Chapter 4

Micellization of Various Surfactants in Deep Eutectic Solvents

Contents

This chapter includes the micellization of various surfactants in a reline-water mixture and aquolines. The effect of potassium and sodium salt on the micellization of DTAB was also studied in this chapter. The fluorescence technique was used to compute CMC of surfactants.
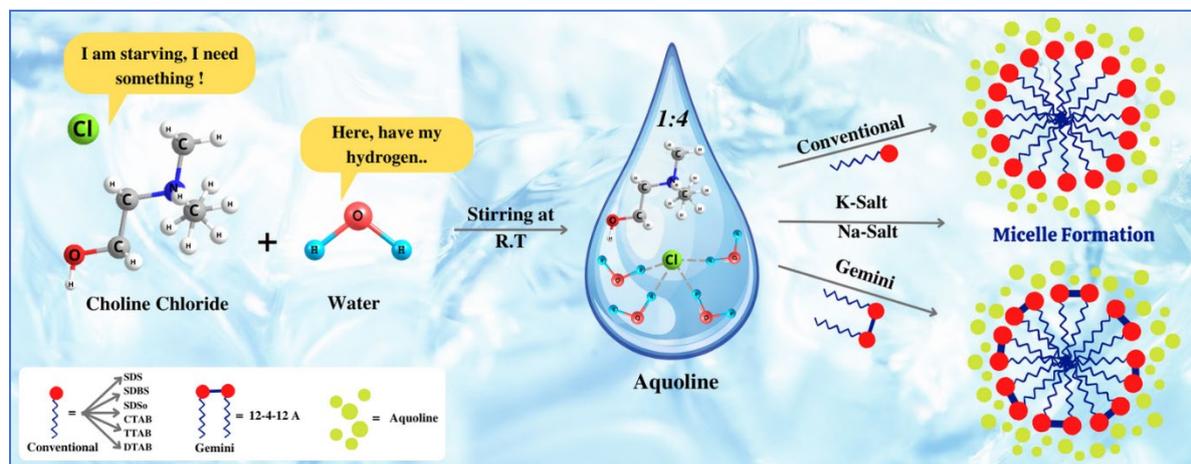
4.1 Introduction

The unique characteristics of surfactants continue to captivate the attention of scientists and technologists, motivating them to develop novel surfactant systems that exhibit exciting solution behaviour [1–3]. Surfactants, which are a class of molecules, exhibit self-assembly behavior due to their unique composition consisting of both hydrophilic (polar) and hydrophobic (non-polar) regions [4,5]. This property is responsible for their tendency to accumulate at interfaces and form different self-assembled structures, including spherical and rod-like micelles and vesicles, in solvent media [6,7]. The characteristics of surfactants, including their ability to form aggregates and their behaviour at interfaces, are influenced by the properties of the solvent environment [8]. Surfactant molecules can aggregate into micelles when subjected to various solvents [9,10]. To achieve this objective, it is crucial to comprehend the self-aggregation of surfactants in new solvents, such as deep eutectic solvents (DESs). This understanding could potentially allow for modifying these unique aggregation systems for different uses. In infancy time, the general belief was that DES should be strictly anhydrous for an application point of view. However, the full potential of reline could not be realized due to its higher viscosity which poses a processing problem during its transfer. The problem has been resolved by heating [11] or by adding water [12]. An upper boundary of hydration was demarcated (up to which it behaves as water in DES) over that system behaves molecular solution of DES components (DES in water). Water has unique characteristics owing to strong

H-bonding interaction [13]. When water is deliberately mixed with DESs, the resulting system can act as a functional fluid with improved properties and higher fluidity. This may be due to the alteration of the hydrogen bond network of reline [14]. Recently, it has been proposed that water can act as an additional HBD which results in a newer DES with additional properties over its precursor DES [15].

The formation of aggregates is a consequence of the interplay between the interactions among the amphiphilic molecules themselves and their interactions with the surrounding dispersing medium [9]. Water is frequently used as a medium to investigate the self-assembly behavior of surfactants. The self-assembly process is driven by the hydrophobic effect, which plays a crucial role in forming organized structures [4,16,17]. At ambient temperature, the formation of micelles is predominantly governed by entropy, where a notable negative contribution to the free energy arises from the transfer of hydrocarbon chains into the micellar interior. The investigation of surfactant aggregation behavior using DES as a medium is of great interest due to the environmentally friendly nature of DES as a solubilizing medium. The fundamental report of self-aggregation of ionic surfactant class within various DESs has been reported in the last decade [8,18]. In contrast to water, DESs exhibit a distinct morphology of micellar aggregates, which are spherical in water but adopt an ellipsoidal to rod-shaped structure in DESs. Arnold *et al.* [19], in their investigations on sodium dodecyl sulfate (SDS) in ChCl: urea, were the first to report that surfactant self-association could be controlled by the nature of the DESs itself. In another report, Atri *et al.* [20] showed that the composition of DES influences the length of rod-like micelles. The presence of water in the DES facilitated the formation of smaller aggregates [21].

The solvation mechanism of the head group and counter ion has an impact on critical micelle concentration (CMC) values in DES media. This is evident from the contrasting trends observed for anionic and cationic surfactants in both ChCl: urea and ChCl: glycerol [22]. The amphoteric class includes compounds with charged groups in their head group and is widely employed in biological systems for interacting with various materials such as proteins and phospholipid membranes. However, the solvation of amphoteric moieties in DESs is a complex phenomenon. Studies utilizing X-ray reflectance, surface tension, and SANS have revealed that positively charged choline ions tend to associate with sulphate or phosphate moieties, primarily driven by Coulombic interactions and hydrogen bonding [23].

Salt addition in an aqueous surfactant solution is a successful tool for tuning micellization or CMC and micellar morphologies [24–26]. The presence of basic inorganic electrolytes in aqueous solutions of ionic surfactants has a known impact on micellization due to the bonding between the counter ion with charged micelles. Typically, this leads to a reduction in the CMC along with an increase in the size of the aggregates. This results in a reduction in surface tension and an increase in the viscosity of the solution [27,28]. With an increase in ionic strength, the CMC of ionic surfactants reduces due to the decrease in electrostatic repulsion among charged head groups. This indicates that the presence of salt promotes the aggregation of surfactants. Additionally, several studies indicate that co-ions may affect the process of micellization, with their influence being dependent upon the characteristics of the co-ions and the structure of the surfactants [29–31]. Surfactants often do not form clusters in solutions with high ionic strength. Therefore, it may be expected that the micellization of surfactants might not take place in DESs due to coagulation, as predicted by the DLVO hypothesis [32]. Consequently, in systems with high ionic strength as DESs, the micellization behaviour will be more complex compared to an aqueous system.

This chapter includes a study on the micellization behaviour of SDS in reline or the reline-water mixture in both ranges of composition [33,34] i.e., water in reline or reline in water. The micellization of a range of conventional and some gemini surfactants has been investigated in aquoline (water-based DES) and compared with micellization in water media. The chapter explains about micellization of surfactants in DESs, variation of CMC and aggregation structures in DESs as compared to water. Additionally, micellization of a cationic surfactant, dodecyl trimethyl ammonium bromide (DTAB), in aquolines (ChCl: water, 1:2 (DES I),1:3 (DES II), 1:4 (DES III) or ChCl: water, 1:5 (DES IV)) with the addition of a few potassium and sodium salts (K-salt (potassium bromide, KBr; potassium chloride, KCl; potassium nitrate, KNO_3); (Na-salt (sodium bromide, NaBr; sodium chloride, NaCl; sodium nitrate, $NaNO_3$)) were also investigated in the present work. Furthermore, salt-induced micellar morphologies were also investigated with the help of polarizing optical microscopy. CMC has been obtained by fluorescence measurements. Fluorescence data were used to compute aggregation parameters, micropolarity, and Stern-Volmer binding constant (Ksv). Such studies may contribute to getting insight into the natural eutectic mixture (water + natural metabolites) that protects animals under extreme conditions.

4.2 Experimental section

The materials and methods used are discussed in chapter 2.

