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Aggregation Properties of Novel Cationic Surfactants with Multiple Pyridinium Headgroups. Small-Angle Neutron Scattering and Conductivity Studies

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Novel single-chain cationic surfactants bearing one, two, and three pyridinium headgroups have been synthesized. These surfactants upon solubilization in water produced micelles or large lamellar structures depending on the number of headgroups they possess. The critical micellar concentrations (cmc) of these surfactants were determined by measuring the specific conductance of the aqueous solution of the surfactants. The cmc values were found to increase with every increase in the number of headgroups in the surfactant. Detailed small-angle neutron scattering (SANS) studies were carried out with their aqueous solutions (D₂O) to study their aggregation properties. The data have been analyzed using the Hayter and Penfold model for macro-ion solution to compute the interparticle structure factor $S(Q)$, taking into account the screened Coulomb interactions between the micelles. SANS analysis clearly indicated that the nature of the aggregate structure of these cationic micelles depends on the number of the headgroups present in the surfactants. It was found that a single-headed new pyridinium amphiphile formed the lamellar structure, whereas surfactants with double and triple headgroups formed micelles in water. The aggregates shrank in size with an increase in the number of headgroups in the surfactants. The aggregation number (N) continually decreased and the fractional charge (α) increased with a greater number of headgroups on the surfactants. The semimajor axis (a) and semiminor axis ($b = c$) of the micelle also decreased with the increase in the number of headgroups in the surfactants. It indicates that hydrocarbon chains in such micelles prepared from multiheaded surfactants adopt a bent conformation and no longer stay in extended conformation. The effects of variation of the concentration and temperature on aggregation properties for all the surfactants have also been investigated. In the case of $h = 1$, the lamellar structure remains approximately the same with the variation of concentration, but with an increase in temperature there was transition from lamellar to rodlike micelles. For other surfactants, with an increase in concentration the aggregation number and the size of the micelles increased. The micelles became progressively smaller in size, the aggregation number decreased, and the fractional charge increased with an increase in temperature.

Introduction

Micelles are formed by the aggregation of the surfactants in their aqueous solution above a certain concentration known as the critical micellar concentration (cmc).¹ The micellization properties of surfactants in solution are modulated by parameters such as concentration, temperature, and the presence of additives, such as electrolytes, alcohols, and amines, etc.² The hydrophobic segments of the surfactant molecules constitute the interior core of the micelles to avoid their exposure to water, and the polar headgroups reside at the micellar exterior interfacing with the bulk water. Various types of surfactants are known that vary in terms of their headgroup charges or in other parts of their molecular architecture. Even among cationic surfactants several variations in their molecular structures are known. For instance cationic surfactants consisting of single-chain/single-headgroup, e.g. cetyl trimethylammonium bromide (CTABr) or cetyl pyridinium bromide (CPB), are known, the

micellar properties of which have been extensively investigated.³ Clearly the differences between trimethylammonium and pyridinium headgroups, the charge distribution, and hydration properties of the cations influence the variation in their micellar properties. While it has been shown that single-chain surfactants bearing one, two, and even three trimethylammonium bromide headgroups form micelles,⁴ nothing is known about the corresponding series of surfactants bearing pyridinium headgroups. Since the micellar solutions have widespread applications, and the study of the structures of micellar solutions is important even from the point of view of fundamental research, detailed investigations of the properties of solutions of surfactants with novel molecular features is of considerable current interest.⁵ Herein we present three new single-chain surfactants possessing one, two, or three pyridinium headgroups (1–3) and compare the properties of their aqueous solutions with that of CPB.

