

## Small-angle neutron scattering study of the effect of *n*-alkanols on interacting micelles

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**Abstract.** Small-angle neutron scattering cross-section distributions of sodium dodecyl sulphate (SDS) and dodecyl trimethyl ammonium bromide (DTAB), each 0.3 M in D<sub>2</sub>O were obtained in the absence and presence of 0.1 M 1-pentanol, 1-hexanol, and 1-octanol at 25°C. The Hayter–Penfold type analysis was adopted. An ellipsoidal model with semiminor axis ( $a = 16.5 \text{ \AA}$ ) and semimajor axes ( $b = 40.7 \text{ \AA}$  and  $29.8 \text{ \AA}$ ) for pure SDS and DTAB micelles has produced best fits. On increasing alkanol chain lengths an increase in  $b$  values was found. Micellar parameters like effective radius ( $R$ ), ( $a, b$ ), fraction of counterions per micelle, and intermicellar distances were obtained. Surfactant aggregation number, additive aggregation number intermicellar interaction potentials and values of Debye screening length were obtained for SDS and DTAB in the presence of alkanols. Implications of partitioning effect, surfactant ionicity and intermicellar potentials on the microstructures are rationalised.

**Keywords.** Small-angle neutron scattering of micellar solution; *n*-alkanol effect; interacting micelles.

### 1. Introduction

Sizes and shapes of ionic micelles are sensitively modified in the presence of electrolyte and non-electrolyte additives<sup>1–3</sup>. Numerous reports involving various techniques for the determination of micellar characteristics in presence of additives like NaCl, KBr, 1-alkanols etc. exist in the literature<sup>4,5</sup>. Infact, the intermicellar potentials (or the so-called intercollidal interactions) viewed from the Derjaguin Landau Verwey Overbeek theory (DLVO) represents the “near-surface” intermicellar interactions like the van der Waals hydration and the short-range part of coulomb forces, and all modified by the presence of additives<sup>6,7</sup>. The availability of small-angle neutron scattering (SANS) technique and the pioneering works on the evaluations of microstructural and interaction potentials of micelles by Chen<sup>8,9</sup> and Hayter–Penfold<sup>10,11</sup> theoretical studies of ionic micelle-additive systems have become straightforward. The very strong interfacial tensiometric and viscometric effects on aqueous solutions of ionic micelles in presence of 1-alkanols indicate the query on whether inter- or intramicellar interactions dominate in micellar

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systems containing additives. Comparatively simpler and widely studied materials, namely, sodium dodecyl sulphate (SDS, anionic) and dodecyl trimethyl ammonium bromide (DTAB, cationic), each consisting of equal hydrophobic chain lengths (dodecyl part), have been chosen.

SANS data are collected particularly for 0.3 M SDS and DTAB separately in D<sub>2</sub>O solutions. Since this concentration value exceeds the sphere-to-rod transition point, non-spherical or rod-like micelles will exist in solution<sup>12</sup>. The additives 1-pentanol, 1-hexanol and 1-octanol, each 0.1 M are added separately and SANS of the micelle-alkanol-D<sub>2</sub>O solutions have been obtained. Various physicochemical parameters of the micelles, such as the effective micelle radius [ $R = (a^2b)^{1/3}$ ], semiminor and semimajor axes ( $a$ ,  $b$ ), number density of micelles ( $N_m$ ), surfactant and additive aggregation numbers ( $N_s$ ,  $N_a$ ), fraction charge per micelle ( $\alpha$ ), micelle concentration [mic], additive partition coefficient ( $K_a$ ), Debye screening length ( $\kappa$ ), and the mean intermicellar interaction potentials ( $U(r)/U(T)$ ) are derived from SANS for the SDS and DTAB systems in the presence and the absence of 1-alkanols at 25°C. Implications of these results are discussed.

