4.1 Introduction

Surfactant solution behavior is substantially altered in the presence of polar additives like alcohols, ketones, amides, diols etc. [1-5]. These additives are often used to modify the properties of surfactants, allowing them to be utilized in diverse applications such as lubrication, oil-wetting cleaners, pharmaceuticals, cosmetics, food and detergent formulations, which require the use of surfactants in a water-poor medium. This has stimulated a significant amount of interest in the micellization of surfactants in polar organic liquids. Surfactant solutions in water-1,2-ethanediol (ED) mixtures have been extensively studied [6-30]. Micellization in water + diol oligomers [31-34] and even in pure diol systems [35-38] has been investigated. Though in most cases, these studies have applied ionic surfactants dissolved in these mixed solvents, a few studies on nonionic and zwitterionic surfactants have also appeared [17,22,37,37].

Nagarajan and Wang [10,11] used a thermodynamic model to predict an increase in critical micelle concentration (CMC), a decrease in the aggregation number ($N_{agg}$) and an increase in the aggregate polydispersity for ionic surfactants in water - ED mixed solvents. From a thermodynamic study for a cationic surfactant in water -ED mixed solvents, Ruiz [7] concluded that the solvophobic effect seems to have the same source as the hydrophobic effect, i.e. the large cohesive energy of the solvent is a main contributor to self-assembly. Using fluorescence spectroscopy, Ruiz observed that the structure of the micellar surface is clearly affected by the presence of ED in the solvent system. The microviscosity in the hydrophobic regions of micelles was roughly constant with ED addition, but at the micellar surface, the microviscosity increased and was attributed to the solvent participation in the solvation layer of the micelle head groups [8]. Palepu and coworkers [18,19,31] reported the effect of ED oligomer on micellization and micellar kinetics from thermodynamic study of alkyltriphenylphosphonium bromides in mixed solvent of water – ED and water-diethylene glycol. Moya and coworkers [20-28] have extensively investigated the micellization of cationic surfactants in water- ED mixtures and examined these systems as reaction media for kinetic studies in mixed solvents containing as high as 50% ethylene glycol. These studies suggest that a progressive increase in the diol concentration makes the aggregation process less
favorable for surfactant monomer and also reduces rate of reaction. Bakshi [29,30] investigated the effect of ED on mixed micelle formation by ionic surfactants and concluded that the non-ideality of the mixed system increases with increasing amount of diol due to the solvation of hydrophobic surfactant tail by the solvent.

In most of these studies listed above, the aggregate formation process was investigated by physical methods, e.g., electrical conductivity, fluorescence and surface tension measurements, in many cases over the entire mole fraction range of diol. Seguin et al. [37] used small angle neutron scattering (SANS) to determine shape and aggregation number of micelles of ionic and nonionic surfactants in water-diol mixtures using ED and 1,3-propanediol (PD) over a wide range of dielectric constants and concluded that self–assembly was strongly dependent on the surfactant type and the identity of the diol. Seguin et al. [38] also observed that for an ethoxylated nonionic surfactant in ED-PD mixtures, their ratio may be effectively used to switch aggregation "on" or "off".

Recent studies by Tomi et al. [35] presented CMC data on dodecyltrimethylammonium bromide in the presence of some $\alpha,\omega$-diols using electrical conductivity. They discussed the interaction of diols with surfactant in aqueous solution and compared with corresponding monohydric alcohols. Marangoni and coworkers [32,33] examined the partitioning of diols in micelles and mixed micelles as a function of alkyl chain length and the position of hydroxyl group (-OH) by calorimetry and NMR. In a previous study we compared the effect of 1-butanol and 1,4-butanediol on micellization and microstructure of micelles of cationic surfactants [39]. However, most of the studies in the literature deal with micellization and micellar characteristics in ED or ED/water systems. There are few studies where the micellar properties of ionic surfactants have been determined in the presence of longer chain $\alpha,\omega$-alkanediols; these studies are limited to the measurement of the effect of the diol on a single property of the aggregate (e.g., partitioning [32]). A comprehensive and systematic study of the effects of various long chain diols on the properties of surfactant micelles is lacking and in fact there is no report on the effect of higher diols on aggregation number and location of diols in micelles from SANS and NMR. Hence, we report our results on the investigation aggregate formation by the cationic surfactant TTAB in the presence of various $\alpha,\omega$-diol/water mixtures.
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CMC values and degree of counterion dissociation (α) of TTAB in the mixed solvents were obtained from electrical conductivity measurements. SANS investigation on 100mM TTAB solution in D₂O and in presence of D₂O + diols was used to determine both size/shape and aggregation number (N_{agg}) of the micelles. ¹³C NMR chemical shifts were used to probe the locus of solubilization of the diols in the surfactant micelles. All these results are interpreted in terms of the impact of the diol on the subtle balance of forces that govern the self-assembly of the cationic surfactant in these mixed solvent systems.