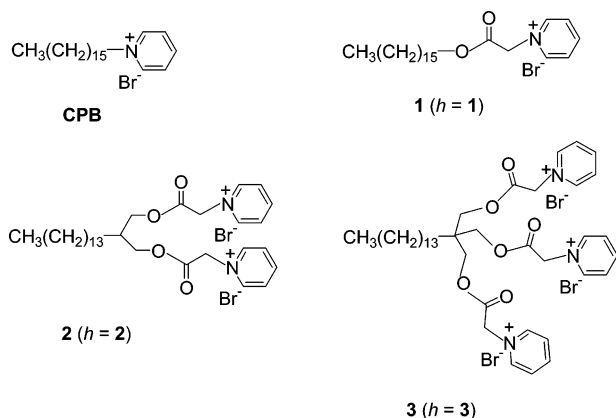
In this paper we report the aggregation properties of these new surfactants in water in detail using small-angle neutron scattering (SANS), conductivity studies, and transmission electron microscopy (TEM). SANS is a good, noninvasive technique for determining the sizes and shapes of micelles,⁶ and this method has been extensively used for the characterization of micellar solutions of different surfactants,⁷ including those

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of gemini surfactants.⁸ We show how the micellar shapes, aggregation number, and ionization, etc., change with an increase in the number of headgroups. We also present the SANS characterization of the solutions of different surfactants at various concentrations and temperatures.

Experimental Section

Materials. All the surfactants with $h = 1, 2$, and 3 were synthesized according to a procedure described previously.^{4a} ¹H NMR, FT-IR, ESI-MS, and elemental analysis confirmed the high purities of these surfactants. Thin-layer chromatography (TLC) on precoated silica gel plates further confirmed that each of these surfactants was highly pure as no other spot was detectable on the TLC plate. The D₂O (99.8 atom % D) was used for the preparation of micellar solutions, by dissolving known amounts of surfactants in D₂O for the neutron scattering studies. All the reagents and solvents used in this study were of the highest grade available commercially. Millipore grade water was used for all physical measurements.

Methods. Critical Micellar Concentration. The critical micellar concentration values for each surfactant solution in water were measured conductometrically by using a conductivity meter (Konduktometer CG855, SCHOTT) and electrode with a cell constant of 0.93 cm^{-1} . Concentrated solutions of individual surfactant systems of known concentration were progressively diluted, and the specific conductivity values at 40°C were measured. The cmc's for each surfactant, corresponding to $h = 1, 2$, and 3 were determined at 40°C by plotting the values of the specific conductivities against the respective surfactant concentrations. For each surfactant, reproducible breaks were observed, indicating the onset of micellization.

Transmission Electron Microscopy. An aqueous solution of $h = 1$ (5 and 20 mM) was examined under TEM by negative staining with 1% uranyl acetate solution. A solid sample was dissolved by heating at 40°C , and an aqueous suspension was drop-coated onto carbon-Formvar-coated copper grids (400 mesh), stained with uranyl acetate, and it was allowed to settle onto the grid. Excess solution was wicked off using filter paper, and the grid was air-dried at 40°C for 30 min . TEM was then performed on a JEOL 200-CX electron microscope, with an accelerating voltage of 120 keV . Micrographs were recorded at $10000\times$ magnification.

Small-Angle Neutron Scattering Measurements. Data Collection. Small-angle neutron scattering (SANS) experiments were performed on aqueous solutions of cationic surfactants containing a single hydrocarbon chain with single-, double-, and triple-pyridinium headgroups. For comparison, SANS experiments were also done with cetyl pyridinium bromide, a well-known single-chain/single-headed cationic surfactant. All the

TABLE 1: Critical Micellar Concentration (cmc), Scattering Length Density, and Volume of Surfactant Monomer for Multiheaded Pyridinium Surfactants^a

| surfactant | cmc (mM) | scattering length density ($\times 10^{10} \text{ cm}^{-2}$) | vol of surfactant (\AA^3) |
|------------|-------------------------|--|--------------------------------------|
| CPB | 0.92 | 0.12 | 589 |
| $h = 1$ | 0.89 (0.3) ^b | 0.35 | 682 |
| $h = 2$ | 3.94 | 0.73 | 933 |
| $h = 3$ | 5.5 | 0.95 | 1184 |

^a The cmc measurements were performed at 40°C . ^b The value shown in parentheses is due to the formation of the premicellar aggregates.