## 2. Experimental

SDS and DTAB from Sigma were used as such. Fluka was the source of 1-pentanol, 1-hexanol and 1-octanol and were dried with fused calcium chloride before use. Sigma D<sub>2</sub>O was used *in lieu* of H<sub>2</sub>O. Quantitatively weighed amounts of the surfactants, alkanols and D<sub>2</sub>O were mixed to prepare the isotropic solutions and were thermostated at 25°C.

### 2.1 SANS measurements

The SANS measurements were carried out on a spectrometer equipped with a position-sensitive X-Y detector, installed at the CIRUS reactor, Trombay, Bhabha Atomic Research Institute, India. The experimental procedure adopted was according to the User's manual<sup>13</sup>. The liquid samples were taken in a quartz cell of path length 1 cm. The BeO filtered neutron beam of mean wavelength  $\lambda = 5.2 \text{ \AA}$  was used. The wave vector transfer  $Q = \text{range}$  accessible from the instrument was 0.02 to 0.08  $\text{\AA}^{-1}$  where ( $Q = 4\pi\sin\theta/\lambda$ ) and  $2\theta$  being the scattering angle. The data were collected for the fast neutron background upto  $Q = 0.18 \text{ \AA}^{-1}$  and the transmission factor was normalised to the absolute cross-section units. Based on the conclusions of Berr<sup>14</sup> the micellar properties in D<sub>2</sub>O were assumed to be unaltered from that of H<sub>2</sub>O solutions, within the limits of experimental error.

The measured SANS distribution was analysed using the method of Hayter-Penfold for an assembly of monodisperse uniform ellipsoidal micelles. The coherent differential cross-section can be expressed as<sup>15</sup>,

$$d\Sigma/d\Omega = N_m V_m^2 (\rho_m - \rho_s)^2 [\langle F^2(Q) \rangle + \langle F(Q) \rangle^2 \{S(Q) - 1\}], \quad (1)$$

where  $N_m$  is the number density of the micelles,  $\rho_m$  and  $\rho_s$  are the scattering length densities of micelle and solvent,  $V_m$  is the micelle volume,  $F(Q)$  is the form factor defined as  $(1/V_m) \int V_m e^{iQ \cdot r}$ , that describes the angular distribution of scattering to the morphology of the micelle with respect to  $Q$ .

The structure factor  $S(Q)$  represents interparticle interferences and has been calculated approximating the ellipsoid to an equivalent sphere of radius  $R = (a^2b)^{1/3}$ . The

concentration of micelles [mic] mol dm<sup>-3</sup> is known from  $N_s$ ,  $C_s$  and cmc as equal to  $(C_s - \text{cmc})/N_s$ . The number density of micelle in solution  $N_m = N_{av}$  [mic]/1000 (ml<sup>-1</sup>).

