

Effect of the Hydrophilicity of Aromatic Counterions on the Structure of Ionic Micelles

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Small-angle neutron scattering experiments have been carried out on aqueous micellar solutions of cationic surfactant cetyltrimethylammonium bromide (CTABr) in the presence of different aromatic salts. The salts with different hydrophilicity of the counterions that have been used are sodium benzoate (NaB), sodium 2-hydroxy benzoate (Na2-HB), sodium 2,6-dihydroxy benzoate (Na2,6-DHB), and sodium 4-hydroxy benzoate (Na4-HB). It is found that cationic CTABr micelles grow strongly with the addition of small amount of NaB, Na2-HB, and Na2,6-DHB salts. The effect of addition of salts on the growth of the micelles is significantly higher for Na2-HB and Na2,6-DHB as compared to that for NaB. On the other hand, the addition of salt Na4-HB is relatively much less effective similar to the effect of inorganic salts (e.g., NaBr) on the growth of the micelles. We explain the propensity of strong growth of the micelles in the presence of NaB, Na2-HB, and Na2,6-DHB because of the high charge neutralization by these salts as the aromatic counterions are adsorbed on the surface of the micelle. In these counterions, the hydrophilicity seems to be important in deciding the location of the charged group of the counterions with respect to the level of the oppositely charged micellar surface. The counterions of Na4-HB are not adsorbed on the micellar surface, and hence, it behaves differently than the above other salts.

Introduction

Surfactant molecules self-assemble into aggregates in aqueous solution to form micelles above the critical micelle concentration.^{1,2} Polar headgroups of these aggregates lie near the bulk aqueous media, whereas the hydrocarbon tails extend inwardly to stay away from the unfavorable water contacts. The micelles are formed by the delicate balance of opposing forces: the attractive tail–tail hydrophobic interaction provides the driving force for the aggregation of the surfactant molecules, whereas the electrostatic or steric repulsion between the polar headgroups limits the size that a micelle can attain. As a result, the characteristics of these aggregates are easily controlled by the small changes in chemical structure of the surfactant molecule and the solution conditions such as concentration, temperature, and ionic strength. The aggregates formed are of various types, shapes, and sizes such as spherical or ellipsoidal, cylindrical, or threadlike micelle; disklike micelle; membrane; and vesicles.^{3–7}

One of the convenient ways to control the structure of the micelles is by the addition of the salts in the micellar solution.^{3–7} It is known that the micelles of cationic surfactants (e.g., cetyltrimethylammonium bromide (CTABr)) grow from spherical to rodlike shapes on the addition of salts such as NaBr, NaSal (sodium salicylate), etc.^{8–16} The charge neutralization by the counterions at the surface of the micelle allows more number of surfactant molecules to aggregate and hence the size of the micelle increases. There are several factors to decide the effect of a salt on the structure of micelles such as chemical structure, nature (inorganic or aromatic), hydrated size of the counterions, etc. Usually, the coions have the negligible effect as compared to that of the variation of counterions. The salts with aromatic counterions are very effective in the micellar growth because of the adsorption of these counterions on the surface of the

micelles. NMR studies have provided the main evidence in support of this connection.^{17–21} On the other hand, inorganic counterions tend to stay around the micelles, and thus, their effect on the growth of the micelles is relatively much less as compared to those of the aromatic counterions. The role of hydrated size of the counterions for inorganic salts is quite well understood to control the structure of micelles. It is believed that the counterions with higher hydrophilicity have more affinity to remain in the bulk of micellar solution and therefore are less effective to screen the charge on the micellar surface.^{22–25} However, such types of studies with aromatic counterions are rare.

This paper reports the effect of salts on the structure of micelles when the hydrophilicity of the aromatic counterions is varied. The effect of salt sodium 2-hydroxy benzoate (Na2-HB), also referred to as NaSal, on the structure of cationic micelles is well studied in the literature.^{26–33} The micelles grow strongly with the addition of a small amount of Na2-HB. We compare the effect of different salts, which have either a smaller or higher hydrophilicity than Na2-HB. The chemical structures of these salts are given in Figure 1. In addition to Na2-HB, the salts have been used are sodium benzoate (NaB), sodium 2,6-dihydroxy benzoate (Na2,6-DHB), and sodium 4-hydroxy benzoate (Na4-HB). Small-angle neutron scattering (SANS) has been used to study the structure of the micelles in these micellar solutions.

