viscosity and refractive index of the solutions.⁶⁵ Number-weighted size distribution of aggregates formed in surfactant–DES plus water mixtures at 298 K is obtained from DLS measurements. In DLS, narrow distribution indicates the amount of light scattered from the various size “segments” present within the solution. Figure 6 shows the DLS spectra of the cationic surfactant’s micellar solution in the absence and presence of DES. The profiles of the hydrodynamic radius ($R_h$) vs scattered intensity are shown in Figure 6. It is observed that the formed aggregates of CDMEAB/CTBPB in the aqueous Gly-based DES solution are relatively smaller as compared to those in water, i.e., bimodal distribution for CDMEAB and CTBPB in the aqueous DES solution. In the DLS studies, the experiments have been performed taking surfactant concentration three and six times the CMC to make sure that micelle formation has already taken place within the system.

The results of DLS signify that the distribution of average-sized CDMEAB/CTBPB micellar particles in the aqueous DES solution shows that the CDMEAB micelles are larger aggregates except CTBPB micelles under similar conditions. Shahrabadi et al.⁶⁶ studied the tendency of asphaltene particles to agglomerate with an increase of solvent aliphaticity; hence, asphaltene particle size in the arrival point can be a dependable method to the reviewer. It provided a monomodal distribution with an average particle size for the inhibitor-free sample and for samples including DES. As result suggests, the distribution with average asphaltene particle size at the n-heptane/toluene ratio of 1 for the inhibitor-free sample is 1419 nm.

As results show, the average peak diameter of the micellar solution is similar for both CTBP and CDMEAB; the diameter appears to increase with 5 wt % DES addition. It is experimental the addition of 5 wt % Gly the peak diameter

| surfactants | DES (ChCl–Gly) | water (ChCl–Gly) |
|-------------|----------------|------------------|
| CDMEAB      | 10.54 ± 0.05   | 6.23 ± 0.02      |
| CTBPB       | 8.75 ± 0.04    | 2.24 ± 0.02      |

Table 2. Aggregation Numbers ($N_{agg}$) and Stern–Volmer Constants ($K_{SV}$) of Aqueous Cationic Surfactants, i.e., CDMEAB and CTBPB, in the Presence of 5 wt % Gly.
(CDMEAB > CTBPB). Surfactant–Gly interaction plays a noteworthy role in varying the characteristics of surfactants, cite with upright polarized light. Modifications in the micelle aggregates within surfactant–Gly (0–5 wt %) are revealed by electrostatic attraction. As clarify previously, electrostatic attraction between OH− groups on CDMEAB moieties within the micelles renders the usual micellar size reasonably large. Within CDMEAB, though, the need for such an interaction, shared with the cationic nature of the surfactant, along with the presence of Br− counterions resulted in much more dense micelles.

3.6. Fourier Transform Infrared Spectroscopy. FTIR spectroscopy is recognized as a useful tool for the examination of formation of complexes. FTIR measurements of the aqueous surfactant and DES systems were conducted using a PerkinElmer FTIR spectrometer in a range of 400–4000 wavenumbers and a four-time scanning repetition. FTIR spectra of Gly alone classified the structural changes on the micellar surface of the surfactants; a preliminary investigation was conducted to recognize the functional groups of DES as functionalizing agents. FTIR spectra of the both cationic surfactants, i.e., CDMEAB/CTBPB, in the presence of Gly-based DES are shown in Figure 7. The FTIR spectra of surfactant solutions in the presence of 5 wt % Gly-based DES, i.e., (A) CDMEAB, (B) CDMEAB–ChCl–Gly, (C) CTBPB, (D) CTBPB–ChCl–Gly.

Table 3. Infrared Absorption Band and Difference Modes of Vibration for CDMEAB and CTBPB in the Presence of Gly-Based DES

| Characteristic band (cm⁻¹) | CDMEAB | CTBPB |
|---------------------------|--------|-------|
| Pure surfactant           | After Gly DES | Pure surfactant | After Gly DES |
| vO−H                      | 3318   | 3221  | 3382 | 3308.77 |
| vCH₂-O−C−H−C             | 2912.53 | 2923.63  | 2917.04 | 2925.78  |
| vC−H                      | 1469.85 | 1476.89  | 1464.33 | 1475.75  |
| vC−H−O−C−C−C−O          | 781.51 | 1039.17 | 1092.47 | 1038.89  |
| vC−O−H, v                | 670.76 | 954.84  | 719.61 | 954.58   |
| vC−C−C, v−C−C−O          | 627.88 |