4.2. Materials

The surfactant TTAB (Aldrich) was purified by recrystallization from acetone/ethanol mixture. The diols (ED, BD, HD, and OD,) were all analytical grade reagents from MERCK/Sigma and were used as received. Table 4.1 shows structural formulae of diols used. Triply distilled water (specific conductivity order of 10⁻³ mScm⁻¹) was used for preparing the solutions. The diol-water mixtures were made on a volume/volume basis for conductance and SANS measurements; the TTAB solutions were prepared on a molar basis by dissolving the appropriate quantity in a given volume of the mixed solvent.

Table 4.1 Structural formulae and octanol-water partition coefficient (log P_{o/w}) α,ω-alkanediols

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>log P_{o/w}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ED</td>
<td>HO—CH₂—OH</td>
<td>-1.93</td>
</tr>
<tr>
<td>BD</td>
<td>HO—CH—OH</td>
<td>-0.83</td>
</tr>
<tr>
<td>HD</td>
<td>HO—CH₂—CH</td>
<td>-0.11</td>
</tr>
<tr>
<td>OD</td>
<td>HO—CH₃—CH</td>
<td>-</td>
</tr>
</tbody>
</table>

Ref. [42]

4.3 Methods
4.3.1 Conductivity

Conductivity measurements were done using an ESICO microprocessor-based conductivity bridge, Model 1601, and a dip-type cell made of platinum black having a unit cell-constant. Temperature equilibrium was maintained via a Haake temperature bath to 0.01°C during the mixing and measurement. The conductivities of the solutions were measured using a successive dilution method in which a TTAB solution of an appropriate concentration was gradually diluted by the addition of a fixed amount of solvent system; for each increment of dilution, the specific conductance was measured as function of surfactant concentration. In all, approximately 50 experimental values were obtained for each titration run. The break in the specific conductance versus concentration plot was used to estimate the CMC value and the ratio of slopes above and below the break point was used to estimate the α for all systems. The uncertainty limits of CMC and α are ± 3 % ± 4% respectively.

4.3.2 $^{13}$C NMR

The proton-decoupled $^{13}$C NMR spectra for the TTAB/mixed-solvent systems were obtained on a Bruker Avance-II NMR spectrometer operating at 400.13 MHz for protons and 100.61 MHz for $^{13}$C. D$_2$O was used as the solvent and the spectra were referenced using an internal standard of 1 wt% TMS dissolved in CDCl$_3$. A pulse length of 4 μs, corresponding to a flip angle of ca. 60° was used with a sweep width of 20500 Hz. The 32K of data points was used and the number of acquisitions was normally 512. A typical $^{13}$C spectrum for the system TTAB/2.0% BD system is given in Fig. 4.1.

![Typical $^{13}$C NMR spectrum for the system 100mM TTAB/2.0 wt% BD.](image)

Fig. 4.1 Typical $^{13}$C NMR spectrum for the system 100mM TTAB/2.0 wt% BD.

4.3.3 Small angle Neutron scattering (SANS)
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The SANS measurements were done at the Dhruva reactor, BARC, Trombay, India [51]. The diffractometer uses a polycrystalline BeO filter as a monochromator; the mean wavelength ($\lambda$) of the incident neutron beam was 5.2 Å with a resolution ($\Delta\lambda/\lambda$) of approximately 15%. The angular distribution of the scattered neutron was recorded by a linear 1 meter long He$^3$ position sensitive detector (PSD), in the Q range 0.017–0.34 Å$^{-1}$. The surfactant solutions were placed in a 0.5cm thick quartz cell with Teflon stoppers and all measurements were carried out at 30° ± 0.1° C and corrected for the background and solvent contributions. The data were normalized to the cross-sectional unit using standard procedures. The scattering cross section per unit volume measured, as a function of scattering wave vector, gives the micellar parameters for the mono dispersed surfactant system [51].