Experimental Section

Surfactant CTABr was obtained from Sigma, and the aromatic salts were obtained from either Sigma or Aldrich. All these chemicals were used as supplied. The samples for SANS experiments were prepared by dissolving a known amount of surfactant and salts in D₂O. The use of D₂O as solvent instead of H₂O provides better contrast in neutron experiments. Small-angle neutron scattering experiments were carried out using

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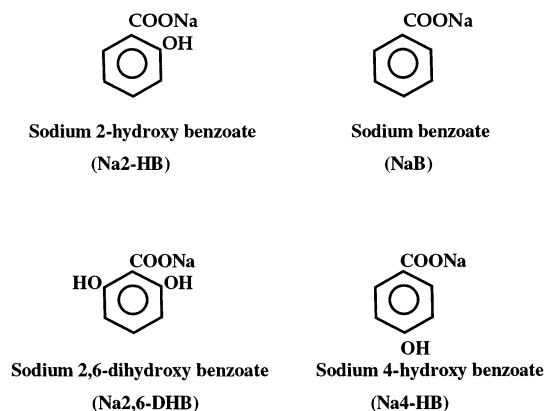


Figure 1. Chemical structures of different aromatic salts with varying hydrophilicity.

SANS diffractometer at the Swiss Spallation Neutron Source SINQ, Paul Scherrer Institut.³⁴ The wavelength of the neutron beam was 8 Å, and the experiments were performed at two different samples-to-detector distances of 2 and 8 m to cover a Q range of 0.005–0.3 Å⁻¹. The scattered neutrons were detected using a two-dimensional 96 cm × 96 cm detector. The measurements were made for the fixed surfactant concentration 100 mM, and the concentration of salts was varied in the range 0–20 mM. In all of the measurements, the temperature was kept fixed at 30 °C. The measurements were also made for 20 mM salt samples at the different temperatures of 45, 60, and 75 °C. The samples were held in quartz sample holder of thickness 1 mm. The measured SANS data have been corrected and normalized to a cross-sectional unit, using standard procedures.

SANS Analysis. In SANS, one measures the differential scattering cross-section per unit volume ($d\Sigma/d\Omega$) as a function of scattering vector Q . For a system of charged interacting micelles, $d\Sigma/d\Omega$ is given by^{35,36}

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

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. $F(Q)$ 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

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

$$\langle F(Q) \rangle^2 = [\int_0^1 F(Q, \mu) d\mu]^2 \quad (3)$$

$$F(Q, \mu) = \frac{3(\sin x - x \cos x)}{x^3} \quad (4)$$

$$x = Q[a^2\mu^2 + b^2(1 - \mu^2)]^{1/2} \quad (5)$$

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

In general, micellar solutions of ionic surfactants show a correlation peak in the SANS distribution.³⁷ The peak arises

because of the corresponding peak in the interparticle structure factor $S(Q)$ and indicate the presence of electrostatic interactions between the micelles. $S(Q)$ specifies the correlation between the centers of different micelles and its Fourier transform of the radial distribution function $g(r)$ for the mass centers of the micelle. Unlike the calculation of $P(Q)$, it is quite complicated to calculate $S(Q)$ for any other shape than spherical. This is because $S(Q)$ depends on the shape and as well as the orientation of the particles. To simplify this, prolate ellipsoidal micelles are assumed to be equivalent spherical. We have calculated $S(Q)$ as derived by Hayter and Penfold³⁸ from the Ornstein–Zernike equation and using the rescaled mean spherical approximation.³⁹ The 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

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

where κ is the Debye–Hückel inverse screening length and is calculated by

$$\kappa = \left[\frac{8\pi N_A e^2 I}{10^3 \epsilon k_B T} \right]^{1/2} \quad (7)$$

defined by the ionic strength I of the solution

$$I = \text{CMC} + \frac{1}{2} \alpha C + C_s \quad (8)$$

I is determined by the CMC, dissociated counterions from the micelles and the salt concentration. The fractional charge α ($=Z/N$, where Z is the micellar charge) is the charge per surfactant molecule in the micelle and is a measure of the dissociation of the counterions of the surfactant in the micelle. C and C_s present the concentrations of the surfactant and salt in the solution, respectively. The contact potential u_0 is given by

$$u_0 = \frac{Z^2 e^2}{\pi \epsilon \epsilon_0 \sigma (2 + \kappa \sigma)^2} \quad (9)$$

where ϵ is the dielectric constant of the solvent medium, ϵ_0 is the permittivity of free space, and e is the electronic charge.