4.3 Result and Discussion

4.3.1 Micellization of SDS in water in reline and reline in water

Micellization results from the breaking and reformation of hydrogen bonds as the alkyl tail of the surfactant comes in contact with water. These reformed H-bonds are again broken when the monomeric surfactant alkyl tail reaches the micellar phase. This happens due to hydrophobic interactions and is driven entropically [9]. Reline can be considered a hybrid system containing a molecular/ionic network with distorted H-bond architecture [35]. Micellization of SDS in pure reline has already been reported using tensiometry [19]. On continuous addition of water to the reline, the complex structures (of reline) are separated due to the presence of water molecules (water in reline). Later, reline structural motifs are gradually destroyed, and molecular solutions of reline components are formed, resulting in reline in water [12]. Therefore, CMC measurements have been performed both in water in reline and reline in water regions. In reline-water systems, one can expect hydrogen bond modifications due to the presence of surfactant and therefore, forces responsible for micellization will remain similar as mentioned above for water. Viscosity decreases with the addition of water and hence facilitates CMC measurement in water in reline region.
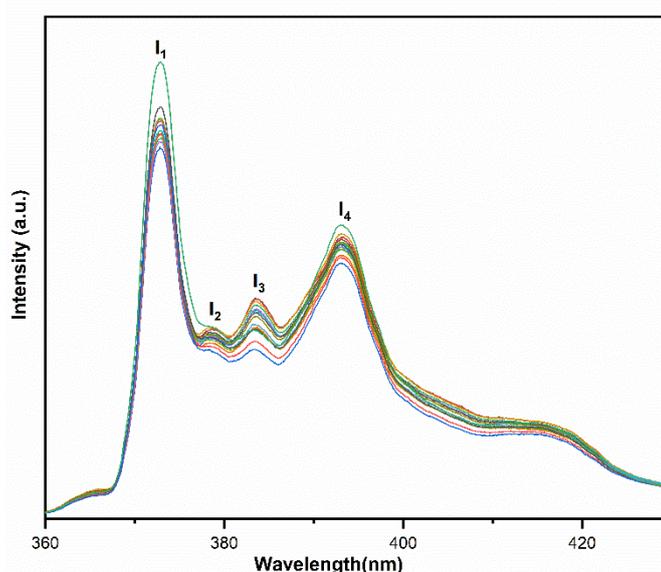
Figure 4.1: Emission spectra of pyrene (intensity vs wavelength) in various concentrations of surfactants in DES (with and without water).

Fluorescence measurement has been reported as an ideal technique to observe micellization in the reline-water mixture [36]. Fluorescence signals of pyrene are well suited to study the phenomenon of micellization because the emission band of pyrene changes with the polarity of the surrounding environment [37]. Fluorescence data from a probe can provide insights into the association of micelles and their interior surroundings. Pyrene has been frequently utilized to collect such data by fluorescence methodology. **Figure 4.1** displays several common intensities versus wavelength graphs. The polarity dependence can be expressed in terms of I_1/I_3, where I_1 is the intensity of the reline-water fluid-dependent peak, and I_3 corresponds to the peak resulting from the reline-water fluid insensitive transition. **Figure 4.2** shows the plot of I_1/I_3 *vs* [SDS] for water in reline and reline in the water region.
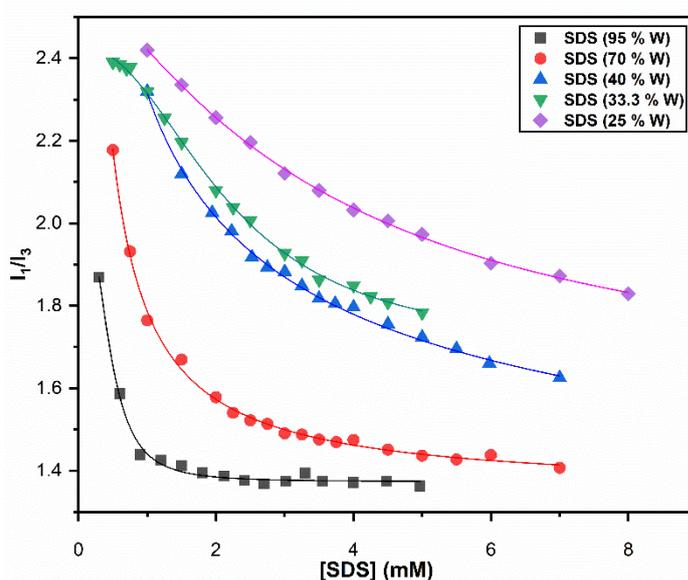
Figure 4.2: Variation of I_1/I_3 (for pyrene) against [SDS] at 303 ± 0.1 K.

The resulting CMC values are compiled in **Table 4.1** and compared with literature values and plotted against wt.% of water (**Figure 4.3**). Literature data nearly fall on the same curve as depicted in **Figure 4.3** and demonstrate the concurrence of CMC data of earlier studies [36]. CMC decreases (region I), increases (region II), and then decreases again with the continuous addition of water in the reline-water mixture (region III). This is probably due to approaching the transition from water in reline to reline in water via transformation region (region II). CMC data in the region I can be understood in the light of H-bonded structures of water in reline, which is modified due to the presence of surfactant monomers. This modification in the H-bonded network is responsible for micellization in region I. However, when the loose motif of reline-urea-water is formed (region II) and releases some urea /choline chloride (ChCl) from the above motifs [12].

Table 4.1: CMC data of SDS in reline-water mixture.

Wt.% of water	CMC of SDS (mM.L^{-1})
5	13.9 [a]
15	9.2 [a]
15	8
25	4.69
33.3	2.74
40	3.96
50	3.8 [a]
70	1.63
95	0.9

[a] values are taken from reference [36].

It has been reported that urea is known for CMC increase as well as for protein denaturation [38,39]. This release of urea and ChCl may affect micellization in opposite ways as ChCl, being a quaternary salt, may reduce CMC. In other studies, on the micellization of SDS, it has been reported that the addition of quaternary ammonium salt decreases the CMC [40,41]. Probably, urea effect on micellization dominates and is responsible for a CMC increase as observed in region II of **Figure 4.3**.
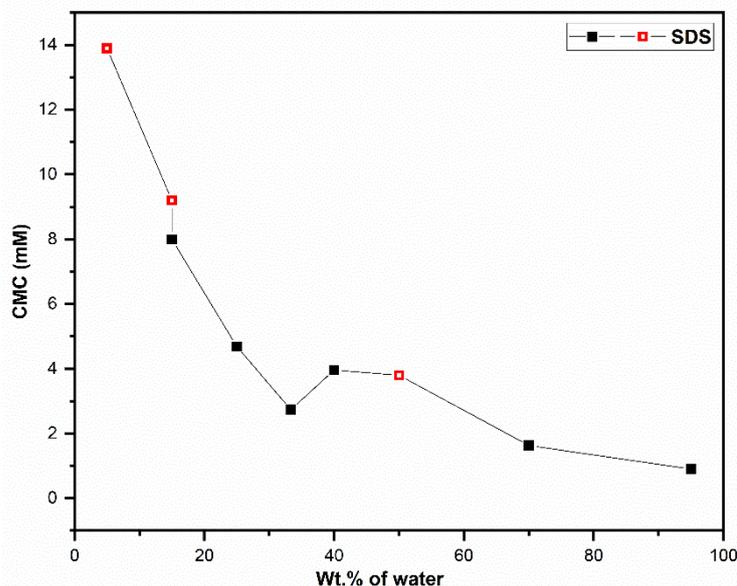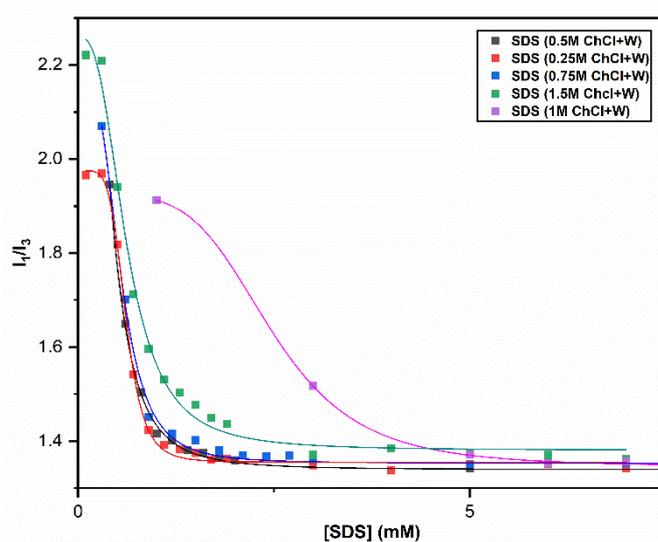

Figure 4.3: Variation of CMC of SDS against wt.% of water in the reline-water mixture (water in reline or reline in water): ■, present study and □, taken from reference [36].

