Counterions in the growth of ionic micelles in aqueous electrolyte solutions: A small-angle neutron scattering study

V. K. Aswal[1] and P. S. Goyal[1,2]

[1]*Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India*
[2]*Inter-University Consortium for the Department of Atomic Energy Facilities, Mumbai Centre, Bhabha Atomic Research Centre, Mumbai 400 085, India*

Ionic micelles in aqueous solution usually grow in size on addition of the electrolytes. This paper deals with the understanding of the reasons for different growths of micelles for different electrolytes. In this connection, small-angle neutron scattering (SANS) experiments on aqueous micellar solutions of ionic surfactants cetyltrimethylammonium chloride (CTAC) and sodium dodecyl sulphate (SDS) in presence of various alkali-metal halide electrolytes are reported. The measurements have been carried out from 0.1 M CTAC for varying concentrations of KBr($=0.0, 0.03, 0.05, 0.07$, and 0.1 M) and KCl($=0.0, 0.05, 0.1, 0.3, 0.5, 0.7$, and 1.0 M). It is found that micelles grow on addition of KBr, but their size is constant over a wide range of KCl concentration. When compared with similar data on CTAB micellar solutions, these data suggest that the differences in the micellar growths in the above systems are not connected with the common ion effect. To examine the effect of size and hydration behavior of ions of the electrolytes on the micellar growth, SANS measurements from SDS micellar solutions have been carried out in presence of alkali halide electrolytes ($AX, A = $Na, K, Cs and $X = $Cl, Br, I) for the fixed concentrations of surfactant ($= 0.3$ M) and the electrolyte ($= 0.1$ M). It is found that micellar growth strongly depends on the counterions and there is negligible effect of the coions. The growth is more when the counterion hydration is smaller.

I. INTRODUCTION

Micelles are formed by the self-aggregation of the surfactant molecules in aqueous solution. Micelles are ionic and nonionic depending on whether the head groups of the surfactant molecules ionize or not. The micelles formed at the low concentrations are spherical and their structure changes with the concentration, temperature, and in presence of the additives, such as electrolytes, alcohols, and amines [1–5]. For example, cationic micelles grow in size and become cylindrical on addition of electrolytes, such as KBr, NaSal to the micellar solutions [6–18]. In general, micellar growth is quite sensitive to the nature of the electrolyte. The reasons for different growth rates for different electrolytes are, however, not fully understood. For example, it is not clear why the micellar growth should be different when similar electrolytes (say, KCl or KBr) are added to cetyltrimethylammonium bromide (CTAB) solution. It has been seen that while the micelle size is constant over a wide range of KCl concentration, there is significant micellar growth on addition of small quantities of KBr [19]. This difference in the micellar growth rates for the above two electrolytes could be either because of the common ion effect or because of the differences in the counterion size of Cl$^-$ and Br$^-$ ions. This paper reports the results of the following small-angle neutron scattering (SANS) measurements.

(i) To see the role of common ion effect, SANS measurements have been carried out on micellar solutions of cationic surfactant cetyltrimethylammonium chloride (CTAC) with varying concentrations of KBr and KCl. The viscosity measurements have also been carried out from CTAC/KCl and CTAC/KBr micellar solutions. The preliminary results of

these studies have been reported earlier [12]. The common ion effect would suggest that micelles should grow in CTAC/KCl and not in CTAC/KBr. This is especially so as it has been already seen that micelles grow in CTAB/KBr and not in CTAB/KCl solutions [19].

(ii) To understand the effect of the varying sizes of the counterion and the coion on the structure of ionic micelles, SANS measurements have been carried out on aqueous micellar solutions of anionic surfactant sodium dodecyl sulfate (SDS) in presence of various alkali-metal halide electrolytes AX ($A = $Na, K, Cs and $X = $Cl, Br, I).