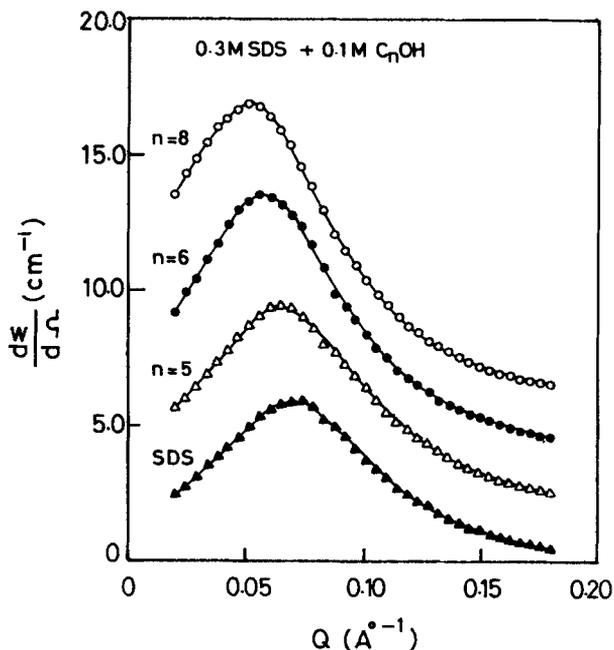
Equation (1) representing Hayter–Penfold theory when best fitted, produces  $N_m$  values of the micelles which are strongly interacting in aqueous medium. The hydrocarbon core of SDS and DTAB micelles in D<sub>2</sub>O can be modelled for prolate ellipsoids with semiminor axis  $a = c$  fixed at 16.5 Å (for fully extended dodecyl chain) and the variable semimajor axis ( $b$ ) computed by assuming a close-packed micellar core ( $V_c$ ),  $V_c = 4\pi a^2 b/3$ . The shell volume ( $S_v$ ) enveloping the micellar core is obtained from  $4\pi(a^2 b_h - a^2 b)/3$ , where  $a_h$  (Å) =  $a + 5.56 + 2.6 + \Delta$  and  $b_h$  (Å) =  $b + 5.56 + 2.6 + \Delta$ . The head group diameter is 5.56 Å, the diameter of counter ion (Na<sup>+</sup>)<sup>16,17</sup> is 2.6 Å and  $\Delta$ (Å) is the diffuse layer thickness for SDS micelles. In the case of DTAB,  $a_h = a + 3.9 + 4.1 + \Delta$  and  $b_h = b + 3.9 + 4.1 + \Delta$  where 3.9 (Å) and 4.1 (Å) are diameters of headgroup and counterion (Br<sup>-</sup>) respectively. The effective number,  $N_w$  of water molecules in the hydration region of the shell is computed as  $[S_v - N_s V_p - (1 - \alpha)N_s V_i]V_w$ , where  $V_p$  is the head group volume,  $V_i$  is the counterion volume,  $N_s(1 - \alpha)$  is the number of counterions bound per micelle, and  $V_w$  the volume of the water molecule. Debye screening length ( $\kappa$ ), which is equal to  $\Delta$ , is given as  $\kappa = (8\pi N_{av} e^2 I / 1000 \epsilon K_B T)^{1/2}$ ,  $I = \text{cmc} + \alpha c/2$ ,  $c$  = molar concentration of SDS or DTAB monomers in the micellar state,  $e$  is the electronic charge,  $\epsilon$  is the dielectric constant of D<sub>2</sub>O = 78.25. The contact potential is given by,

$$U(T) = 1.6711 \times 10^5 Z^2 / (1 + k/2)^2 T \sigma, \quad (2)$$

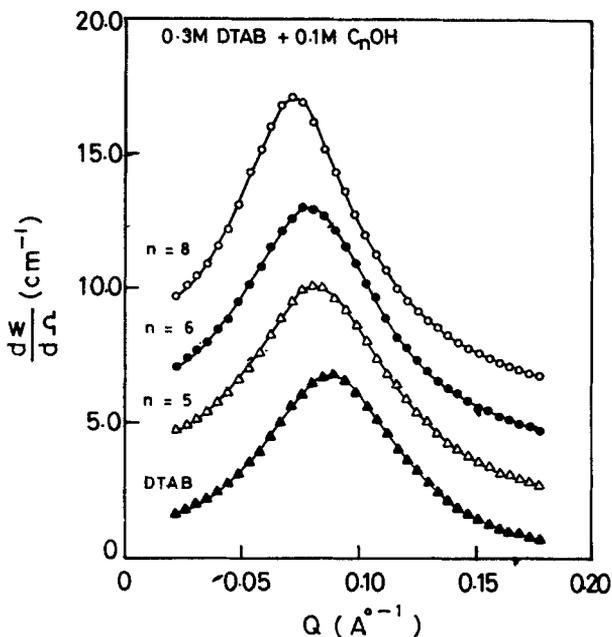
where  $Z = N_s \alpha$  i.e. the number of charges on a micellar surface,  $k$  is the screening parameter =  $\kappa \sigma$ , and  $\sigma$  is the effective hard core diameter =  $2R$ , where  $R = (a^2 b)^{1/3}$  respectively. The  $\sigma$  value is best computed by the method outlined by Ishihara considering the excluded volume of a rigid prolate ellipsoid<sup>18</sup> which leads to  $\sigma^3 = 2(\delta + 1) a_h^2 b_h$ , where  $\delta = \frac{3}{4}[1 + \sin^{-1}(e)/e(1 - e^2)^{1/2}][1 + 1 - e^2/2e(\ln 1 + e)/(1 - e)]$  and  $e^2 = (b_h^2 - a_h^2)/b_h^2$ . The area per head group ( $A_{HG}$ ) located at the interface between the polar heads and the core is considered from the area between middle of -CH<sub>2</sub>-N and -CH<sub>2</sub>-O in case of DTAB and SDS. In case of prolate ellipsoid, this is known from the surface area  $S = 4\pi R^2/N_s$ , where  $R$  = effective radius of the micelle. The screened coulomb potential of ionic micelles  $U(r)$  may be obtained by considering  $\sigma$ , and contact potential  $U(T)$  as  $U(r) = U(T) \exp[-\kappa(r - \sigma)]/r$ , where  $r$  denotes the intermicellar distance, which is considered as equivalent to  $d$ , since  $d \gg R$ .