As mentioned above, region III (reline in water) belongs to a molecular solution of reline components (ChCl and urea) and cholinium ion (Ch$^+$) may interact with an anionic SDS

micelle electrostatically as well as hydrophobically (due to the presence of alkyl part) and responsible for facilitating the process of micellization with a concomitant decrease in CMC as observed in region III of **Figure 4.3**. It has been reported that counter-ion binding follows a similar trend in DES as reported in water [42]. However, DES provides strengthened binding of counter ions which assists in the micellization process. It may be mentioned here that reline (or reline-water mixture) provides a favorable environment for counter-ion association and responsible here for cholinium dodecyl sulphate formation with a concomitant decrease in CMC [20]. The replacement process of sodium ion by cholinium ion should increase with the increase in water content of the reline-water mixture and is responsible for a continuous decrease in the CMC of the SDS [21].

4.3.2 Micellization of SDS in a molecular solution of ChCl

Micellization of SDS was studied in an aqueous solution of ChCl with different molar concentrations of ChCl by using fluorescence spectroscopy. Pyrene is commonly utilized as a probe to study micellization in surfactant solutions. Pyrene typically exhibits four vibrational peaks (I, II, III, and IV) in aqueous solution when exposed to photoluminescence (fluorescence), as seen in **Figure 4.1**. Fluorescence measurements at a specific surfactant concentration show significant alterations in the third vibration peak of pyrene) both above and below the CMC as a result of its solubilization site, polarity, and microenvironment. Micellization can be determined by analyzing the intensity ratio of I to III vibration peaks (I_1/I_3). **Figure 4.4** represents a plot of I_1/I_3 vs [surfactant] which gives the CMC value after sigmoidal fitting in the plot. The CMC data are compiled in **Table 4.2**.

Figure 4.4: Variation of I_1/I_3 (for pyrene) against [SDS] in a molecular solution of ChCl at 303 ± 0.1 K.

Table 4.2: CMC data of SDS in a molecular solution of ChCl.

[ChCl] (M)	Molar ratio ChCl: water	Mole % of water	Wt. % of water	CMC of SDS (mM.L^{-1})
0.25	1:220	99.5	96.6	1.10
0.5	1:111	99.1	93.5	1.35
0.75	1:74	98.6	90.5	1.33
1	1:55	98.2	87.7	1.95
1.5	1:37	97.3	82.6	1.28

4.3.3 Micellization of conventional and some gemini surfactants in aquolines

Association behaviour of conventional (SDS, sodium dodecyl benzene sulfonates (SDBS), sodium 1-dodecane sulfonate (SDSo), cetyltrimethylammonium bromide (CTAB), tetradecyl trimethyl ammonium bromide (TTAB), dodecyl trimethyl ammonium bromide (DTAB)) and gemini (P, P'-1,4-butanedieyl, P, P'-didodecylester, disodium salt (12-4-12A)) surfactants in different aquoline systems (DES I-DES IV) has been studied by fluorescence measurements by using pyrene as a probe and representative plot is given in **Figure 4.1**. These plots are used to obtain the ratio of intensities of Ist vibronic peak to IIIrd vibronic peak (I_1/I_3). Later, I_1/I_3 *vs* [surfactant] curves are plotted (some of them are shown in **Figure 4.5 (a-c)**) to obtain CMC of particular surfactant-aquoline combinations. CMC data for various conventional and gemini anionic surfactants are compiled in **Table 4.3.** As the surfactants SDSo, 12-4-12A, and CTAB do not dissolve in DES I, the CMC values were not investigated for that particular system.

The CMC of SDS varies non-linearly with a continuous increase in the molar ratio of water in the aquoline mixture. However, all other surfactants show a clear decrease in CMC with an increasing number of moles of water in a particular aquoline. Data do not allow any further generalization on CMC variation. Micellization depends on two counter effects, one promotes association and the other retard it. Hydrophobic interactions promote micellization which is driven by the polarity of the solvent (e.g., water) which compels the hydrocarbon chain to go into the micellar interior, thereby free energy decrease of the system [43]. All DESs are more polar solvents in comparison to water (polarity data are given in chapter 3). However, micellization was observed in almost each DES though the formation of micelle is DES selective [20,44–46]. In the present study, micellization is observed for both anionic and cationic surfactants and CMC values as compiled in **Table 4.3**.
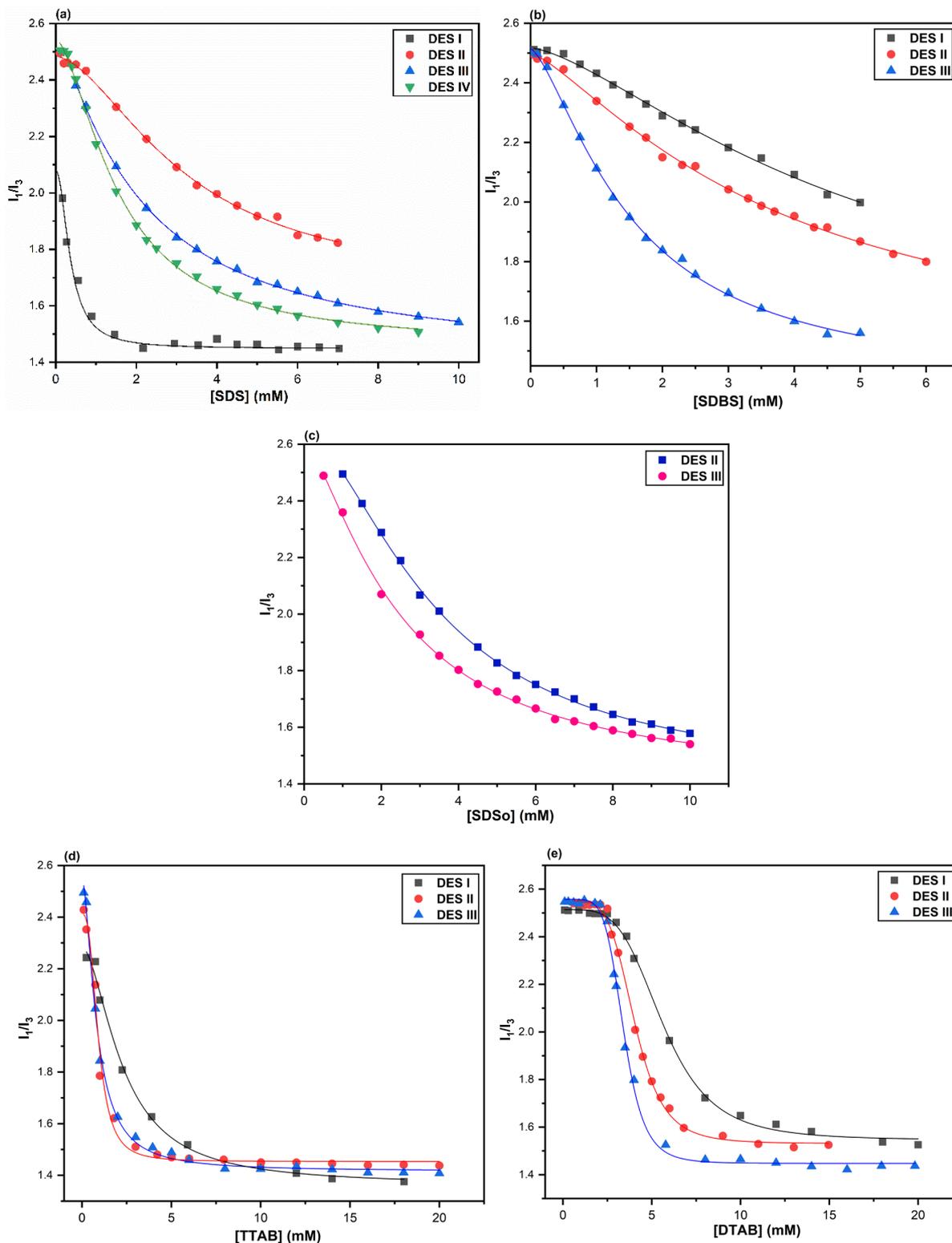
Figure 4.5: Variation of I_1/I_3 (for pyrene) against surfactant concentration: a) SDS; b) SDBS; c) SDSo; d) TTAB; and e) DTAB.