II. EXPERIMENT

CTAC was purchased from Aldrich, SDS, and the alkali-metal halide electrolytes were purchased from Sigma. The D$_2$O (99.4 atom % D) was obtained from Heavy Water Division, BARC. These chemicals were used as supplied. The micellar solutions were prepared by dissolving known amounts of surfactants and electrolytes in D$_2$O. The use of D$_2$O instead of H$_2$O for preparing micellar solutions provides a better contrast in SANS experiments. Small-angle neutron scattering measurements were carried out using SANS spectrometer at CIRUS reactor, Trombay [20]. The spectrometer makes use of BeO filtered beam and has a resolution $\Delta Q/Q$ of 15% at $Q = 0.05$ Å^{-1}. The angular distribution of the scattered neutrons was recorded using one dimensional position sensitive detector. The accessible wave vector transfer Q ($= 4\pi \sin\theta/\Lambda$, where Λ is the wavelength of the incident neutrons and 2θ is the scattering angle) range of the instrument is between 0.02 to 0.32 Å^{-1}. The mean neutron wavelength was $\Lambda = 5.2$ Å. Experiments were carried out on 0.1 M CTAC for varying concentrations of
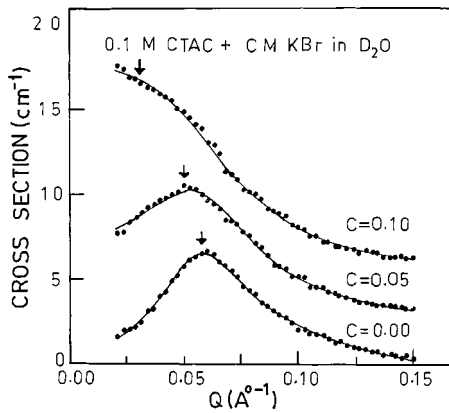
FIG. 1. SANS distributions from 0.1 M CTAC solution with varying concentration of KBr. The distributions for KBr concentrations $C=0.05$ and 0.1 M are shifted vertically by 2 and 4 units, respectively.

KBr ($=0.0, 0.03, 0.05, 0.07$, and 0.1 M) and KCl ($=0.0, 0.05, 0.1, 0.3, 0.5, 0.7$, and 1.0 M). The samples during the SANS experiments were held in quartz cell of thickness 0.5 cm. Viscosity measurements were made using Brookfield cone/plate viscometer. The viscosity experiments were carried out on 0.1 M CTAC as a function of the concentration of KCl and KBr in the concentration range of 0–2 M. The temperature of the samples were maintained at 30 ± 1 °C both for SANS and viscosity measurements.

In the case of SDS micellar solutions, the measurements were made on the fixed concentrations of the surfactant ($=0.3$ M) and the electrolyte ($=0.1$ M). The temperature of samples were maintained at 35 ± 1 °C. The samples thickness was once again 0.5 cm.

The measured SANS distributions were corrected for the background, empty cell scattering and the sample transmission. The resulting corrected intensities were normalized to absolute cross section units [20]. The absolute calibration has an estimated uncertainty of 10%. SANS data are shown in Figs. 1–3, 5, and 6. The data are plotted in the limited Q range of 0.02–0.15 Å^{-1} for Figs. 1–3 and 0.02–0.2 Å^{-1} for Figs. 5 and 6. This is because the signal to background ratio is poor for the higher Q values.
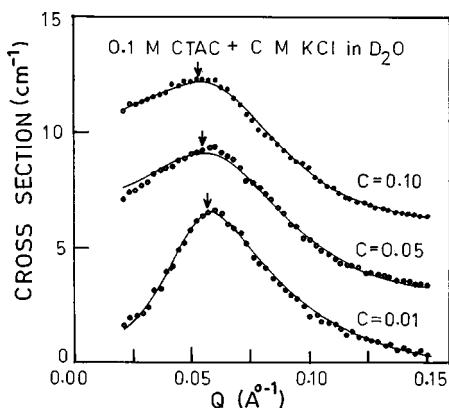

FIG. 2. SANS distributions from 0.1 M CTAC solution with varying concentration of KCl. The distributions for KCl concentrations $C=0.05$ and 0.1 M are shifted vertically by 2 and 4 units, respectively.
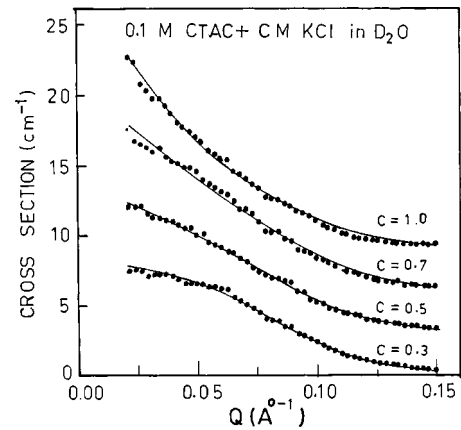

FIG. 3. SANS distributions from 0.1 M CTAC solution with varying high concentration of KCl. The distributions for KCl concentrations $C=0.5$, 0.7, and 1 M are shifted vertically by 2, 4, and 6 units, respectively.