Although micelles may produce 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.^{40,41} The dimensions of the micelle, aggregation number, and the fractional charge have been determined from the analysis. The semimajor axis (a), semiminor axis ($b = c$), and the fractional charge (α) are the parameters in analyzing the SANS data. The aggregation number is calculated by the relation $N = 4\pi ab^2/3v$, where v is the volume of the surfactant monomer.

Throughout the data analysis, corrections were made for instrumental smearing.⁴² For each instrumental setting, the scattering profiles as given by eq 1 were smeared by the appropriate resolution function to compare with the measured data. The parameters in the analysis were optimized by means of nonlinear least-squares fitting program.⁴³

Results and Discussion

Figure 2 shows the SANS data from 100 mM CTABr micellar solution with varying concentration (0–20 mM) of the salt Na2-HB. The SANS distribution from a pure 100 mM CTABr shows

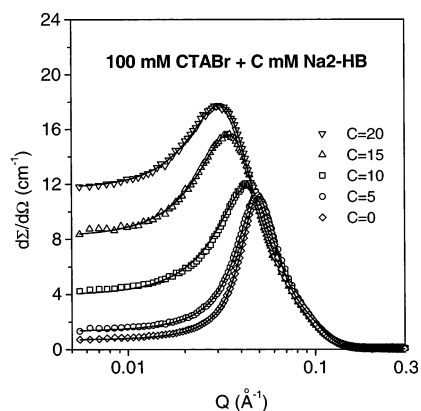


Figure 2. SANS data from 100 mM CTABr micellar solution with varying concentration of salt Na2-HB.

TABLE 1: Micellar Parameters from 100 mM CTABr with Varying Concentration of Salt Na2-HB^a

salt conc (mM)	temp (°C)	aggregation number, N	fractional charge, α	semiminor axis, $b = c$ (Å)	semimajor axis, a (Å)	axial ratio, a/b
0	30	173	0.23	24.0	40.2	1.68
5	30	185	0.20	24.3	42.9	1.77
10	30	254	0.13	24.1	61.0	2.53
15	30	448	0.11	24.2	108.8	4.50
20	30	568	0.09	24.5	137.1	5.60
20	45	403	0.11	23.0	110.4	4.80
20	60	190	0.14	22.5	54.0	2.40
20	75	121	0.20	22.0	36.1	1.64

^a The parameters from 100 mM CTABr with 20 mM Na2-HB at different temperatures are also given.

a well-defined correlation peak at the wave vector transfer $Q \sim 0.05 \text{ \AA}^{-1}$. This correlation peak is an indication of strong repulsive interaction between the positively charged CTABr micelles. The correlation peak usually occurs at $Q_{\text{max}} \sim 2\pi/d$, where d is the average distance between the micelles and Q_{max} is the value of Q at the peak position.³⁷ In Figure 1, the cross-section increases and the peak position shifts to lower Q values with the increase in the salt concentration. This suggests the formation of larger micelles and hence the smaller number density with the addition of the salt. The micellar parameters in these systems are given in Table 1. It is seen that the fractional charge on the micelles α decreases from 0.23 to 0.09 and the aggregation number N increases from 173 to 568 when the salt is increased from 0 to 20 mM. The strong growth of the micelles is believed to be due to the adsorption of aromatic 2-HB[−] counterions on the micelle. This is supported by the variation in the fractional charge on the micelle, which decreases sharply with the increase in the salt concentration. It could be mentioned that the parameters obtained for high values of axial ratios of the micelles (Table 1) may not be very reasonable because of the assumption of the prolate ellipsoidal micelles as the equivalent spherical in the calculation of $S(Q)$. In fact, this is the reason we have limited the SANS measurements to the low salt concentrations. It would be interesting to make the use of Cryo-TEM to compare the structures of CTABr micelles in the presence of different salts at high concentrations.

Figure 3 shows the SANS data from 100 mM CTABr with the addition of 20 mM Na2-HB at different temperatures. The general trends in these data with increasing temperature are opposite to that of increasing the salt concentration (Figure 2). The cross-section decreases and the peak position shifts to higher Q values with the increase in the temperature. This suggests the formation of shorter micelles with the increase in the

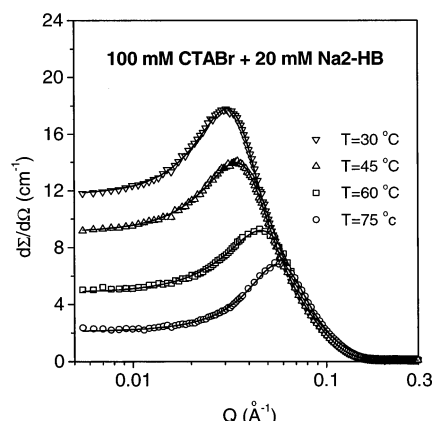


Figure 3. SANS data from 100 mM CTABr micellar solution with the addition of 20 mM Na2-HB salt at different temperatures.