It may be mentioned here that all aquoline mixtures are highly polar materials (like other DESs) but initiate micellization behaviour as observed in pure water. Not much is known about the micellization of different surfactants in highly polar DESs. Probably, high polarity

may facilitate the removal of the hydrophobic portion of surfactant from the bulk medium to the micelle through electrostatic interactions between the head groups may facilitate a reverse process (de-micellization). However, 12-4-12A shows higher CMC in DES III in comparison with pure water. The molecular architecture of 12-4-12A may contribute (two polar heads) with a concomitant effect on the association process.

Table 4.3: CMC data of various conventional and gemini surfactants in different aquolines (DES I to DES IV).

| Surfactants	CMCs (mM.L^{-1})				
	Water	**DES I**	**DES II**	**DES III**	**DES IV**
SDS	7.90[a]	3.08	4.69	3.75	2.98
SDBS	2.30[a]	3.31	2.73	2.48	-
SDSo	10.65[a]	-	6.72	5.0	-
12-4-12 A	0.55[b]	-	-	1.40	-
CTAB	0.87[c]	-	1.42	0.82	-
TTAB	3.62[c]	4.45	2.70	2.56	-
DTAB	14.7[c]	8.38	6.07	5.26	-

Values are taken from [a] ref [47]; [b] ref [16]; and [c] ref [48].

Among anionic surfactants (except 12-4-12A) CMC shows an order: SDSo>SDS>SDBS (**Table 4.3**) in DES II and DES III. With the same dodecyl chain in these surfactants, the head group contributes differently towards micellization, which may depend on the head group – counter ion interaction [49]. A similar type of order was observed in earlier studies [47,50]. CTAB, TTAB, and DTAB show lower values of CMCs in aquolines than in water (except TTAB in DES I). This behaviour is similar to that observed for most anionic surfactants and can be interpreted similarly as discussed above. Moreover, an increase in the chain length of the hydrocarbon chain in cationic surfactants (DTAB to CTAB) causes a decrease in CMC which is again a similar behaviour as observed with pure water as a solvent [9]. These observations suggest that the phenomenon of micellization follows a similar mechanism of association in both water and aquoline though the degree of H-bonding in two types of solvents can be different. Even for contrast charge surfactants of the same alkyl chain length (SDS and DTAB) CMC value trend is similar as observed in pure water and corroborates the above proposed interpretation of micellization in aquoline (and water).

4.3.4 Influence of salts on solution behaviour of DTAB in aquolines

Micellization of DTAB in *aquolines* (DES I to DES III), with salt, is investigated using a spectrofluorometer at 303±0.1 K and representative plots (with *aquoline*-salt media) of intensity vs. wavelength **(Figure 4.1)**, is used to acquire an intensity ratio of the first vibronic

peak to the third vibronic peak (I_1/I_3). The variation of I_1/I_3 with [DTAB], with K-salt and Na-salt, (sigmoidal plot, **Figure 4.6 (a-b)**) has been used to compute CMC. The acquired CMC data of DTAB in pure *aquolines* and *aquolines* + salt mixture is compiled in **Table 4.4**. CMC of DTAB decreases with the presence of several molecules of water in a typical *aquoline*. It has been further observed that CMC in *aquoline*(s) are lower than the CMC of DTAB observed in pure water [51,52]. However, a comparison of Gordon parameter (G values; given in chapter 3) for water and *aquolines* suggests that CMC should be higher in *aquoline* than in water. Probably, the presence of chloride of ChCl plays a role and modifying electrostatic interactions and hence the micellization process/CMC.
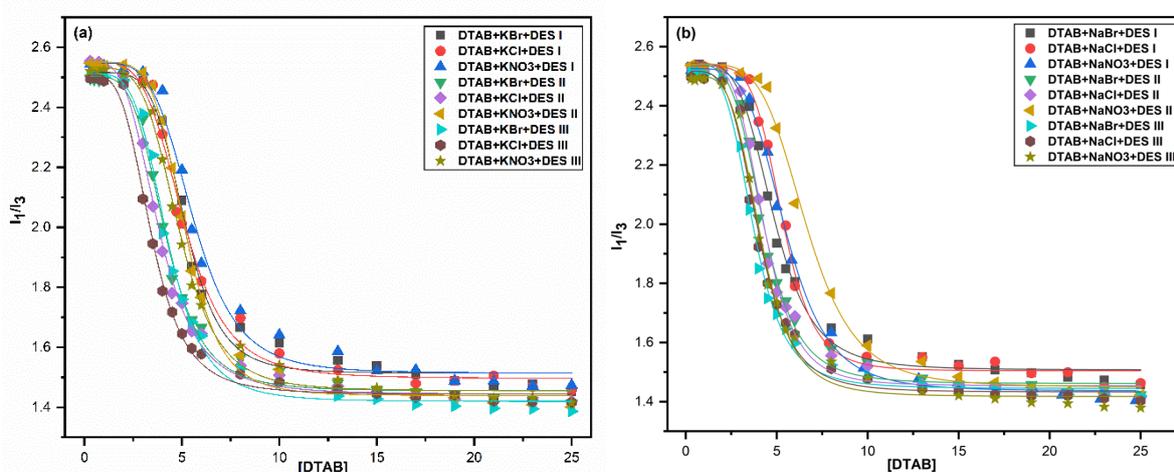
Figure 4.6: Variation of I_1/I_3 against [DTAB] in a) K-salt + aquolines, and b) Na-salt + aquolines at 303±0.1 K.

It has been reported that the solubilities of NaBr in DESs are lower in comparison to those in water [53]. Similarly, ionic surfactants show a choice of DES for dissolution and other related phenomena [36]. In this direction, *aquoline* holds a special place as it dissolves both cationic and anionic surfactants judiciously. Therefore, *aquolines* could be a better medium for the study of the association behaviour of surfactants with and without salt. DTAB + *aquoline* system has a Br^- or Cl^- as counter ions while Ch^+ can be considered as a co-ion. It may be mentioned here that the dissociation process of DTAB would also be changed in *aquoline* as compared to water. Therefore, the addition of salt effect cannot be as direct as has been reported in aqueous medium [54,55]. The salt effect can be studied in terms of *(i)* salt concentration, *(ii)* nature of co-ion, and *(iii)* nature of counter ion. Recently, the solubility of the alkali halides in *aquolines* follows the order: NaF < NaI < NaBr < NaCl and KCl < NaCl < LiCl [56]. In another study, it has been reported that the solubility of NaBr increases in *reline* by partial

substitution of urea with glycerol [53]. In the same study, it is also observed that NaBr solubility shows an order: *reline* < *reline* + glycerol < glycerol < water. This means the presence of glycerol or water may increase salt solubility in a typical DES (*reline* + glycerol in comparison to pure *reline*). This analogy can be further extended to *aquolines* having different water molecules. This is indeed observed in our case where the salt solubility order was: DES I < DES II < DES III (dissolution of salt has been found easier in DES III than DES II or DES I). Based on the solubility data it was concluded that the solubilities of the alkali halides decrease considerably in the *aquolines* than in water. The ion pair repulsion between ChCl and the alkali halides governs the overall solubility.

Table 4.4: Co-ion effect on CMC of DTAB in aquolines.