III. SANS ANALYSIS

The coherent differential scattering cross section ($d\Sigma/d\Omega$) for a system of monodisperse interacting micelles can be expressed as [21,22]

$$\frac{d\Sigma}{d\Omega} = n(\rho_m - \rho_s)^2 V^2 [\langle F^2(Q)\rangle + \langle F(Q)\rangle^2 [S(Q) - 1]] + B,$$

(1)

where n denotes the number density of the micelles, ρ_m and ρ_s are, respectively, the scattering length densities of the micelle and the solvent, and V is the volume of the micelle. The aggregation number N of the micelle is related to the micellar volume V by the relation $V=Nv$, where v is the volume of the surfactant monomer. The volume of surfactant monomers of CTAC and SDS with the head groups as determined using Tanford's formula are 560 and 410 Å^3, respectively. The volume of the corresponding head groups $N^+(CH_3)_3$ and OSO_3^- are 102 and 60 Å^3, respectively. The scattering length densities of CTAC and SDS micelles have been estimated to be -0.38×10^{10} cm^{-2} and 0.30×10^{10} cm^{-2}, respectively. The scattering length density of D_2O is 6.38×10^{10} cm^{-2}.

$F(Q)$ is the single particle form factor and $S(Q)$ is the interparticle structure factor. B is a constant term that represents the incoherent scattering background, which is mainly due to hydrogen in the sample. The single particle form factor has been calculated by treating the micelle as prolate ellipsoidal. For such an ellipsoidal micelle

$$\langle F^2(Q)\rangle = \int_0^1 [F(Q,\mu)]^2 d\mu,$$

(2)

$$\langle F(Q)\rangle^2 = \left[\int_0^1 F(Q,\mu) d\mu\right]^2,$$

(3)

$$F(Q,\mu) = \frac{3(\sin x - x\cos x)}{x^3},$$

(4)

$$x = Q[a^2\mu^2 + b^2(1-\mu^2)]^{1/2}.$$

(5)

where a and b are, respectively, the semimajor and semiminor axis of the ellipsoidal micelle. μ is the cosine of the angle between the directions of a and the wave vector transfer Q.

$S(Q)$ specifies the correlation between the centers of different micelles and it is the Fourier transform of the radial distribution function $g(r)$ for the mass centers of the micelle. In the analysis of the data, $S(Q)$ has been calculated using mean spherical approximation (MSA) as developed by Hayter and Penfold [21,23]. This theory is applicable if there is no angular correlation between the particles. This assumption is quite reasonable for charged micelles especially when the surfactant concentration is low and the ratio of the axes is not much greater than unity. It may be mentioned that satisfactory data analysis procedures for ellipsoidal particles have not been developed. Though the approximation of treating ellipsoid as a sphere has been often used in the literature, its consequences on size parameters are not fully understood. In this approximation micelle is assumed to be a rigid equivalent sphere of diameter $\sigma = 2(ab^2)^{1/3}$ interacting through a screened Coulomb potential, which is given by

$$u(r) = u_0 \frac{\sigma}{r} \exp[-\kappa(r-\sigma)], \quad r > \sigma, \qquad (6)$$

where κ is the Debye-Huckel inverse screening length (which depends on the CMC, fractional charge on the micelle, and the concentration of the added electrolyte) and u_0 is the contact potential. The fractional charge α ($=z/N$, where z is the micellar charge) is an additional parameter in the calculation of $S(Q)$.