### 3. Results and discussion

The measured and fitted SANS distribution for SDS and DTAB micelles, each in 0.3 M D<sub>2</sub>O solutions, obtained in the absence and presence of additives are shown in figures 1 and 2. Best fit results are seen for ellipsoidal model of the SDS and DTAB micelles. The SANS distributions develop correlation peaks around 0.05–0.07 Å<sup>-1</sup> with SDS micelle peak shifting to shorter  $Q$  values indicating micellar group process in SDS to be in greater extent than in the DTAB system. The average intermicellar distances ( $d = 2\pi/Q_{\max}$ ) are known from the peak positions ( $Q_{\max}$ ). The micellar parameters obtained from SANS data applying the Hayter–Penfold type analysis and other derived parameters are presented in table 1 for SDS, and in table 2 for DTAB. The ellipsoidal model of pure SDS and DTAB micelles with semiminor axis ( $a = 16.5$  Å) and semimajor axis ( $b = 40.7$  Å and 29.8 Å) respectively, seem to produce best fits on SANS distributions. The effective radii  $R$  values



**Figure 1.** SANS cross-section distribution curves of 0.3 M SDS  $D_2O$  solution in absence and in presence of 0.1 M each of alkanol  $C_n$  OH: 1-pentanol ( $n = 5$ ); 1-hexanol ( $n = 6$ ); 1-octanol ( $n = 8$ ).  $T = 25^\circ C$ .



**Figure 2.** SANS cross-section distribution curves of 0.3 M DTAD  $D_2O$  solution in absence and in presence of 0.1 M each of alkanol  $C_n$  OH: 1-pentanol ( $n = 5$ ); 1-hexanol ( $n = 6$ ); 1-octanol ( $n = 8$ ).  $T = 25^\circ C$ .

**Table 1.** Micellar parameters from SANS data adopting Hayter–Penfold type analysis for 0.3 M SDS in D<sub>2</sub>O and containing 0.1 M of 1-alkanols. *T* = 25°C.

Parameters	SDS			
	–	1-pentanol	1-hexanol	1-octanol
<i>R</i> (Å)	22.3	24.1	27.2	29.0
<i>a</i> (Å)	16.5	16.5	16.5	16.5
<i>b</i> (Å)	40.7	51.2	74.4	89.8
<i>N<sub>s</sub></i>	113	125	178	206
<i>N<sub>a</sub></i>	–	42	60	70
[mic] mol dm <sup>-3</sup>	2.5	2.3	1.6	1.4
<i>α</i>	0.076	0.066	0.058	0.045
<i>N<sub>s</sub>/N<sub>a</sub></i>	–	2.98	2.97	2.94
<i>b/a</i>	2.5	3.0	4.5	5.4
<i>d</i> (Å)	89.8	96.7	114.3	123.7
<i>U(r)/U(T)</i> (× 10 <sup>-5</sup> ) ( <i>K<sub>B</sub>T</i> ) units	2.040	0.558	0.012	0.002
<i>N<sub>m</sub></i> (× 10 <sup>18</sup> dm <sup>-3</sup> )	1.59	1.44	1.01	0.88
<i>A<sub>p</sub></i> (Å <sup>2</sup> )	17	8	8	8
<i>A<sub>i</sub></i> (Å <sup>2</sup> )	1	0	0	0