[Salt]	NaCl			KCl		
	DES I	DES II	DES III	DES I	DES II	DES III
0	8.4	6.0	5.3	8.4	6.0	5.2
10	4.9	4.1	3.7	4.7	3.9	4.5
20	5.2	5.5	4.4	5.1	3.9	3.3
30	5.3	4.3	4.0	5.0	3.7	3.4

An increase in [salt] seems responsible for decreasing the CMC value followed by a level off (**Table 4.4**). This behaviour was similar as observed with the aqueous surfactant–salt system [57]. In a previous study, it was reported that specific DES-cationic head group interactions are absent and, therefore, have little interfering chance with the salt [58]. The decreasing effect of CMC is more pronounced with KCl than NaCl. K^+ is less hydrated than Na^+ [59] and hence would respond *aquoline* network differently. Since *aquolines* are water-based DESs, co-ions (Na^+ or K^+) may interact with water present in the network. At higher salt concentrations, Cl^- can also contribute to the overall network effect. Moles of water in a typical *aquoline* have specific effects on the *aquoline* network (H-bonding) which also contribute to the resultant CMC. Additionally, G values (given in chapter 3) are lower in *aquolines* which may work against micellization. CMC will be decided by the dominance of one factor over another and responsible for the absence of any regular trend. This is indeed observed from the data in **Table 4.4**.

The nature of the counter ion has been reported to influence the micellization process [60]. This is because counter ions can interact with micellar surfaces via electrostatic attractive forces and cause depletion of micellar surface charge with consequent lowering of CMC in aqueous solution. **Figure 4.7** shows the variation of CMC of DTAB with the nature of

counter ion. CMC data follows the trend: $Cl^- < Br^- < NO_3^-$. This trend is opposite to the one observed in aqueous solution ($Cl^- > Br^- > NO_3^-$). The key lies in the hydrophilicity of counter ions and in this context, NO_3^- is the least hydrophilic and expected to disturb less the *aquoline* network than the other
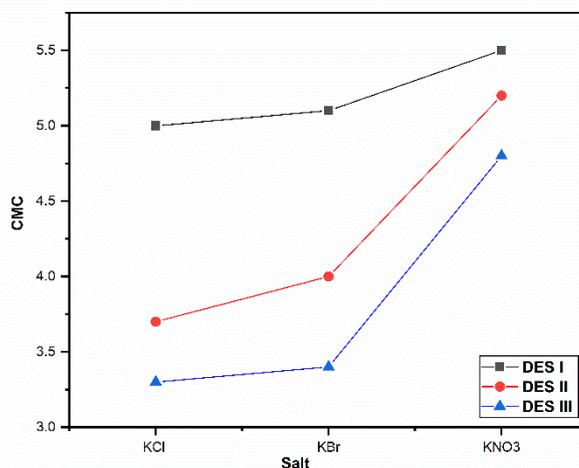

Figure 4.7: Variation of CMC of DTAB with the nature of counter ion in aquolines.

Counter ion binding seems less effective in influencing the micellar surface and only modification of *aquoline* network plays a role in decreasing the CMC. Further, Cl^- may occupy a favorable position in the *aquoline* network and assist the micellization phenomenon. If this is correct, CMC with Cl^- should be lower than the other ones. This is indeed observed in **Figure 4.7**. Not a single study on salt-induced micellization in DESs is available for comparison to the present data. However, in one of the studies on micellization, it has been shown that changing the counter ion of an anionic surfactant from Li^+ to Cs^+ facilitates the micellization process in *reline* as well as *glyceline* (ChCl + glycerol, 1:2) [42]. The present data on K-salt, in a way, corroborates the above observation. These aspects are further explored in terms of aggregation number (N_{agg}) and micellar morphology in the following sections.

4.3.5 Aggregation number and micellar environment

The aggregation number (N_{agg}) of micelles was determined by reducing the fluorescence intensity of pyrene while changing the concentration of the quencher (CPC) at constant concentrations of pyrene and surfactant. A quenching experiment was performed to calculate N_{agg}, Stern-Volmer constant (K_{sv}), micro polarity (I_1/I_3), and apparent dielectric constant (ε) for various surfactants in aquolines (DES I- DES III) and for 10 mM DTAB with K-salt in aquolines. Representative fluorescence emission spectra (**Figure 4.8 (a-b)**, shown only for SDS and for 10mM DTAB + 30mM K-salt) of pyrene, in the presence of CPC as a quencher, can be applied to acquire plots of ln I_0/I_q vs. [CPC].
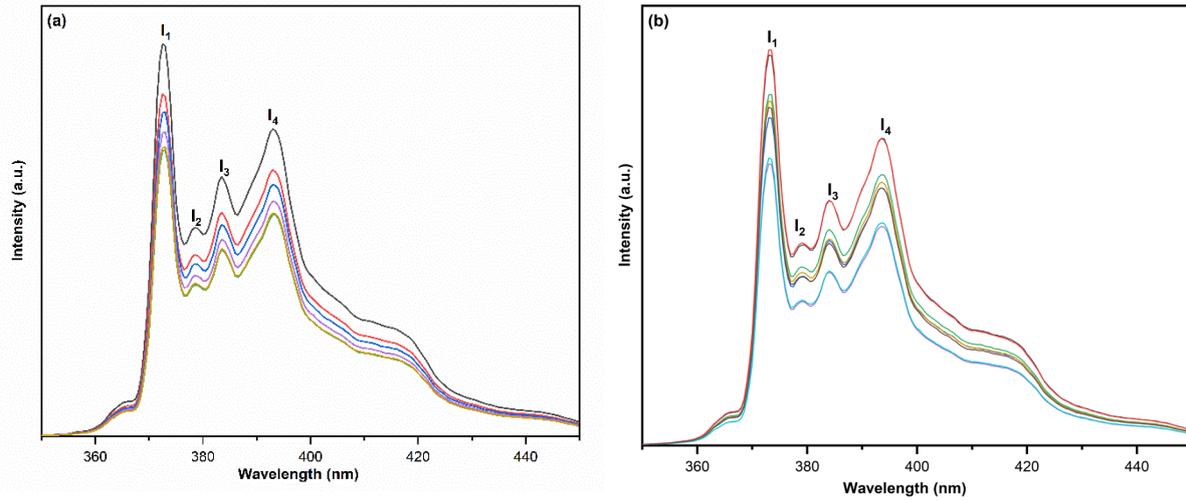
Figure 4.8: Emission spectra of pyrene with different CPC concentrations in: a) SDS + DES III; b) 10mM DTAB in DES I + KCl.

Figure 4.9 (a-b) represents plots of ln I_0/I_q vs. [CPC] for some of the systems. These plots are used to obtain data regarding N_{agg} and the micellar environment experienced by the probe [61]. The Stern-Volmer constant (K_{sv}) can be obtained by the following equation [62].

$$\frac{I_0}{I_q} = 1 + K_{sv}\,[CPC] \qquad \text{(Equation 1)}$$

where, I_q and I_0 are intensities (for I^{st} vibronic peak of the plot of intensity vs wavelength, (**Figure 4.8**) of pyrene in the presence and absence of CPC. A linear plot was the result of the variation of I_0/I_q with [CPC]. N_{agg} of micelle has been calculated using a well-known mathematical relation (Eq.2) [63],

$$ln\left(\frac{I_0}{I_q}\right) = N_{agg} \times \frac{[CPC]}{C_m} \qquad \text{(Equation 2)}$$

where C_m is [surfactant] in micellar form. Equation 2 represents a straight line (**Figure 4.9 (a-b)**) passing through the origin and its slope used to compute N_{agg}.