The above approach to calculate $S(Q)$ (Hayter and Penfold type analysis) assumes a screened Coulomb repulsion between the micelles, but neglects the attractive van der Waals interaction. This is a reasonable approximation for ionic micellar solutions since the van der Waals interaction is much weaker than the Coulomb interaction. However, the situation is different when the large amount of an electrolyte is added to the micellar solution. The increase in the ionic strength of the solution screens out the Coulomb forces thereby making it comparable to the van der Waals interaction. Thus the total interaction potential can be expressed as

$$u(r) = u_c(r) + u_{vW}(r). \qquad (7)$$

The second term $u_{vW}(r)$ is the van der Waals interaction and for spherical particles it is given by [22]

$$u_{vW}(r) = -\frac{A}{12}\left[\frac{\sigma^2}{r^2-\sigma^2} + \frac{\sigma^2}{r^2} + 2\ln\frac{r^2-\sigma^2}{r^2}\right] \qquad (8)$$

where A is the Hamaker constant. While analytical expressions are available for the calculation of $S(Q)$ in the MSA for the screened Coulomb potential, it has been calculated numerically under the Rogers and Young (RY) approximation [24] when both the types of interactions are present.

Although micelles are known to form polydisperse systems, we have assumed them as monodisperse for the simplicity of the calculation and to limit the number of unknown parameters in the analysis. The analysis of the data involves calculating $d\Sigma/d\Omega$ and comparing it with an experimental
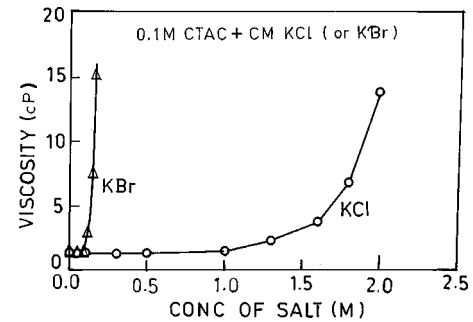

FIG. 4. The viscosity of CTAC/KBr and CTAC/KCl micellar solutions with varying concentration of salts.

data. The unknown parameters are determined by the nonlinear least squares fitting. We have analyzed the data assuming micelles to be monodisperse ellipsoids with dimensions $a \times b \times b$. The fits give $a > b$, which suggests that micelles are prolate ellipsoidal. The similar method of data analysis has been used earlier also [6–10,17,19,21,22,25–27]. The dimensions of the micelle, aggregation number, and the fractional charge have been determined from the analysis. The Hamaker constant has also been determined. The aggregation number (N), semiminor axis ($b=c$), and the fractional charge (α) are the parameters in analyzing the SANS data in terms of Eq. (1). The semimajor axis is calculated by the relation $a = 3V/4\pi b^2$.

IV. RESULTS AND DISCUSSION

A. Comparison of micellar growth in CTAC/KBr and CTAC/KCl

The SANS distribution from a pure 0.1 M CTAC micellar solution (Fig. 1) shows a well defined correlation peak at the wave vector transfer $Q \sim 0.06$ Å^{-1}, and is in good agreement with the literature [25–27]. This correlation peak is an indication of strong repulsive interaction between the positively charged CTAC micelles. The peak usually occurs at $Q_m \sim 2\pi/d$, where d is the average distance between the micelles. The peak position is related to the concentration and the aggregation number or the size of the micelle. The width of the peak gives the charge on the micelles. When the concentration of the surfactant molecules is increased, the peak shifts to the higher Q values due to decrease in the average distance between the micelles. Similarly, at constant concentration if the micelles grow with the change in the solution conditions, the peak will shift to lower Q values due to increase in the average distance between the micelle [5].

When KBr is added to the 0.1 M CTAC micellar solution, the peak in the measured distribution broadens and shifts to lower Q as shown in Fig. 1. The peak shifts to lower Q is an indication of the growth of CTAC micelles with the addition of KBr. The broadening of the peak is due to the screening of the repulsive interaction between the micelles in presence of electrolyte. The same is not the case in CTAC/KCl solutions, where the peak broadens without a significant shift in the peak position (Fig. 2). This shows that CTAC micelles do not grow with the addition of KCl. At high KCl concentrations (Fig. 3), where the Coulomb interaction has been screened out, the measured distributions do not show any peak in the Q range of the experiment. The monotonically

TABLE I. Micellar parameters for 0.1 M CTAC + C M KBr solutions.