Hence, IR spectra were studied for both cationic surfactants CDMEAB and CTBPB in the presence of the Gly-based DES solution. Figure 1 shows the FTIR spectra for Gly DES along with their entity components, i.e., ChCl and Gly. IR spectra (Figure 7A,B) of CDMEAB in the presence of Gly show that vO−H at 3318 cm⁻¹ shifts to 3321 cm⁻¹; vC−H at 2912.53 and 2846.75 cm⁻¹ shifts to 2923.63 cm⁻¹; vC−H at 1469.85 cm⁻¹ shifts to 1476.89 cm⁻¹; and vC−H−C, vC−O, vC−OH, vC−C−C, and vC−C−O at 781.51, 670.76, and 627.88 cm⁻¹ shift to 1039.17 and 954.84 cm⁻¹. IR spectra (Figure 7C,D) of CTBPB in the presence of Gly show that vO−H at 3382 cm⁻¹ shifts to 3308.77 cm⁻¹; vC−H at 2917.04 and 2849.37 cm⁻¹ shifts to 2925.78 cm⁻¹; vC−H at 1464.33 cm⁻¹ shifts to 1475.75 cm⁻¹; and vC−H−C, vC−O, vC−OH, vC−C−C, and vC−C−O at 1092.47 and 719.61 cm⁻¹ shift to 1038.89 and 954.58 cm⁻¹.

Table 3 illustrates the infrared absorption band and difference modes of vibration for CDMEAB and CTBPB in the presence of Gly-based DES.

Furthermore, the asymmetric vibration of C−H in the CDMEAB/CTBPB/Gly solution shifts slightly to a lower frequency with increasing CDMEAB/CTBPB concentration, implying stronger hydrogen-bonding interactions. The development of the hydrogen-bonding strength draws CDMEAB/CTBPB molecules dispersed in the aggregates strongly and simultaneously promotes the dissociation of head group counterions on the surface of aggregates, resulting in a closer deal of micelles. The conventional cationic surfactants, i.e., CDMEAB/CTBPB with Gly-based DES micellization behavior, are studied by different techniques such as surface tension, conductometry, fluorescence, and FTIR, along with advanced NMR spectroscopy techniques, i.e., 1H NMR and NOESY.

Zhang et al.32 studied the interaction of DES with long-chain ionic liquid C₁₆mimCl and observed a characteristic band at around 3382 cm⁻¹ for the O−H stretching vibration of C₁₆mimCl/glycine solutions, which was clearly increasing in comparison with that of glycine alone. It confirms the reality of stronger intermolecular hydrogen-bonding interactions between DES and micelles. The asymmetric vibration of C−H in C₁₆mimCl/glycine solution shifts slightly to a lower frequency with increasing C₁₆mimCl concentration, implying stronger hydrogen-bonding interactions.

3.7. Interaction of ChCl-Based DES with Cationic Surfactants. The impact of ChCl-based DES on the formation of micelles can be expressed by the following interaction factors (i.e., hydrogen-bonding, electrostatic, hydrophobic, and van der Waals interactions), which are involved in the spontaneous micellization behavior. Surfactants contain hydrophobic and hydrophilic groups, which interact freely with the water molecules in aqueous surroundings and...
are responsible for the micellization behavior of surfactants. DES has emerged as a green solvent, which has shown great impact on modifying the micellization properties of surfactants. Both surfactants used here interact with Gly-based DES depending on their (1) hydrophobic part and (2) hydrophilic part. Bromide is an counterion of both the surfactants, and the hydrophilic group of CTBPB is a tributylphosphonium group, but CDMEAB has a dimethylethanolammonium group. In the present study on DES, ChCl contains N+, Cl−, CH2−CH2−OH, (CH3)3 and glycerol (C3H8O3) contains 3-OH groups. The interactions between the hydrophilic part (P+) of CTBPB and DES are electrostatic and H-bonding interactions, and also hydrophobic groups, known as hydrophobic interactions, and both counterions, i.e., Br− and Cl−, are responsible for electrostatic interactions. The interactions between the hydrophilic part (N+) of CDMEAB and DES are electrostatic, H-bonding, and hydrophobic interactions. CDMEAB shows more H-bonding association as compared to CTBPB due to the presence of an ethanol (−CH2−CH2−OH) group attached to the surfactant hydrophilic group.