The micellar environment mapping has been performed in terms of micropolarity which has been obtained from an average of I_1/I_3 (**Figure 4.8**). The micropolarity (I_1/I_3) and apparent dielectric constant (ε) can be correlated by employing the equation (Eq. 3) as follows:

$$\frac{I_1}{I_3} = 1.000461 + 0.01253 \times \varepsilon \qquad \text{(Equation 3)}$$
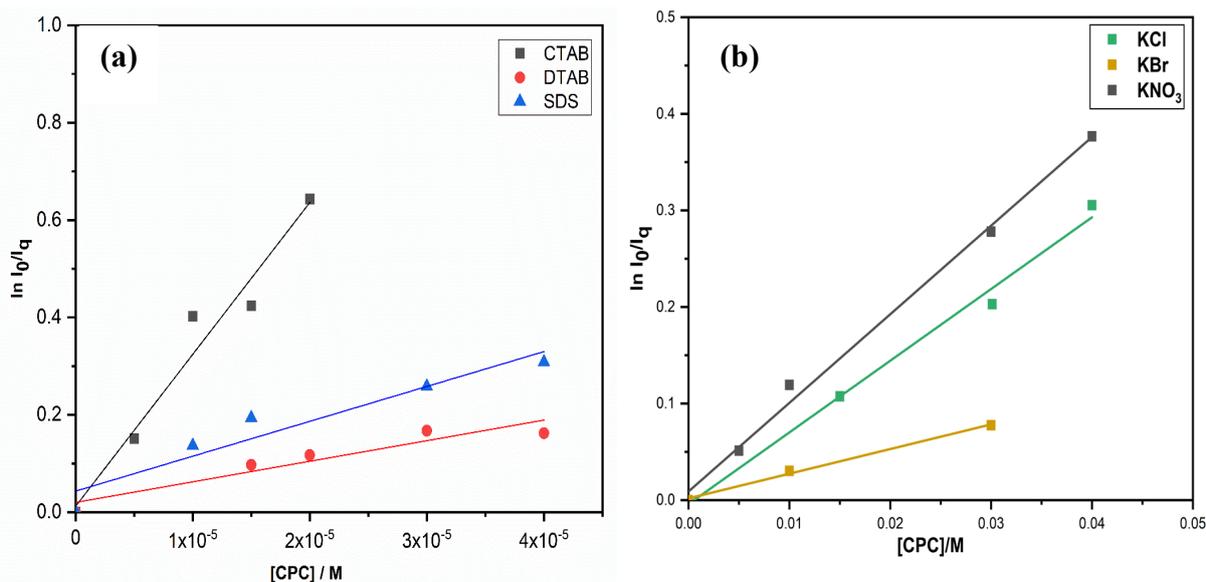
Figure 4.9: Plots of ln I_0/I_q vs [CPC] for a) CTAB, DTAB and SDS + DES III; b)10mM DTAB in K-salt + DES I.

All the data, N_{agg}, K_{sv}, micro polarity (I_1/I_3), and ε for various surfactants in aquolines (DES I- DES III) and for 10 mM DTAB with K-salt in aquolines are compiled in **Table 4.5.** K_{sv} and the quenching process can be correlated and the K_{sv} value dictates the rate of fluorescence quenching by the presence of CPC. Depending on the micellar environment produced by different surfactants, probe and quencher may be at the same or dissimilar sites. However, the micellar environment experienced by the probe has been found more polar than expected in pure water [61,64]. Further, N_{agg} has been found lower than observed in an aqueous medium [65] which can be explained on the basis of the micellar environment (which is more polar in an *aquoline*-based micellar system). However, the presence of salt usually causes an increase (with a few exceptions) in N_{agg} which also shows counterion nature dependence as reported for micelles in aqueous media [66,67].

Salt-induced micellar environment governs the presence of pyrene and CPC at the same site or at different sites. It may be mentioned based on the data compiled in **Table 4.5**, that the micellar environment is more polar with *aquolines* (with and without K-salt) than in aqueous micelle [64,68]. The ε value of salt-induced DTAB micelles suggests a less polar environment as one moves higher moles of water (DES I to DES III) in a typical *aquoline*. However, salt counter ion has a marginal bearing on the micellar environment. Aquoline polarity can be exploited to produce reverse micelle [69,70] which are generally used as nano reactors for the synthesis of organic compounds/ nanomaterial [71,72].

Table 4.5: Aggregation number (N_{agg}), Stern-Volmer constant (K_{sv}), micro polarity (I_1/I_3), and apparent dielectric constant (ε) for various surfactants and for 10 mM DTAB with K-salt in *aquolines*.

System	Aquoline	Aggregation Number (N_{agg})	K_{sv} 10^4	Micro polarity (I_1/I_3)	Apparent dielectric constant (ε)
SDS	DES I	31	3.50	1.80	64.17
	DES II	16	2.67	1.63	50.34
	DES III	34	0.67	1.53	41.97
SDSo	DES II	19	2.66	1.57	45.78
	DES III	57	2.14	1.80	63.75
SDBS	DES I	58	8.90	1.85	68.46
	DES II	54	8.01	1.80	63.95
	DES III	168	7.15	1.69	55
12-4-12 A	DES III	4	1.72	1.98	78.01
CTAB	DES II	53	23.86	1.73	58.48
	DES III	37	10.07	2.26	100.54
TTAB	DES I	56	6.71	2.31	89.29
	DES II	91	7.07	1.78	62.41
	DES III	118	20.12	1.52	42.18
DTAB	DES I	10	0.64	1.72	58.20
	DES II	25	1.04	1.56	45.36
	DES III	27	1.55	1.54	43.33
DTAB + KCl	DES I	37	0.81	1.63	50.26
	DES II	22	0.96	1.57	45.24
	DES III	54	0.86	1.52	41.76
DTAB + KBr	DES I	13	0.98	2.03	82.38
	DES II	46	0.87	1.55	43.37
	DES III	21	0.55	1.53	42.71
DTAB + KNO$_3$	DES I	41	1.02	1.66	52.87
	DES II	68	1.52	1.57	45.82
	DES III	52	1.88	1.56	45.02

4.3.6 Salt-induced micellar morphologies in aquolines

DTAB is known to form nearly spherical micelles in pure water [73]. The magnified POM images (**Figure 4.10**) have been acquired for 10mM DTAB + 30mM K-salt in water and *aquolines* (DES I and DES III). No structures were seen with DTAB + K-salt in water or DTAB in pure *aquolines*. However, DTAB aggregates are seen when DTAB micelles form in *aquoline* – salt medium. Such surfactant structures (probably vesicles) have been seen for the first time microscopically in DESs. In a separate study, it has been reported that micellar elongation takes place in *reline* in comparison to aqueous media [42,74]. This suggests that the presence of counter ion together with *aquoline* provides ideal conditions for the formation of higher-order surfactant aggregates (diameter ranges from 1.3 µM- 3.3 µM, as depicted in **Table 4.6**).
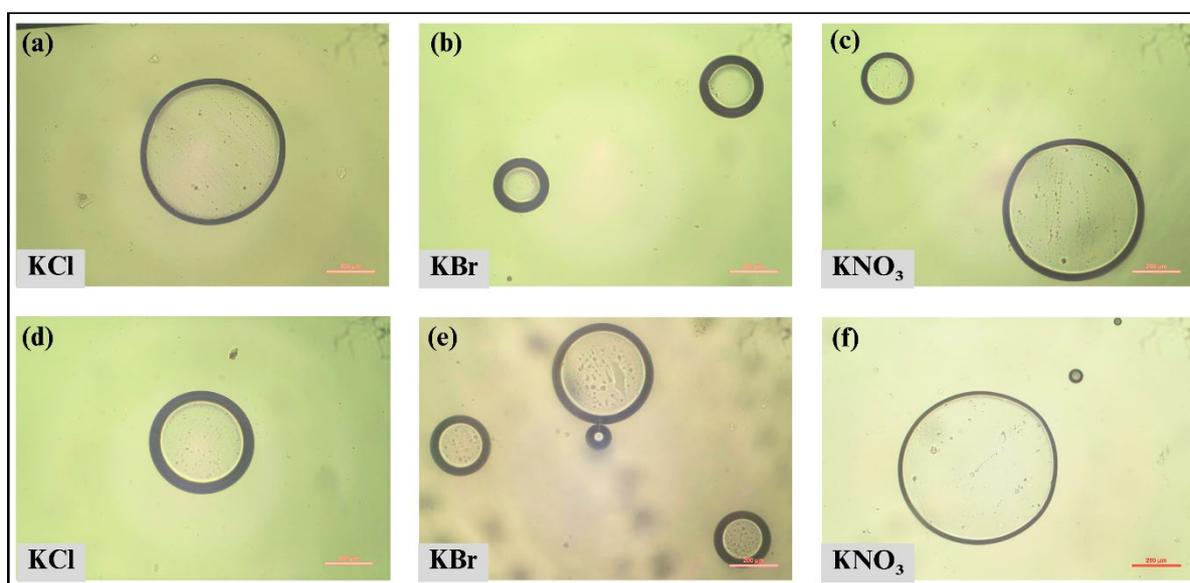
Figure 4.10: Magnified POM image of 10mM DTAB - aquoline (DES I, a-c and DES III, d-f) – K-salt.