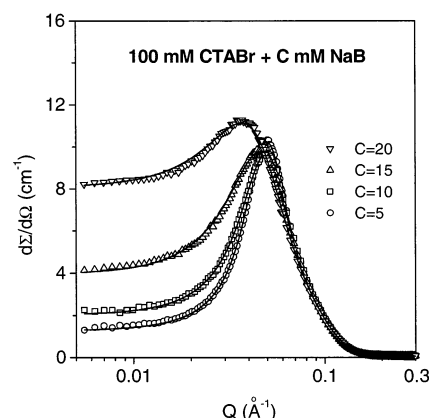


Figure 4. SANS data from 100 mM CTABr micellar solution with varying concentration of salt NaB.

temperature. The micellar parameters in these systems are given in Table 1. We find that the fractional charge on the micelles increases and the aggregation number decreases with the increase in the temperature. It is believed that increase in the dissociation of Br[−] counterions with the increase in the temperature results in the stronger repulsion between the charged headgroups and hence the formation of smaller micelles. At higher temperatures, the adsorption of the small amount of aromatic counterions seems to be insufficient to maintain the growth of the micelles.

Figure 4 shows the SANS data from 100 mM CTABr micellar solution with varying concentration (0–20 mM) of the salt NaB. SANS data from 100 mM CTABr with the addition of 20 mM NaB at different temperatures are shown in Figure 5. The general trends on the SANS data of the addition of the NaB (Figure 4) or increasing temperature (Figure 5) are similar to that of Na2-HB but less pronounced. The micellar parameters in these systems are given in Table 2. The comparison of the micellar parameters (Tables 1 and 2) shows that the addition of NaB is less effective in the neutralization of the charge on the micellar surface. It has been known from NMR measurements that 2-HB[−] anions are intercalated between CTA⁺ surfactant cations.^{17–21} The presence of the −OH group close to the COO[−] group in 2-HB[−] would make these groups remain on the outside of the micelle surface (close to water and far from the hydrophobic tails) and, therefore, are very effective to neutralize the charge on the micelle. The B[−] counterions similar to the 2-HB[−] are expected to adsorb on the micellar surface. The fact that the hydrophilicity of the B[−] counterions is less than that of the 2-HB[−] means that the intercalation of the benzene ring more toward the core of the micelles seems to be making B[−]

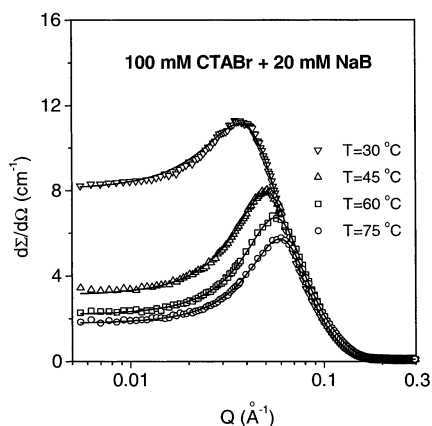


Figure 5. SANS data from 100 mM CTABr micellar solution with the addition of 20 mM NaB salt at different temperatures.

TABLE 2: Micellar Parameters from 100 mM CTABr with Varying Concentration of Salt NaB^a

salt conc (mM)	temp (°C)	aggregation number, <i>N</i>	fractional charge, α	semiminor axis, $b = c$ (Å)	semimajor axis, a (Å)	axial ratio, a/b
5	30	176	0.20	24.1	41.2	1.71
10	30	184	0.17	23.7	45.6	1.92
15	30	214	0.13	24.1	51.8	2.15
20	30	290	0.10	24.0	72.2	3.01
20	45	165	0.15	23.2	44.2	1.91
20	60	125	0.17	22.4	35.7	1.59
20	75	107	0.21	21.7	32.5	1.50

^a The parameters from 100 mM CTABr with 20 mM NaB at different temperatures are also given.