System	Aggregation number N	Fractional charge α	Semiminor axis $b=c(\text{Å})$	Semimajor axis a (Å)	a/b
0.1 M TAC	120	0.13	21.5	34.7	1.61
0.1 M CTAC+0.05 M KBr	148	0.11	21.5	42.8	1.99
0.1 M CTAC+0.1 M KBr	227	0.07	21.5	65.6	3.05

decreasing distributions in Fig. 3 are very similar to those from nonionic micellar solutions where the interactions are dominated by the van der Waals forces.

The viscosity of CTAC micellar solutions in presence of KBr and KCl is shown in Fig. 4. It is seen that the viscosity of CTAC/KBr solutions is almost constant up to electrolyte concentration of 0.1 M and thereafter it increases rapidly. On the other hand, viscosity of CTAC/KCl solutions does not alter up to a concentration which is ten times higher. This also suggests that on the addition of electrolyte micelles grow in size for CTAC/KBr and not for CTAC/KCl. It may be mentioned however that the viscosity of micellar solutions responds to the changes in both the structure and their mutual interactions. Thus one should be careful in analyzing the viscosity data in terms of the shape transition because the different equiviscous solutions of a surfactant system could have micelles which differ in their sizes [28,29].

The quantitative analysis of the SANS data involved comparing the measured distribution with calculated cross section as given by the Eq. (1). It may be noted that SANS distributions at large $Q(>0.07 \text{ Å}^{-1})$, where $S(Q)\sim 1$, are mainly decided by the intraparticle structure factor $P(Q)$ of the micelle. It is observed that the measured distributions and thus $P(Q)$ are independent of the electrolyte concentration for $Q>0.07 \text{ Å}^{-1}$. This is possible if micelles are ellipsoidal and the smaller dimension is independent of the electrolyte concentration. Micelles were assumed to be prolate ellipsoidal ($a\neq b=c$). The measured distributions were first calculated by using the method of Hayter and Penfold and it worked reasonably well for KBr and KCl in the concentration range 0–0.1 M. However, it produced very poor fit for the high KCl concentrations (>0.1 M). This is due to the omission of van der Waals interaction. The solid lines in Figs. 1 and 2 are the fits of the Hayter and Penfold type analysis and the solid lines in the Fig. 3 are obtained using the method which takes account of Coulomb as well as van der Waals interactions. In the van der Waals interaction, the value of the Hamaker constant was determined from the data corresponding to $C=1.0$ M for CTAC/KCl, as the Coulomb effects are small at such a high concentration of KCl. The

value has been found to be $14.7 k_B T$, and it is comparable to that reported in the literature [30].

The analysis shows that CTAC micelles are ellipsoidal with the dimensions $a=34.7$ Å and $b=21.5$ Å in pure CTAC solutions. The aggregation number is 120 and the fractional charge on the micelle is 0.13. The parameters for CTAC micellar solutions in presence of KBr and KCl are given in Tables I and II, respectively. To fit the data at high KCl concentrations (Fig. 3), we have used the fixed aggregation number, fractional charge, and semiminor axis as obtained from the data of low KCl concentrations (Table II) but taking account of both the screened Coulomb and van der Waals interactions. It is seen that the value of a/b in CTAC/KBr increases by a factor of about 2 on varying the KBr concentration from $C=0.0-0.1$ M. However, a/b is found to be independent of KCl concentration in CTAC/KCl, even when the KCl concentration is increased to 1.0 M. These observations, together with the viscosity measurements, suggest that CTAC micelles grow on addition of small quantities of KBr and not with KCl. It may be mentioned that fits in Figs. 1–3 assuming micelles as monodisperse ellipsoids may not be unique, as polydisperse spheres could also fit the data. However, the large changes in viscosity in CTAC/KBr system with the increase in KBr concentration (Fig. 4) are reflection of prolate ellipsoidal micelles. This will not happen if the micelles were polydisperse spheres.