Table 4.6: Vesicle diameter of 10 mM DTAB in aquoline - K-salt system.

Salt	Diameter ± 0.1 µM	
	DES I	DES III
KCl	2.95	2.20
KBr	1.30	2.10
KNO$_3$	2.90	3.30

Such types of giant unilamellar vesicles (GUVs) have been reported in aqueous lipid mixtures with and without cholesterol [75]. However, more surfactant systems should be

studied in order to make a generalization. At present, counterion binding seems a predominant reason in *aquoline* and rationalizes micellar structural transition into higher-order aggregates [76]. The above giant amphiphile aggregates have already been reported by POM [77,78] and validate the present data.

4.4 Conclusion

The micellization behavior of various surfactants in DESs, reline-water mixtures, and aquolines, has been extensively investigated. From the data presented here, it can be concluded that micellization can be observed in the reline-water mixtures as in an aqueous solution. The CMC values show that water in reline converts to reline in water through the medium region (region II). CMC decrease in water in reline region via formation/breaking of H-bonded structures in ChCl-urea-water motifs. However, CMC decreased in region III (in reline in water) due to the molecular solution of ChCl, which furnished a Ch+ counter ion. This Ch+ ion can interact with the head groups of the micelle and is responsible for lowering CMC in region III. Data obtained from the fluorescence study allow concluding that the micellization process, of a variety of surfactants, can be observed in aquoline (DES I to DES IV) as seen in pure water. CMC decreases with an increasing number of water molecules per mole of ChCl in a typical aquoline. Further, CMC values are lower in most of the cases when compared with water. Micelles show a lower aggregation number (N_{agg}) and higher polar environment experienced by the probe (pyrene). However, gemini (12-4-12A) surfactant shows higher CMC and lower aggregation number than in water. This can be understood in light of architectural differences between gemini and conventional surfactants. The study demonstrates that micellization phenomenon can occur with both types of ionic surfactants (anionic and cationic) in aquoline which is rare for other DESs (e.g. reline, ethaline or glyceline) as observed in pure water. Aquolines were also used to study the association behaviour of a cationic surfactant, DTAB, with and without salt. Salt addition facilitates the micellization phenomenon with a concomitant lowering of CMC. CMCs were varied with the nature of counter ions (Cl^-, Br^- or NO_3^-) and co-ions (Na^+ or K^+). POM data suggest the formation of giant aggregates in salt + *aquoline* media. However, they were absent in pure water or pure *aquolines* at the same solution composition. Being a biocompatible medium (*aquoline*) together with the presence of giant aggregates, the reported systems can be used as good biotechnological models for synthetic biology and pharmaceuticals. This approach of getting higher-order aggregates (e.g., giant vesicles), in such novel media (*aquolines*), may find applications in various fields of research

(e.g., ultrafiltration [79], drug delivery vehicle [80], microreactor [81], biochemistry [82] among others [83].

4.5 References

[1] P. Mukherjee, S. K. Padhan, S. Dash, S. Patel, and B. K. Mishra, Adv Colloid Interface Sci **162**, 59 (2011).

[2] S. Chowdhury, S. Shrivastava, A. Kakati, and J. S. Sangwai, Ind Eng Chem Res **61**, 21 (2022).

[3] M. Palmer and H. Hatley, Water Res **147**, 60 (2018).

[4] S. Kumar, S. Singh, A. Bhadoria, K. Parikh, S. K. Yadav, S. Kumar, and V. K. Aswal, Journal of Physical Chemistry B **121**, 8756 (2017).

[5] L. Sreejith, S. Parathakkat, S. M. Nair, S. Kumar, G. Varma, P. A. Hassan, and Y. Talmon, J Phys Chem B **115**, 464 (2011).

[6] B. Patel, S. Singh, K. Parikh, V. Chavda, D. Hirpara, D. Ray, V. K. Aswal, and S. Kumar, J Mol Liq **359**, 119242 (2022).

[7] B. Patel, S. Singh, K. Parikh, V. Chavda, D. Ray, V. K. Aswal, and S. Kumar, J Mol Liq **363**, 119885 (2022).

[8] R. Mohammed and M. Azaga, Surfactant Aggregation in DESs, 2018.

[9] Milton J. Rosen, *Surfactant and Interfacial Phenomena*, third (2012).

[10] H. Hoffmann and G. Ebert, Angewandte Chemie International Edition in English **27**, 902 (1988).

[11] G. H. Abdullah and M. A. Kadhom, Studying of Two Choline Chloride's Deep Eutectic Solvents in Their Aqueous Mixtures, 2016.

[12] O. S. Hammond, D. T. Bowron, and K. J. Edler, Angewandte Chemie - International Edition **56**, 9782 (2017).

[13] Ralf Ludwig, Angewandte Chemie International Edition **40**, 1808 (2001).

[14] S. Sarkar, A. Maity, and R. Chakrabarti, Physical Chemistry Chemical Physics **23**, 3779 (2021).

[15] N. López-Salas, J. M. Vicent-Luna, S. Imberti, E. Posada, M. J. Roldán, J. A. Anta, S. R. G. Balestra, R. M. Madero Castro, S. Calero, R. J. Jiménez-Riobóo, M. C. Gutiérrez, M. L. Ferrer, and F. del Monte, ACS Sustain Chem Eng **7**, 17565 (2019).

[16]   S. K. Yadav, K. Parikh, and S. Kumar, Colloids Surf A Physicochem Eng Asp **514**, 47 (2017).

[17]   S. Singh, S. K. Yadav, K. Parikh, A. Desai, S. Dixit, and S. Kumar, J Mol Liq **272**, 413 (2018).

[18]   S. Trivedi, S. Juneja, V. Khokhar, and S. Pandey, in *Green Sustainable Process for Chemical and Environmental Engineering and Science* (Elsevier, 2023), pp. 145–192.

[19]   T. Arnold, A. J. Jackson, A. Sanchez-Fernandez, D. Magnone, A. E. Terry, and K. J. Edler, Langmuir **31**, 12894 (2015).

[20]   R. S. Atri, A. Sanchez-Fernandez, O. S. Hammond, I. Manasi, J. Doutch, J. P. Tellam, and K. J. Edler, Journal of Physical Chemistry B **124**, 6004 (2020).

[21]   A. Sanchez-Fernandez, K. J. Edler, T. Arnold, R. K. Heenan, L. Porcar, N. J. Terrill, A. E. Terry, and A. J. Jackson, Physical Chemistry Chemical Physics **18**, 14063 (2016).

[22]   A. Pandey, R. Rai, M. Pal, and S. Pandey, Physical Chemistry Chemical Physics **16**, 1559 (2014).

[23]   A. Sanchez-Fernandez, G. L. Moody, L. C. Murfin, T. Arnold, A. J. Jackson, S. M. King, S. E. Lewis, and K. J. Edler, Soft Matter **14**, 5525 (2018).

[24]   Kabir-ud-Din, D. Sharma, Z. A. Khan, V. K. Aswal, and S. Kumar, J Colloid Interface Sci **302**, 315 (2006).

[25]   S. Kumar, A. Z. Naqvi, and Kabir-ud-Din, Langmuir **16**, 5252 (2000).

[26]   S. Manet, Y. Karpichev, D. Bassani, R. Kiagus-Ahmad, and R. Oda, Langmuir **26**, 10645 (2010).

[27]   A. A. Ivanova, C. Phan, A. Barifcani, S. Iglauer, and A. N. Cheremisin, J Surfactants Deterg **23**, 327 (2020).

[28]   M. J. Qazi, S. J. Schlegel, E. H. G. Backus, M. Bonn, D. Bonn, and N. Shahidzadeh, Langmuir **36**, 7956 (2020).

[29]   V. Srinivasan and D. Blankschtein, Langmuir **19**, 9932 (2003).

[30]   J. Aslam, U. S. Siddiqui, W. H. Ansari, and Kabir-ud-Din, J Surfactants Deterg **16**, 693 (2013).

[31] A. L. Kwiatkowski, V. S. Molchanov, A. S. Orekhov, A. L. Vasiliev, and O. E. Philippova, J Phys Chem B **120**, 12547 (2016).