In small angle neutron scattering experiment, the differential scattering cross-section per unit volume as a function of scattering vector Q is obtained, and for monodisperse system of micelles it can be expressed as [52].

$$\frac{d\sigma}{d\Omega} = n_m V_m (\rho_m - \rho_s)^2 \left[ <F^2(Q)> + <F(Q)>^2 [S(Q) - 1] \right] + B$$  \hspace{1cm} (1)

Here $n_m$ is the number density of the micelles, $\rho_m$ and $\rho_s$ are the scattering length densities of the micelle and solvent, respectively, $V_m$ is the volume of micelle, and $(\rho_m - \rho_s)^2$ is a contrast factor that represents the difference between the average scattering length density of the micelle and solvent. $F(Q)$ and $S(Q)$ are single particle form factor and the inter-particle structure factor, respectively. The inter-particle structure factor $S(Q)$ depends upon the spatial arrangement of particles and hence gives information about the inter-particle interaction. B is a constant term that represents the incoherent scattering background, which is mainly due to the hydrogen atoms in the sample. The detailed analysis procedure can be found in literature [52-55], but for the present purpose no such analysis of SANS data is required.

4.4 Results and Discussion

4.4.1 CMC and $\alpha$ values

The effect of diols on the CMC and $\alpha$ of TTAB at 30°C is shown in Fig. 4.2. The values in water are in good agreement with those reported previously [47]. Fig. 4.2a displays that as the content of ED and BD increases, the CMC is increased while for HD and OD, CMC decreased. However, for all diol the $\alpha$ values increase with diol
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concentration. Among the diols used in this work, ED and BD have high cohesive forces, dielectric constants, and hydrogen bonding abilities [40]. These diols also possess the ability to form hydrogen bonds with themselves or with other hydrogen bond donors like water [41]. On the other hand, relatively longer chain diols HD and OD behave differently due to their more hydrophobic nature [32]. The presence of short chain diols (ED and BD) decreases cohesive energy density of water resulting in an increase in the aqueous solubility of the surfactant and thus the CMC increases [7]. Also, these diols decrease the dielectric constant of aqueous phase which would favour the mutual repulsion of the ionic heads in the micelle, thus opposing micellization and thereby increasing the CMC. The decreased dielectric constant in the water-diol mixture pushes away the bromide counterion from the trimethylammonium head group and thus leads to an increase in the $\alpha$ value. Water structure breakers like ED and BD have a significant impact on the structure of the water molecules that surround the hydrophobic chains of the surfactant [49]. This decreases the hydrophobic interaction and destabilizes the micelles. It is observed that for ED and BD, these effects are acting cooperatively to oppose micelle formation, and thus the CMC is increased with increasing diol concentration in the mixed solvent.

For ED and BD, the hydrogen bonding ability (with water) of their terminal hydroxyl groups will anchor these molecules towards the outermost part of the palisade layer [34]. Further, when compared to HD and OD, their short methylene chain is not sufficient to have favorable interactions with the hydrophobic core of the TTAB micelle. Thus, the hydrogen bonding ability (water structure breaking ability) and short methylene chain of these diols does not favour the transfer of these molecules toward the micelle core. Thus, the high aqueous solubility of the short chain diols dictates their role as a cosolvents; modifying the characteristic structure of water (solvent). Also, when comparing the solvent properties of ED and BD, we can conclude that the latter is a better cosolvent despite the fact that is relatively less hydrophilic. Here, due to the four carbon methylene chain on the BG backbone, we conclude that BG has a stronger tendency to interact with the hydrophobic tails of the surfactant when compared to ED (in line with their partition constant in the literature [32]) which makes it relatively good cosolvent.
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Fig. 4.2 (a) Critical micelle concentration (b) Degree of counterion dissociation of micelle (α) of TTAB in presence of different concentration of (●) ED, (□) BD, (△) HD and (◊) OD at 303.15K.