However, here, the various factors, i.e., electrostatic and hydrophobic interactions, that influence the micellization behavior of surfactants in the presence of DES and the impact of Gly on CMC are somehow crucial. A schematic model of such hydrogen bonding is shown in Scheme 2. These interactions, besides the electrostatic attraction among the surfactant hydrophilic groups and anions, result in the entrapment of oppositely charged anions at the micelle’s polar shell and are expected to create a DES effect that decreases the CMC.

3.8. Proton Nuclear Magnetic Resonance Spectroscopy. 1H NMR spectral investigations were studied to gain more widespread information about the intermolecular interactions and thus to determine the location of DES and surfactant moieties in the micellar solution. DES and surfactants interactions result in the change in chemical shifts of the protons as a result of the shielding effects. In the presence of additives like DES to micellar solution will influence the protons of the region they are interacting with. The 1H NMR spectra of both cationic surfactants display three characteristics peaks; the terminal CH3 protons of the hexadecyl chain appear at 0.854 ppm, and bulk (CH2) protons appear at 1.279 ppm. The terminal CH3 and bulk CH2 protons of CDMEAB in the absence of Gly appear at 0.854 and 1.279 ppm, respectively.

The chemical shift values in ppm of 5 wt % of Gly-based DES in CDMEAB micellar solutions, terminal CH3 and bulk CH2 groups are shown the different chemical shift values i.e., 0.803, 1.221, 1.278, 1.297, 1.669, 2.812, 2.929, 3.024, 3.112, 3.224, 3.289, 3.345, 3.363, 3.439, 3.454, 3.467, 3.483 ppm the surroundings of surfactant protons are shown in Figure 8A. Chemical shift values in ppm of 5 wt % of Gly-based DES in
CTBPB micellar solutions, terminal CH₃ and bulk CH₂ groups are shown the different chemical shift values i.e., 0.788, 0.804, 0.818, 0.858, 0.875, 0.892, 1.206, 1.398, 1.414, 1.432, 1.447, 1.476, 1.494, 2.153, 2.186, 2.923, 3.105, 3.250, 3.268, 3.284, 3.295, 3.350, 3.360, 3.411, 3.433, 3.448, 3.461, 3.478 ppm as shown in Figure 8B.

The examination of spectra reveals that with DES having the concentration of CDMEAB beyond CMC, the values of all protons of terminal carbon atoms of CDMEAB/CTBPB shift upfield. The effect is more obvious for higher wt % of DES, representing increased interactions between DES and tail protons of the cationic surfactant; it is most likely that some DES molecules have entered the micellar interior and screened protons from the tail region besides interacting on the surface. ¹H NMR and ¹H-¹H 2D NOESY spectroscopy methods have been used to study the changes in structures of both surfactants in the presence of Gly-based DES. Those are interconnected to every proton to overlapping to another molecule, and the obtained spectra are shown in Figures 8 and 9. Changes in the chemical shift of unusual protons of ChCl–Gly DESs due to the role of water reveal modifications in the surroundings of DES components. In the case of Gly, all protons of Gly show as a singlet in ¹H NMR spectra and a continuous upfield shift along with a peak increase while moving from neat DES to DES–water (50% w/w) mixture (Figure 8A). An upfield shift, changeable in size, is also experimental for all protons of cholinium ions present in Gly. As lying side by side to other protons, −CH₃ group protons at position (1) show maximum upfield shift in Gly–water (5 wt %) mixture as compared to that in neat Gly.

3.9. Nuclear Overhauser Effect Spectroscopy. Nuclear Overhauser effect spectroscopy (2D NOESY) analysis confirms signals for specific hydrogens in close proximity, even if they continue to be nonbonded. The 2D NOESY spectrum shows correlations through spin–spin relaxations, which confirm the interaction of both surfactants within Gly DES. Rotating-frame Overhauser spectroscopy (2D NOESY) in Figure 9 shows no correlations among H-1 to H-9 of CDMEAB and hydrogens H-1 to H-7 of the surfactant. However, a noticeable correlation is observed in hydrogen pairs of H-2, H-3 and H-3, H-5. Cross peaks within the spectra are developed from the strong correlation obtained from surfactants. NOESY experiments were achieved for the system of 0.01 M CDMEAB/CTBPB mixed with a 5 wt % solution of ChCl–Gly DES. NOESY experiments have revealed to give tremendous nearby into the environment of the self-assembly procedure in a amount of aggregated systems. NOESY spectra are revealed in Figure 9. In reciprocal cases, we tend to study strong cross peaks between the protons within the head group regions of the both surfactants within the cation aggregates.