**Table 2.** Micellar parameters from SANS data adopting Hayter–Penfold type analysis for 0.3 M DTAB in D<sub>2</sub>O and containing 0.1 M of 1-alkanols. *T* = 25°C.

Parameters	SDS			
	–	1-pentanol	1-hexanol	1-octanol
<i>R</i> (Å)	20.1	21.5	22.5	25.0
<i>a</i> (Å)	16.5	16.5	16.5	16.5
<i>b</i> (Å)	29.8	36.4	41.8	57.6
<i>N<sub>s</sub></i>	75	81	92	122
<i>N<sub>a</sub></i>	–	28	32	42
[mic] mol dm <sup>-3</sup>	3.8	3.6	3.2	2.5
<i>α</i>	0.182	0.145	0.140	0.138
<i>N<sub>s</sub>/N<sub>a</sub></i>	–	2.89	2.87	2.90
<i>b/a</i>	1.8	2.2	2.5	3.5
<i>d</i> (Å)	69.77	73.88	78.50	83.73
<i>U(r)/U(T)</i> (× 10 <sup>-5</sup> ) ( <i>K<sub>B</sub>T</i> ) units	3.33	2.18	0.91	0.88
<i>N<sub>m</sub></i> (× 10 <sup>18</sup> dm <sup>-3</sup> )	2.4	2.2	2.0	1.5
<i>A<sub>p</sub></i> (Å <sup>2</sup> )	48	8	8	8
<i>A<sub>i</sub></i> (Å <sup>2</sup> )	2.3	0	0	0

of SDS and DTAB micelles seem to be in good agreement with literature reports<sup>19,20</sup>. The SANS distributions exhibit correlation peaks around 0.05–0.07 Å<sup>-1</sup> (*Q*<sub>max</sub>) from which the mean intermicellar distance *d* is known. The value of *d* is calculated only when *R* << *d*.

In the case of pure surfactant solutions  $X_n + X_1^n \exp(-\Delta\mu^0 n/K_B T)$ , where *X<sub>n</sub>* is the mole fraction of the micelle formed by association of *n*-monomers, *X<sub>1</sub>* is the monomer mole fraction in solution, *T* is the temperature in Kelvin, *K<sub>B</sub>* is the Boltzmann constant and  $\Delta\mu^0 n$  is the change in the standard chemical potential of a micelle and that of a surfactant monomer. The standard state refers to infinite dilute solutions. Considering earlier works<sup>21,22</sup>, the free energy change of micellization results as the summation of the