The earlier studies on CTAB/KCl and CTAB/KBr had shown that micelles grow on addition of KBr and not KCl [19]. In view of this and the results reported above, we conclude that the common ion effect is not the reason for the differences in the micellar growth in CTAC/KBr and CTAC/KCl solutions. We believe that the intermicellar interactions are different in CTAC/KBr and CTAC/KCl for similar electrolyte concentrations, leading to the differences in micellar growth and the viscosities. It seems that Cl^- and Br^- ions screen the head group charges differently because of their different sizes and the hydration behavior and thus effect the intermicellar interaction differently. In the following, we examine the effect of varying sizes of the counterions and coions on the structures of ionic micelles. SANS measure-

TABLE II. Micellar parameters for 0.1 M CTAC + C M KCl solutions.

System	Aggregation number N	Fractional charge α	Semiminor axis $b=c(\text{Å})$	Semimajor axis $a(\text{Å})$	a/b
0.1 M CTAC	120	0.13	21.5	34.7	1.61
0.1 M CTAC + 0.05 M KCl	120	0.13	21.5	34.7	1.61
0.1 M CTAC + 0.1 M KCl	122	0.12	21.5	35.2	1.64

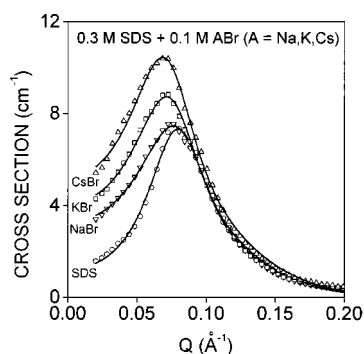FIG. 5. SANS distributions from 0.3 M SDS and in presence of 0.1 M NaBr, 0.1 M KBr, and 0.1 M CsBr.

FIG. 6. SANS distributions from 0.3 M SDS and in presence of 0.1 M KCl, 0.1 M KBr, and 0.1 M KI.

ments have been carried out from the micellar solutions of SDS in presence of various alkali halide electrolytes AX (A=Na,K,Cs and X=Cl,Br,I). It may be noted that unlike CTAC which is positively charged, SDS micelles are negatively charged, and thus it is the variation in cation which will mainly decide the growth of the SDS micelles.

B. Growth of SDS micelles with various alkali halide electrolytes

SANS distributions from 0.3 M SDS micellar solution, and in presence of 0.1 M NaBr, 0.1 M KBr, and 0.1 M CsBr are shown in Fig. 5. These electrolytes have the same coion but the different counterions. All the SANS distributions show a correlation peak, which is an indication of a repulsive interaction between the ionic micelles. The 0.3 M SDS data has the peak at $Q_m \sim 0.07$ Å^{-1}, and is in good agreement with the literature [31,32]. The parameters of 0.3 M SDS as obtained by Hayter and Penfold type analysis are given in Table III. Micelles have the aggregation number N = 106 and the fractional charge α=0.15. The semimajor and semiminor axes of the micelles are 17.0 and 35.8 Å, respectively.

When the above electrolytes are added to the micellar solution, it is observed that there is shifting and the broadening of the correlation peak. These observations are similar to those found in CTAC/KBr solutions. The shifting of peak to lower Q indicates the micellar growth on the addition of electrolyte. The broadening of the peak is due to the screening of the repulsive interaction between the micelles in presence of electrolyte. The effect becomes more important as we go from NaBr to CsBr. In all the cases, it is seen that aggregation number increases and the fractional charge decreases with the addition of electrolyte (Table III). The minor axis does not change on the addition of electrolyte. The ag-
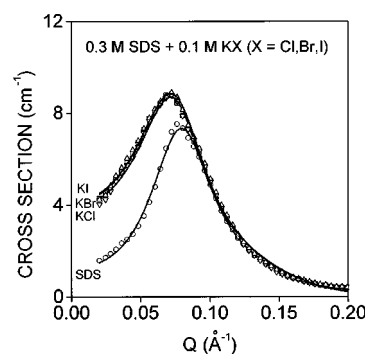
gregation number in presence of NaBr, KBr, and CsBr are 122, 145, and 170, respectively. The corresponding fractional charge on the micelles are 0.13, 0.11, and 0.10, respectively. These results thus show that micellar growth depends on the counterions.