Compared to ED and BD, both HD and OD have longer methylene chains between two the terminal –OH groups. Thus, their hydrogen bonding ability and polarity is diminished in comparison to the shorter chain diols. Also, as shown by Mullally et al.[32] for these diols in sodium dodecylsulfate (SDS) and dodecyltrimethylammonium bromide (DTAB), the thermodynamic tendency for the diols to partition between pseudomicellar phase and bulk phase increases as a function of methylene chain length. Hence, as was demonstrated previously, we would expect that the addition of longer chain diols (HD and OD) favours micellization and decreases the CMC. Mullally et al. and Fukui et al.[32,50] have indicated that the
most likely locus of solubilization for the α,ω-alkanediols (HD and OD) would be in the micelle palisade layer region. These diols would adopt a wicket-like configuration much like that adopted by bolaform surfactants [51-53]. Thus, from the fact that HD and OD have an increased partitioning into the micelles, we may expect more normal mixed micellar behaviour i.e., increasing the diol concentration will decrease the electrostatic contributions to micelle formation as the –OH group will be interspersed amongst the TTAB head groups in the micelle palisade layer. As well, the longer chain of the diol makes a greater contribution to the hydrophobic interactions. Both of these contributions together can explain the observed behaviour for the longer chain methylene diols. However, it should also be noted that the partitioning/penetration of the longer chain diols in the ionic surfactant micelle (both the magnitude of the partition and where the diol is solubilised in the micelle) can make a substantial contribution to the reduction in the electrostatic interactions felt by the surfactant molecules in the micelle. Here, due to placement of hydrophilic –OH group at micelle surface, the interaction between adjacent surfactant molecules is shielded which leads to the reduction in the charge density at the micellar surface and, consequently, α increase. For the higher diols, we expect that the contribution to the hydrophobic interactions (i.e., the higher partitioning) would be the dominant contributor to the increased α value. Since partition of long chain diols increases with chain length it is clear that why OD (C₈) is dominant in decreasing CMC and increasing α as compared to HD (C₆).

The trends in the CMC values of the surfactant in the presence α,ω-alkanediols can be qualitatively linked with their octanol-water partition coefficient (log $P_{o/w}$) values, which provides degree of hydrophobicity of alcohol. The diol with higher log $P_{o/w}$ contains large nonpolar regions in molecule and will have a higher tendency to partition into the micelle, specifically towards the nonpolar interior of micelle. Since in all cases the -OH groups remain at the micelle surface, the length of methylene chain plays a decisive role in the interactions these molecules have with the surfactant micelles. As listed in Table 4.1 in case of ED low value of log $P_{o/w}$ (-1.93) suggests that ED remains in the aqueous bulk phase. The short methylene chain (C₂) and the ability of two -OH group to form H-bond with water do not allow ED molecules to interact strongly with the surfactant micelle. BD has higher log $P_{o/w}$ (= -0.83) than ED;
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The short hydrophobic chain of the BD molecules means that it largely affects micelle formation in the same fashion as ED. It is apparent that only a small number BD molecules will interact with the micelle head group region; the vast majority of the BD molecules will remain mixed in the bulk of the solution, (attributed from increase CMC) for similar reasons as in case of ED. The comparison of log $P_{o/w}$ for ED and BD suggests that magnitude of increase in CMC should be higher in presence of ED but as shown in Fig. 4. 2a, the results are quite opposite. As discussed earlier, BD due to its C4 chain has a higher affinity for the for surfactant’s hydrophobic tail and hence opposes micellization more as compared to ED. The log $P_{o/w}$ HD (=-0.11) and OD (> HD) indicate that these two diols due to their higher hydrophobicity (six and eight carbon long methylene chain, respectively) get incorporated into the surfactant micelle and form true mixed micelles. Further, OD, being the most hydrophobic of all four diols studied, would be substantially dispersed in the micelle interior (hydrophobic) and exhibit a prominent decrease in the CMC of the mixed micelles with increasing diol concentration.

4.4.2 $^{13}$C NMR chemical shift changes of TTAB molecule from water to the water/diol mixtures

The $^{13}$C chemical shift changes upon micellization can give information about conformational changes that surfactant molecules undergo when forming micelles. Generally, we interpret a high-frequency shift with an increase in the number of trans conformers, while a low-frequency shift means an increasing probability of gauche form [54-58]. Weerd et al. [59] have stated that the chemical shift changes upon micelle formation can be discussed in terms of the difference in the van der Waals interactions between the surfactant chains in the micelle versus the interaction of the surfactant chains in the bulk of the solution. It has also been discussed that contributions to the $^{13}$C chemical shift changes ($\Delta \delta$) upon micelle formation may be due to head group interactions and hydration changes [60]. However, the conformational arguments for these chemical shift changes are supported by independent techniques [61-63]. For the TTAB/diol system, we define the chemical shift changes as follows.