following: (1)  $N_s \Delta\mu^0_{HC/w}$  which represents the standard free energy change when a molecule is transferred from water to the liquid-like hydrocarbon core phase, (2)  $N_s \Delta\mu^0_C$ , represents the micellization involving constraints on hydrocarbon tail orientations wherein the polar head groups occupy micellar core-water interface, (3)  $N_s \sigma(A-A_0)$ , represents the free energy of formation of hydrocarbon core and water.  $\sigma$  is the interfacial tension between hydrocarbon and water which is 50 dynes/cm for dodecane/water system,  $A$  and  $A_0$  are the surface areas per micellar amphiphile shielded and unshielded from contact with water by the polar head group, where  $A = 4\pi R^2/N_s$ , (4)  $-N_s K_B T \ln(1 - A_p/A)$  represents the surface exclusion effects due to the finite size of the head groups, which restricts the surface mobility of the head groups. This effect decreases the overall entropy of the process.  $A_p$  represents the effective cross-sectional area of the head group, (5)  $n^2_{ion} e^2 \beta [(1 + (A_1 + \kappa r))/2\epsilon r]$ , represents the coulombic repulsions of the ionic head groups at the micellar surface,  $e$  is the electronics charge,  $\epsilon$  is the dielectric constant of D<sub>2</sub>O equal to 78.25,  $r$  is the radius of the micellar surface which equals the radius of micellar core and the distance of separation between the core and the surface where the charges are located,  $\kappa$  is the reciprocal Debye length given by  $\kappa^2 = 8\pi e^2 N_{av} I / \epsilon K_B T 1000$ , where  $N_{av}$  is the avagadro number,  $I$  is the ionic strength,  $\epsilon$  the dielectric constant of D<sub>2</sub>O.  $A_1$  is the radius of counterion and  $\beta$  is the empirical correction factor which equals the 0.5 suggested by Tanford<sup>23</sup>. Based on empirical investigations of solubility of hydrocarbon in water at 25°C, first term equals  $-K_B T [2.05 + 1.49n_c]$  where  $n_c$  is the number of carbon atoms in the chain length, second term equals  $K_B T (-0.5 + 0.25n_c)$ , if  $A_p \gg 21 \text{ \AA}^2$  (the hydrocarbon chain area) then  $A_0$  equals to  $21 \text{ \AA}^2$ . If  $A_p < 21 \text{ \AA}^2$  then  $A_0$  equals to  $A_p$ <sup>24</sup>.

The overall free energy of micellization after summing up the terms (1)–(5) lies around  $-8.91 \text{ kJ/mole}$  and  $-7.3 \text{ kJ/mole}$  for SDS and DTAB systems. Despite the semiminor axes being equal, the differences in  $b$ ,  $\alpha$  and  $N_s$  between SDS and DTAB may be considered as follows. The  $b$  length proportionates to the micellar growths and to the extent of screened coulomb forces. As the size of the macroion (charged micelle) increases, the thickness of the shell in proportion to the macroion radius increases. The counterion condense onto the surface, thus effectively lowering the charge of the macroion when the radius becomes large compared to the Debye length<sup>25</sup>. Increase in  $b$  results in  $N_s$ . The charge condensation phenomenon occurs to an extent of  $\alpha$  per micelle for the factor  $(\alpha N_s / 4\pi R^2)$  reaching a minimum. The trimethyl ammonium head group being more hydrophobic, the coulomb interaction is weaker than the sulphate head groups in SDS.

Thus  $\alpha$  of DTAB is  $>\alpha$  of SDS and  $N_s$  of DTAB  $< N_s$  of SDS. Independent assessment on computation of potentials on counterions at the micellar surface [ $U(T)$ ], the following may be said, when  $U(T) < K_B T$  the counterion binds to the micellar surface, when  $U(T) > K_B T$ , it is freely moving and when  $U(T) = K_B T$ , charge condensation phenomenon occurs.  $U(T) = U(r) = U_0 2R \exp[-\kappa(d-2R)]/d$ , where  $2R$  is the equivalent particle diameter,  $U_0$  is the contact potential which is a constant at a particular temperature. Under such conditions charge condensation on SDS micelles occurs to a larger extent than DTAB.