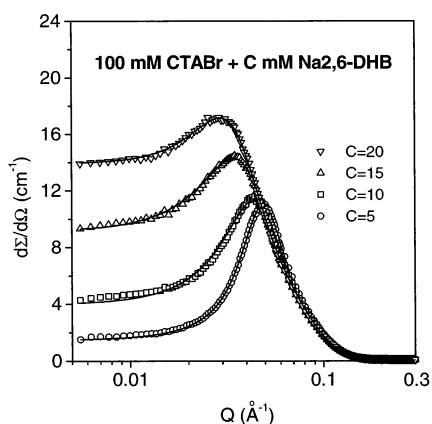


Figure 6. SANS data from 100 mM CTABr micellar solution with varying concentration of salt Na₂,6-DHB.

counterions less effective in the charge neutralization on the micellar surface.

Figure 6 shows the SANS data from a 100 mM CTABr micellar solution with varying concentration (0–20 mM) of the salt Na₂,6-DHB. SANS data from 100 mM CTABr with the addition of 20 mM Na₂,6-DHB at different temperatures are shown in Figure 7. The general trends on the SANS data of the addition of the Na₂,6-DHB (Figure 6) or increasing temperature (Figure 7) are very much similar to that of Na₂-HB. The micellar parameters in these systems are given in Table 3. The comparison of the micellar parameters (Tables 1 and 3) shows that, although the addition of Na₂,6-DHB is equally effective to that of Na₂-HB in the neutralization of the charge on the micellar surface, the increase in the size of the micelles is slightly smaller for Na₂,6-DHB. It seems that both 2-HB[−] and 2,6-DHB[−] counterions maintain their charged headgroup (COO[−])

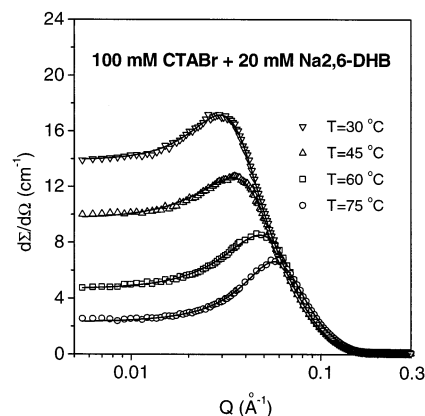


Figure 7. SANS data from 100 mM CTABr micellar solution with the addition of 20 mM Na₂,6-DHB salt at different temperatures.

TABLE 3: Micellar Parameters from 100 mM CTABr with Varying Concentration of Salt Na₂,6-DHB^a

salt conc (mM)	temp (°C)	aggregation number, <i>N</i>	fractional charge, α	semiminor axis, $b = c$ (Å)	semimajor axis, a (Å)	axial ratio, a/b
5	30	185	0.18	24.3	42.7	1.76
10	30	242	0.11	23.7	60.0	2.53
15	30	391	0.09	24.1	96.5	4.01
20	30	545	0.07	24.2	134.9	5.57
20	45	338	0.09	23.0	92.9	4.04
20	60	173	0.12	22.5	50.0	2.22
20	75	120	0.17	22.2	35.6	1.60

^a The parameters from 100 mM CTABr with 20 mM Na₂,6-DHB at different temperatures are also given.

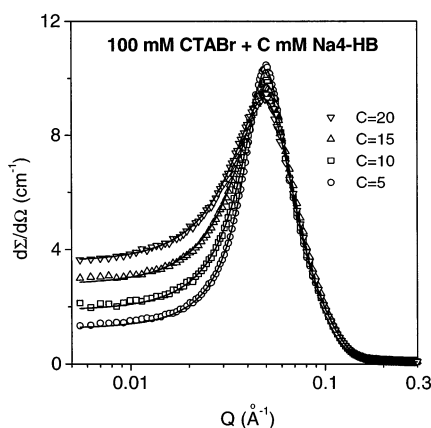


Figure 8. SANS data from 100 mM CTABr micellar solution with varying concentration of salt Na₄-HB.

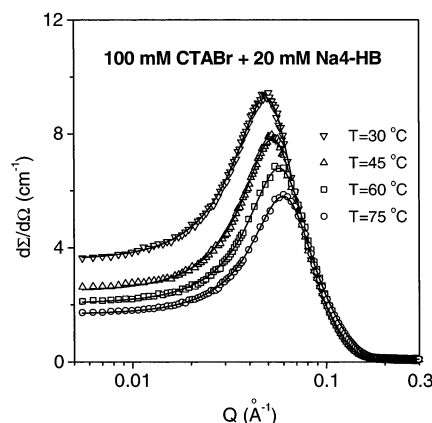
at the same level of the oppositely charged micellar surface, so that they are equally effective in the charge neutralization. The fact that the hydrophilicity of the 2,6-DHB[−] countetions is more than that of the 2-HB[−] means that the increase in the effective physical size of the headgroup (surfactant + counterion) may be the reason for slightly smaller micelles in the presence of Na₂,6-DHB.