$$\Delta \delta = \delta(100 \text{ mM TTAB in } 2.0 \text{wt } \% \text{ diol}) - \delta(100 \text{ mM TTAB in D}_2\text{O})$$

(2)
Here, $\delta$(100mM TTAB in 2.0wt% diol) is the $^{13}$C chemical shift of TTAB in wt% diol/D$_2$O mixture and $\delta$(100mM TTAB) is the chemical shift of TTAB in the absence of diol (i.e., D$_2$O only). The $^{13}$C chemical shift changes upon micelle formation for three carbons of TTAB, the N-methyl carbons, the methylene carbon adjacent to the head group, and the $\omega$-carbon are plotted in Fig. 4.3. We note from Fig. 4.2 that a relatively smooth transition seems to occur from ED through to OD, in that OD exhibits a larger interaction with the carbons in the interior of the TTAB micelles, in agreement with higher partitioning of these diols in the micelle. In all cases, we observe positive $^{13}$C chemical shift changes for the $\alpha$-methylene (-NCH$_2$) carbon, in agreement with trans type conformational changes taking place in the head group region of the mixed micelles. We note that as the chain length of the diol increases, the amount of re-ordering in the micellar interior is increased, in agreement with increased partitioning as the diol chain length (n) increases. For the TTAB/OD and the TTAB/HD systems, the magnitude of $\Delta\delta$ for the TTAB $\omega$-methyl carbons is larger than it is for the smaller diols, again an indication of penetration of these diols in the micellar interior. This indicates that in order to accommodate the methylene groups of the longer diols, there is a slightly larger tendency for the $\alpha$-CH$_2$ of the surfactant to adopt a gauche conformation (negative chemical shift changes). Further, larger magnitudes of $^{13}$C shifts in the presence of OD indicate the diol molecule adopts a wicket-like conformation as the eight carbon chain will be more readily able to penetrate the micelle palisade layer and interact with the carbons in the TTAB interior.

In terms of the micellar thermodynamic properties, it is fairly clear from the $^{13}$C chemical shift changes for the TTAB carbons that the effects of the added diols are indeed localized in the head group regions of the micelles. For the smaller chain length diols, these effects are primarily due to the disruption of the solvent structure by the diol, and the subsequent shift in the hydrophobic effects in the direction of micelle destabilization. For the longer chain diols, this is consistent with our explanation of the larger diol altering the thermodynamics of the system due to the more negative Gibbs transfer energy, and the substantial lessening of electrostatic effects as more hydroxyl groups get interspersed among TTAB head groups at the micelle surface. The wicket-like conformation adopted by the longer diols is very
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effective in screening the electrostatic repulsions between neighboring head groups. This allows for enhanced interactions between the alkyl chains of the surfactants, which leads to increased hydrophobic interactions and a reduction in the CMC values.

**Fig. 4. 3** Chemical shift change ($\Delta \delta$) values of $^{13}$C chemical shifts of selected carbons for 100mM TTAB/2 wt % diols solutions as a function of diol chain length (n). -NCH$_2$ (○), -NCH$_3$ (□) and -CH$_3$ (△) at 303.15 K.

**4.4.3 Effect of diol on micelle size and aggregation number**

The SANS distribution of the micellar solution of ionic surfactant generally shows a correlation peak [52] which corresponds to a peak in the inter particle structure factor, $S(Q)$ and indicates the presence of repulsive interaction between micelles. $S(Q)$ specifies the correlation between the centers of the micelle. Since $S(Q)$ depends on both the shape and the orientation of the particles, its calculation is quite complicated for any other shape than spherical. In order to simplify the calculations, prolate ellipsoidal micelles are assumed to be equivalent to spherical. We have calculated $S(Q)$ as derived by Hayter and Penfold [64] by using the Ornstein–Zernike equation and the mean spherical approximation. The micelle is assumed to be a rigid...
equivalent sphere of diameter, \( \sigma = 2(ab^2)^{1/3} \) interacting through a screened Coulombic potential.

SANS experiment was performed to investigate effect of ED, BD, HD and OD on the size/shape of TTAB micelles in 100mM solution at 30°C. The semi major axis (a), semi minor axis (b) and fractional charge (\( \beta \)) were estimated and using the relation \( N_{agg} = \frac{4\pi ab^2}{3v} \), (where \( v \) is the volume of the surfactant monomer) \( N_{agg} \) was calculated. Throughout the data analysis, corrections were made for instrumental smearing [46]. The parameters in the analysis were optimized by means of a nonlinear least-square fitting program and the errors of the parameters were calculated using standard methods [46]. The micellar parameters obtained from the fit are shown in Table 2. The micelle size for 100mM TTAB in D₂O are in agreement with that reported previously [65].