### 3.1 Presence of additives

For mixed micelles of surfactant-additive containing  $N_s$  and  $N_a$  molecules of surfactant and additive per micelle  $X_{N_s, N_a} = X_s^{N_s} X_a^{N_a} \exp[(\mu^0_{N_s, N_a} - N_s \mu^0_s - N_a \mu^0_a) / K_B T]$  where  $X_{N_s, N_a}$  is the mole fraction of the mixed micelle,  $\mu^0_{N_s, N_a}$ ,  $\mu^0_s$  and  $\mu^0_a$  are the standard chemical

potentials of the micelle and single molecules of surfactant and additive respectively. In analogy to the pure surfactant systems it is equal to:

$$\begin{aligned} \mu_{N_s, N_a}^0 - n_s \mu_s^0 - N_a \mu_a^0 / K_B T = & N_s [\Delta \mu_{HC, w}^0 / K_B T + \Delta \mu_C^0 / K_B T]_s \\ & + N_a [\Delta \mu_{HC, w}^0 / K_B T + \Delta \mu_C^0 / K_B T]_a + (N_s + N_a) 2R [A - N_s A_{os} + N_a A_{oa}] / \\ & (N_s + N_a) \ln [1 - (N_s A_{ps} + N_a A_{pa}) / (N_s + N_a) A] + (\alpha N_s)^2_{\text{ion}} e^2 \beta / 2 \epsilon \kappa T r \\ & (1 + \kappa A_1 + \kappa r)] + (N_s \ln (N_s V_{os} / N_s V_{oa} + N_a V_{oa}) \\ & + N_a \ln ((N_a V_{oa}) / (N_s V_{os} + N_a V_{oa})), \end{aligned} \quad (3)$$

where  $V_{os}$  and  $V_{oa}$  are the molecular volumes of surfactant and the additive. The calculated values in presence of alkanols are tabulated in tables 1 and 2. The  $K_a$  values tending to infinity infer complete solubilization of the alkanol molecule into the micelles. The increase in the micelle size in presence of alkanols indicates the alkanol molecules to be located at the surface layer of the micelles such that the average distance between the ionic head groups increases. The increased entropy due to the mixing of the hydrocarbon tails of the surfactant and alkanol molecules in the micellar core directs the formation of mixed surfactant-additive micelles. Also, with increase in  $b$  values, as the 1-alkanol chain length increases from pentanol to octanol, charge condensation increases in proportion showing a steady  $\alpha$  decrease. This is true for both SDS and DTAB systems. The same are reflected from the  $U(T)$  values. In short, additives like 1-alkanols increase the intermicellar interaction potentials (attractive) screening the coulomb forces. Presence of electrolyte type additives (NaCl) brings in a similar effect. Considering only the SDS micelle, the behaviour of 1-alkanols similar to electrolytes is brought by the hydrogen bonding effect between the  $-\text{OH}$  of the alkanol and the negative sulfate group at the stern layer. This effect screens the coulomb forces and increases the intermicellar attractive potentials resulting in a size increase. The size increase is more than two-fold comparing the  $b$  values of SDS in presence of octanols. Regarding DTAB-alkanol systems, the increase in  $b$  is comparatively lower than the SDS system. The size increase has resulted in  $\alpha$  decrease. For both SDS and DTAB systems the intercalation ratio ( $N_s/N_a$ ) indicates that every alkanol molecule intercalates three surfactant molecules in the micelle. One can visualize the intercalation being directed by the oxygen atom of  $-\text{OH}$  of the alkanol and the partial attractive forces from the positive head groups of the surfactants at the stern layer.

#### 4. Conclusions

In the presence and absence of 1-alkanols, micelles of SDS and DTAB in 0.3 M solutions exist as ellipsoids. There is a steady growth in the micellar size upon increasing the additive chain length from pentanol to octanol. The charge per micelle decreases with additive chain lengths. When the intermicellar attraction potentials prevail, micellar size increases and in proportion to the increment, the charge condensation increases i.e. alkanols ( $C_5-C_8$ ) when used in 0.1 M concentration, an electrolyte type behaviour which screens the coulombic interactions bringing in a size increase is noticed. Therefore the surface potential can be tuned by controlling the relative amounts of 1-alkanols or by choosing the appropriate chain length. SANS data has helped us in deriving various micellar parameters that dictate the sizes and growth of micelles. The derived parameters, ofcourse need refinement from polydispersity from the view point of sizes.

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