[32] R. M. Pashley and B. W. Ninham, J Phys Chem **91**, 2902 (1987).

[33] H. Zhang, M. L. Ferrer, M. J. Roldán-Ruiz, R. J. Jiménez-Riobóo, M. C. Gutiérrez, and F. Del Monte, Journal of Physical Chemistry B **124**, 4002 (2020).

[34] M. J. Roldán-Ruiz, R. J. Jiménez-Riobóo, M. C. Gutiérrez, M. L. Ferrer, and F. del Monte, J Mol Liq **284**, 175 (2019).

[35] O. S. Hammond, D. T. Bowron, and K. J. Edler, Green Chemistry **18**, 2736 (2016).

[36] M. Pal, R. Rai, A. Yadav, R. Khanna, G. A. Baker, and S. Pandey, Langmuir **30**, 13191 (2014).

[37] L. Séro, L. Sanguinet, S. Derbré, F. Boury, G. Brotons, S. Dabos-Seignon, P. Richomme, and D. Séraphin, Langmuir **29**, 10423 (2013).

[38] S. Kumar, N. Parveen, and Kabir-Ud-Din, Journal of Physical Chemistry B **108**, 9588 (2004).

[39] L. S. Romsted, J. Zhang, I. M. Cuccovia, M. J. Politi, and H. Chaimovich, Langmuir **19**, 9179 (2003).

[40] J. H. Lin, W. S. Chen, and S. S. Hou, Journal of Physical Chemistry B **117**, 12076 (2013).

[41] S. Singh, S. K. Yadav, K. Parikh, A. Desai, S. Dixit, and S. Kumar, J Mol Liq **272**, 413 (2018).

[42] A. Sanchez-Fernandez, O. S. Hammond, K. J. Edler, T. Arnold, J. Doutch, R. M. Dalgliesh, P. Li, K. Ma, and A. J. Jackson, Physical Chemistry Chemical Physics **20**, 13952 (2018).

[43] Clarke and Steven, The Hydrophobic Effect: Formation of Micelles and Biological Membranes, 2nd Edition (Tanford, Charles), 1981.

[44] I. Manasi, S. J. Bryant, O. S. Hammond, and K. J. Edler, in *Advances in Botanical Research*, Vol. 97 (Academic Press Inc., 2021), pp. 41–68.

[45] R. K. Banjare, M. K. Banjare, K. Behera, S. Pandey, and K. K. Ghosh, ACS Omega **5**, 19350 (2020).

[46] Komal, G. Singh, G. Singh, and T. S. Kang, ACS Omega **3**, 13387 (2018).

[47] S. K. Yadav, R. B. Yadav, and S. Kumar, J Surfactants Deterg **19**, 1063 (2016).

[48] K. Parikh, S. Singh, A. Desai, and S. Kumar, J Mol Liq **278**, 290 (2019).

[49] A. Sanchez-Fernandez, ab O. S Hammond, K. J. Edler, T. Arnold, abd J. Doutch, R. M. Dalgliesh, P. Li, K. Ma, and A. J. Jackson bf, Phys. Chem. Chem. Phys **20**, 13952 (2018).

[50] S. Kumar, H. Patel, and S. R. Patil, Colloid Polym Sci **291**, 2069 (2013).

[51] S. Chauhan, M. Kaur, K. Kumar, and M. S. Chauhan, J Chem Thermodyn **78**, 175 (2014).

[52] S. K. Shah, S. K. Chatterjee, and A. Bhattarai, J Mol Liq **222**, 906 (2016).

[53] R. S. Atri, A. Sanchez-Fernandez, O. S. Hammond, I. Manasi, J. Doutch, J. P. Tellam, and K. J. Edler, J Phys Chem B **124**, 6004 (2020).

[54] P. Lianos, J. Lang, and R. Zana, J Colloid Interface Sci **91**, 276 (1983).

[55] P. Lianos and R. Zana, J Colloid Interface Sci **88**, 594 (1982).

[56] M. S. Rahman and D. E. Raynie, J Mol Liq **324**, 114779 (2021).

[57] A. S. Rafique, S. Khodaparast, A. S. Poulos, W. N. Sharratt, E. S. J. Robles, and J. T. Cabral, Soft Matter **16**, 7835 (2020).

[58] A. Sanchez-Fernandez, T. Arnold, A. J. Jackson, S. L. Fussell, R. K. Heenan, R. A. Campbell, and K. J. Edler, Physical Chemistry Chemical Physics **18**, 33240 (2016).

[59] S. G. Oh and D. O. Shah, J Phys Chem **97**, 284 (1993).

[60] S. Manet, Y. Karpichev, D. Bassani, R. Kiagus-Ahmad, and R. Oda, Langmuir **26**, 10645 (2010).

[61] N. Azum, M. A. Rub, and A. M. Asiri, J Mol Liq **196**, 14 (2014).

[62] K.K.R. Mukherjee, *Fundamentals of Photochemistry* (Wiley Eastern, New Delhi, 1992).

[63] Martin J Schick, J Pharm Sci **56**, 663 (1967).

[64] N. J. Turro, P.-L. Kuo, P. Somasundaran, and K. Wongt, Surface and Bulk Interactions of Ionic and Nonionic Surfactants, 1986.

[65] K. Beyer, D. Leine, and A. Blume, Colloids Surf B Biointerfaces **49**, 31 (2006).

[66] P. Lianos and R. Zana, J Colloid Interface Sci **84**, 100 (1981).

[67] B. B. Mondal, R. Banik, and S. Ghosh, J Taiwan Inst Chem Eng **149**, 104982 (2023).

[68] N. Azum, M. A. Rub, and A. M. Asiri, J Mol Liq **196**, 14 (2014).

[69] A. Khoshnood and A. Firoozabadi, Langmuir **31**, 5982 (2015).

[70] N. M. Correa, J. J. Silber, R. E. Riter, and N. E. Levinger, Chemical Reviews.

[71] W. K. Fong, A. Sánchez-Ferrer, F. G. Ortelli, W. Sun, B. J. Boyd, and R. Mezzenga, RSC Adv **7**, 4368 (2017).

[72] T. Nakanishi, B. Ohtani, and K. Uosaki, Fabrication and Characterization of CdS-Nanoparticle Mono-and Multilayers on a Self-Assembled Monolayer of Alkanedithiols on Gold, 1998.

[73] W. A. Ducker and E. J. Wanless, Langmuir **12**, 5915 (1996).

[74] T. Arnold, A. J. Jackson, A. Sanchez-Fernandez, D. Magnone, A. E. Terry, and K. J. Edler, Langmuir **31**, 12894 (2015).

[75] T. Bhatia, P. Husen, J. Brewer, L. A. Bagatolli, P. L. Hansen, J. H. Ipsen, and O. G. Mouritsen, Biochimica et Biophysica Acta (BBA) - Biomembranes **1848**, 3175 (2015).

[76] T. Kijima, Y. Nishida, D. Fujikawa, M. Uota, T. Yoshimura, and G. Sakai, J Mol Liq **133**, 54 (2007).

[77] A. Manova, J. Viktorova, J. Köhler, S. Theiler, H. Keul, A. A. Piryazev, D. A. Ivanov, L. Tsarkova, and M. Möller, ACS Macro Lett **5**, 163 (2016).

[78] S. G. Oh and D. O. Shah, Effect of Counterions on the Interfacial Tension and Emulsion Droplet Size in the Oil/Water/ Dodecyl Sulfate System, 1993.

[79] F. Pena-Pereira and J. Namieśnik, ChemSusChem **7**, 1784 (2014).

[80] M. Hayyan, Asian J Pharm Sci **18**, 100780 (2023).

[81] P. Liu, J.-W. Hao, L.-P. Mo, and Z.-H. Zhang, RSC Adv **5**, 48675 (2015).

[82] P. A. Shah, P. S. Shrivastav, V. S. Sharma, and V. Chavda, Bioanalysis **15**, 815 (2023).

[83]   M. M. Abdelquader, S. Li, G. P. Andrews, and D. S. Jones, European Journal of Pharmaceutics and Biopharmaceutics **186**, 85 (2023).