The effect of varying coions on the 0.3 M SDS is shown in Fig. 6. SANS distributions in presence of 0.1 M KCl, 0.1 M KBr, and 0.1 M KI are shown. These distributions are very similar, indicating that there are no significant changes in the micellar parameters (Table IV). In particular, it is seen that micelles in these solutions have almost the same aggregation number and the fractional charge.

It may be recalled that the micelles are formed by the competition of two opposing forces, namely, the attractive hydrophobic interaction of the tails and ionic or steric repulsion of the head groups. The geometry of the micelle is given by the packing parameter $p = v/Al$, where v is the volume, A is the effective head group area, and l is the length of the surfactant molecule [33]. The effective head group area A is the measure of the repulsion and depends on the the nature of the head group. For ionic micelles, the effective head group area is decided by the fractional charge on the head group. When the electrolyte is added to the ionic micellar solution, it has a tendency to neutralize the charge on the micelle. The neutralization of the head group charge results in a smaller effective head group area and hence there is a change in the micellar size.

The effect of different electrolytes on the micellar structure is different. This is because they have the different tendency to neutralize the charge on the micelle. The SANS results (Tables III and IV) show that micelle grow on addition of electrolytes in the SDS solutions. The structure of micelle varies when the counterion is changed. The effect of counterions is in the same order as given by the lyotropic series [34]. This series denotes the relative order of influence

TABLE III. Micellar parameters for 0.3 M SDS + 0.1 M ABr (A=Na,K,Cs) solutions.

System	Aggregation number N	Fractional charge α	Semiminor axis $b=c$(Å)	Semimajor axis a (Å)	a/b
0.3 M SDS	106	0.15	17.0	35.8	2.11
0.3 M SDS + 0.1 M NaBr	125	0.13	17.0	42.4	2.49
0.3 M SDS + 0.1 M KBr	147	0.11	17.0	49.7	2.92
0.3 M SDS + 0.1 M CsBr	165	0.10	17.0	55.8	3.28

TABLE IV. Micellar parameters for 0.3 M SDS + 0.1 M KX (X = Cl, Br, I) solutions.

System	Aggregation number N	Fractional charge α	Semiminor axis $b = c$ (Å)	Semimajor axis a (Å)	a/b
0.3 M SDS + 0.1 M KCl	145	0.12	17.0	49.0	2.89
0.3 M SDS + 0.1 M KBr	147	0.11	17.0	49.7	2.92
0.3 M SDS + 0.1 M KI	147	0.11	17.0	49.7	2.92

exerted by ions on various phenomenon. The effect of variation of coions is negligible as the coions do not alter the micellar charge.

There are several studies which deal with the investigation of the micellar properties and their structures in presence of alkali halide electrolytes [7–10,12,13,19,35–39]. The present studies show that the interaction of ion with water most certainly plays an important role in deciding the growth of the micelle in aqueous electrolyte solution. It seems if the hydrated size of the counterion is smaller, it has higher tendency to screen the charge on the micelle. The hydrated size of the Na$^+$, K$^+$, and Cs$^+$ ions are 3.6, 3.3, and 3.3 Å, respectively [40]. The fact that the bare sizes of Na$^+$, K$^+$, and Cs$^+$ ions are 0.95, 1.33, and 1.69 Å, respectively, shows that smaller ions are more hydrated than than larger ions. Our studies show that aggregation number of the SDS micelles increase as the hydration of the counterion decreases. In short, we find that micellar growth depends on the hydrated

ionic size of the counterion and the growth is more when the counterion hydration is smaller.

V. CONCLUSIONS

Small-angle neutron scattering and viscosity measurements from CTAC micellar solutions with varying concentrations of KBr and KCl have been discussed. It is seen that micelles grow on the addition of KBr, but their size is constant over a wide range of KCl concentration. When compared with similar data on CTAB micellar solutions, these results suggest that the differences in the micellar growths in the above systems are not connected with the common ion effect. To examine the role of size and hydration behavior of counterions and coions on the micellar growth, SANS measurements from SDS micellar solutions in presence of various alkali halide electrolytes have also been discussed. It is seen that micellar growth strongly depends on the counterions and there is negligible effect of the coions. We further find that smaller the size of the hydrated counterion, larger is the growth of the micelles.

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