Further, 2D ¹H–¹H NOESY measurements give idea that correlation peaks obtained from the interaction of protons of water with Gly DES become more and more stronger with increasing water content in DES. The feasible structural arrangements in the self-assembled structures of the cationic surfactants, viz., cetyltrimethylammonium bromide (CDMEAB), cetyltributylphosphonium bromide (CTBPB), with ChCl–Gly DES have been further investigated through nuclear Overhauser effect spectroscopy (NOESY), which is a 2D spectroscopy method to classify spins undergoing cross relaxation and to measure their cross-relaxation rates. In NOESY spectra, the cross peaks show which protons of the molecule are close to each other in holes. The transfer of several resolvable peaks in the 2D NMR spectrum of CDMEAB/CTBPB is shown in Figure 9. Outline plots of the 2D NOESY spectrum for the CDMEAB/CTBPB/D₂O system are also shown in Figure 9.

Figure 9 shows the cross peaks between protons on neighboring carbon atoms (H1–H9 for CDMEAB and H1–H7 for CTBPB), which are observed obviously at the Gly DES concentrations lower than the CMC due to intramolecular NOESY transfer. However, it should be noted that these peaks can contain intermolecular contributions as well. Indeed, there are cross peaks that are most likely due to intermolecular NOE transfer. For example, H2 for CTBPB, which is almost separated across the alkyl part, still shows cross peaks with H2, H6, and H7 and H1, H5, H6, and H3 also show some cross peaks with H2–H7, although some of them are rather weak. Contacts of all of the surfactant protons with D₂O molecules are also observed in Figure 8. The cross peaks of H2 with H1 and H3 suggest that intermolecular rather than intramolecular contacts occur above the CMC.

4. CONCLUSIONS

A compressive fundamental investigation would advance our understanding of behavior of surfactants in different solvent systems. This study would also facilitate the design and...
optimization of new surfactant–DES systems for better performance. CMCs of conventional cationic surfactants, i.e., CDMEAB and CTBPB, were determined in aqueous media as a function of Gly-based DES concentration via surface tension, conductivity, fluorescence, DLS, FTIR, $^1$H NMR, and 2D NOESY NMR techniques. The micellization process in the aqueous solution is affected by Gly-based DES. It has been observed that the CMC values of all surfactant systems decrease with the addition of DES, thus favouring the micellization process. This may be due to the presence of polar groups of DES in the proximity of the cationic head group region of surfactants, resulting in surfactant–DES interactions. Micellization of both CDMEAB and CTBPB was significantly influenced via hydrophobic, electrostatic, and H-bonding interactions with DES. The micellar sizes of CDMEAB–DES and CTBPB–DES show bimodal distribution, and the micellar sizes of both the cationic surfactants are effectively tuned by the addition of DES. The basic understanding of physicochemical properties of micellization is necessary for the art of management of their diverse applications in chemical, biochemical, pharmaceutical, and industrial fields. The CMC can serve as a measure of micelle formation. The surface tension technique was very helpful in determining the interfacial parameters, which explain the interfacial behavior of the cationic surfactants within the aqueous DES solution. The present study on the micellization properties is essential to better understand how to develop stable micelles for use in pharmaceutical and industrial applications. It will open novel avenues for the potential applications of these environmentally benign solvents as well.

ASSOCIATED CONTENT

1. Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00866.

Surface activity of the system (SI 1); surface excess concentration ($\Gamma_{\text{ex}}$), surface pressure at CMC ($\pi_{\text{CMC}}$), minimum surface area per molecule ($A_{\text{min}}$), efficiency of absorption ($p_{\text{abs}}$) of some cationic surfactants in water–Gly mixed media at 298 K (Table S1); thermodynamics of micellization (SI 2); degree of ionization ($\alpha$), counterion binding ($\beta$), Gibbs free energy of micellization ($\Delta G_{\text{mic}}$), standard Gibbs energy of adsorption ($\Delta G_{\text{ads}}$), Gibbs energy of transfer ($\Delta G_{\text{trans}}$), free energy at the air–water interface ($\Delta G_{\text{min}}$), Gibbs energy of micellization per alkyl tail ($\Delta G_{\text{tail}}$) for cationic surfactants, i.e., CDMEAB and CTBPB within Gly at 298 K temperature (Table S2); and fluorescence spectra of 1-PyCHO (1 $\mu$M) within aqueous CDMEAB media ($\lambda_{\text{em}} = 365$ nm and slit width = 5 nm) (Figure S1) (PDF)

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Notes
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