Figure 8 shows the SANS data from the 100 mM CTABr micellar solution with varying concentration (0–20 mM) of the salt Na₄-HB. The general trends on the SANS data of the addition of the Na₄-HB (Figure 8) are quite different as have been observed with the other three salts (Figures 2, 4, and 6). The micellar parameters in these systems are given in Table 4. The comparison of the micellar parameters (Tables 1–4) shows that the addition of Na₄-HB is much less effective to that of Na₂-HB or NaB in the neutralization of the charge on the

TABLE 4: Micellar Parameters from 100 mM CTABr with Varying Concentration of Salt Na4-DHB^a

salt conc (mM)	temp (°C)	aggregation number, <i>N</i>	fractional charge, α	semiminor axis, <i>b</i> = <i>c</i> (Å)	semimajor axis, <i>a</i> (Å)	axial ratio, <i>a/b</i>
5	30	175	0.20	24.4	39.2	1.61
10	30	179	0.18	24.2	40.9	1.69
15	30	181	0.16	23.9	42.7	1.78
20	30	192	0.15	24.0	44.7	1.86
20	45	155	0.18	23.2	38.5	1.66
20	60	124	0.20	22.7	32.1	1.41
20	75	107	0.22	21.9	29.8	1.36

^a The parameters from 100 mM CTABr with 20 mM Na4-DHB at different temperatures are also given.

**Figure 9.** SANS data from 100 mM CTABr micellar solution with the addition of 20 mM Na4-HB salt at different temperatures.

micellar surface. We believe that the *p* position of $-\text{OH}$ group at the 4-HB^- counterions makes it difficult to adsorb them on the surface of the micelle. This salt therefore behaves more like the inorganic salt (e.g., NaBr), where the counterions prefer to remain in the bulk or condensed around the charged micelles. SANS data from 100 mM CTABr with the addition of 20 mM Na4-HB at different temperatures are shown in Figure 9. The micelles become smaller with the increase in the temperature similar to those that have been observed in other systems (Figures 3, 5, and 7).

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 electrostatic or steric repulsion of the headgroups. The growth of the ionic micelles with the addition of salts can be understood in terms of the geometrical packing parameter (*p*) of the surfactant molecule.⁴⁴ The parameters are given as $p = v/Al$, where *v* is the volume, *A* is the effective headgroup area, and *l* is the length of the surfactant molecule. For $p < 1/3$, spherical micelles are formed. There is growth of the micelles when *p* is increased. Spherical micelles convert to the ellipsoidal and rodlike micelles for $1/3 < p < 1/2$. The effective headgroup area *A* is the measure of the repulsion and depends on the nature of headgroup and counterions. For ionic micelles, the effective headgroup area is decided by the fractional charge on the headgroup. When the salt is added to the ionic micellar solution, it has a tendency to neutralize the charge on the micelles. The neutralization of the headgroup charge results in a smaller headgroup area, and this increases the packing parameter or the micellar size. In present studies, it has been found that the charge neutralization on the micelles depends on the hydrophilicity of the aromatic counterions, and hence, they show the different growth of the micelles.

Conclusions

The effect of aromatic counterions with varying hydrophilicity on the growth of cationic CTABr micelles has been studied using small-angle neutron scattering. The hydrophilicity of the aromatic counterions was varied by appropriately selecting such salts where $-\text{OH}$ groups are attached to the different positions in the benzene ring of the counterions. It is found that both the amount of hydrophilicity and the position of the hydrophilic groups in the aromatic counterions play an important role in deciding the charge neutralization by these counterions on the micellar surface and hence the growth of the micelles. The strong growth of CTABr micelles in the presence of NaB, Na2-HB, and Na2,6-DHB salts occurs because of the adsorption of the aromatic counterions on the surface of the micelles. The growth of the micelles is much more with the addition of 2-HB^- and $2,6\text{-DHB}^-$ as compared to that for B^- counterions. On the other hand, 4-HB^- counterions are not adsorbed on the micellar surface, and hence, Na4-HB salt has the similar effect to those of the inorganic salts in the micellar solutions.

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