Fig. 4.4 clearly demonstrates that normalized neutron scattering cross-section \((d\Sigma/d\Omega)\) or peak height, decreases in the presence of 10% ED, BD, HD and 5% OD that suggests decrease in micelle size. However, close observation of Fig. 4.4 and Table 4.2 manifests that order of this decrease does not follow the trend with the length of methylene chain in diols. Considerations of peak height, \( N_{agg} \) and axis (semi minor and major) for TTAB micelle in presence of 5% OD clearly suggest that micelle size increases but aggregation number decrease in presence of 5% OD as compare to that in 10% HD. These results are quite contrasting. One of the possible explanations for this behavior is formation of loose or less compact micelle. The shift in the correlation peak (\( Q_m \)) towards the high Q region indicates decrease in intermicellar distance (\( Q_m = \frac{2\pi}{d} \), where \( Q_m \) is the value of Q at the peak position). The order of this shift was ED < BD < HD~OD.

In the presence ED and BD, the solution-hydrocarbon interfacial tension decreases, and hence the transfer of the surfactant tail from bulk phase to micellar phase is less favorable. Hence, we observe that the \( N_{agg} \) decreases since a smaller number of surfactant monomers transfers from the bulk to the micellar phase [11,12]. Although the lower diol-hydrocarbon interfacial tension would have an effect on the CMC of surfactant (i.e., we would expect the CMC to decrease), but due to the decrease in \( N_{agg} \) and increase area per molecule of surfactant cause CMC to increase.
The decrease in $\beta$ and increase in $N_{agg}$ supports the growth of micelle of cationic surfactant [66]. But, it seems from Table 2 in presence of 10% HD and 5% OD when compared to TTAB in D$_2$O, $\beta$ increases and $N_{agg}$ decreases which is attributed to formation of smaller micelle in presence of these diol. It may be possible that at higher HD and OD concentrations (10% and 5% respectively), the solubility of the nonpolar tail of TTAB is increased (due to interaction with long methylene hydrophobic chain of HD and OD). This helps to overcome the hydrophobic interactions between the nonpolar tails of TTAB molecules and shifts the monomer-micelle equilibrium towards monomers and hence, the hydrophobic interactions between the surfactant tails are reduced which will affect the amount of surfactant assembling into micelles and the volume fraction of the micelles. This will reduce $N_{agg}$ as well as lead to a decrease in the micellar size.
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Table 4.2 Semi major axis (a), Semi minor axis (b), fractional charge (β) and Aggregation number ($N_{agg}$) for 100 mM TTAB in presence of different α,ω-alkanediols at 30°C

<table>
<thead>
<tr>
<th>[diol] %</th>
<th>a Å</th>
<th>b Å</th>
<th>β</th>
<th>$N_{agg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$O</td>
<td>38.1±1.0</td>
<td>18.3±0.5</td>
<td>0.20±0.02</td>
<td>106±5</td>
</tr>
<tr>
<td>10% ED</td>
<td>35.9±1.2</td>
<td>17.6±0.5</td>
<td>0.20±0.02</td>
<td>92±5</td>
</tr>
<tr>
<td>10% BD</td>
<td>34.8±1.2</td>
<td>16.6±0.5</td>
<td>0.21±0.02</td>
<td>80±4</td>
</tr>
<tr>
<td>10% HD</td>
<td>28.4±2.0</td>
<td>13.9±0.8</td>
<td>0.29±0.05</td>
<td>38±3</td>
</tr>
<tr>
<td>5% OD</td>
<td>29.1±2.0</td>
<td>14.2±0.8</td>
<td>0.33±0.05</td>
<td>33±2</td>
</tr>
</tbody>
</table>

Values of β attribute the head group polarity [67]; lower β reflects less electrostatic repulsion between charged head groups. The data on fraction charge, β (Table 2) for TTAB micelles in D$_2$O and in presence of diol reveal that with increase in diol chain, electrostatic repulsion between charged head group increase which results micelles with less aggregation number. This explanation also supports lower $N_{agg}$ and micellar size in case of short chain diol and in presence of higher concentration of HD and OD.

4.5 References

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Work described in this chapter has been accepted in J. Surfact Deterg.