surfactant solutions used in the neutron-scattering experiments were prepared in D₂O in place of H₂O because of good contrast between the micelles and solvent. SANS experiments were performed using a SANS diffractometer at the Swiss Spallation Neutron Source SINQ, Paul Scherrer Institute.¹⁰ The wavelength of the neutron beam was 8 \AA , and the experiments were performed at two different sample-to-detector distances of 2 and 6 m to cover a Q range of $0.008\text{--}0.4 \text{ \AA}^{-1}$. The scattered neutrons were detected using a two-dimensional $96 \text{ cm} \times 96 \text{ cm}$ detector. The solutions were held in a 1 mm path length, UV-grade, quartz sample holders with tight-fitting Teflon stoppers. The effect of different concentrations on the SANS distribution was studied for an aqueous solution of concentration in the range of $25\text{--}100 \text{ mM}$ at 40°C for CPB and double- ($h = 2$) and triple-headed ($h = 3$) surfactants. For single-headed surfactant ($h = 1$) the concentration range was chosen as $5\text{--}25 \text{ mM}$ because beyond this concentration it was difficult to obtain a clear solution. The effect of temperature in the range of $40\text{--}70^\circ\text{C}$ was also investigated at a fixed surfactant concentration at 10 mM for $h = 1$ and 50 mM for the other three surfactants. The measured distributions were corrected for the background, empty cell scattering, and sample transmission and were normalized to cross-section units. The experimental points were fitted using a nonlinear least-squares routine as described below. Comparisons between the experimental and the calculated cross-sections are shown in Figures 2 and 5–8.

SANS Analysis. In small-angle neutron scattering one measures a coherent differential cross-section ($d\Sigma/d\Omega$) per unit volume. For a system of monodisperse interacting micelles, $d\Sigma/d\Omega$ is given by¹¹

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

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. 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 volumes of the surfactant monomer of CPB, single-, double-, and triple-headed surfactants are 589 , 682 , 933 , and 1184 \AA^3 , respectively (Table 1). It is calculated by taking into account the volume of the hydrocarbon chain up to the 15th carbon to be 431 \AA^3 , as obtained from Tanford's formula.¹² The volume of each pyridinium headgroup $^+\text{NC}_5\text{H}_5$ is 131 \AA^3 , and the volume of each linker ($-\text{CH}_2\text{OCOCH}_2-$) part is 120 \AA^3 (volume of the headgroup and linker $v = M/dN_A$, where $M = 79$ and 72 is the molecular weight of the headgroup and linker respectively, $d = 1 \text{ g cm}^{-3}$ is the density, and N_A is Avogadro's number).¹³ The scattering length densities of CPB, $h = 1\text{--}3$ surfactants are 0.12×10^{10} , 0.35×10^{10} , 0.73×10^{10} , and $0.95 \times 10^{10} \text{ cm}^{-2}$, respectively (Table 1). The scattering

length density of D₂O is $6.38 \times 10^{10} \text{ cm}^{-2}$, $F(Q)$ 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,

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

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

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

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

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

For a cylindrical micelle of length $L = 2l$ and radius R ,¹⁴

$$\langle F^2(Q) \rangle = \int_0^{\pi/2} \frac{\sin^2(Ql \cos \beta)}{Q^2 l^2 \cos^2 \beta} \frac{4J_1^2(QR \sin \beta)}{Q^2 R^2 \sin^2 \beta} \sin \beta d\beta \quad (6)$$

where β is the angle between the axis of the cylinder and bisectrix. J_1 is the Bessel function of order unity. In the case of planar aggregates $L \ll R$. It can be shown that for rodlike micelles $\langle F^2(Q) \rangle$ varies as $1/Q$ in the Q range of $1/l < Q < 1/R$ and as $1/Q^2$ for planar aggregates in the Q range of $1/R < Q < 1/l$.

In general, micellar solutions of ionic surfactants show a correlation peak in the SANS distribution. The peak arises because of the corresponding peak in the interparticle structure factor $S(Q)$ and indicates the presence of electrostatic interactions between the micelles. $S(Q)$ 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. Unlike the calculation of $F(Q)$, it is quite complicated to calculate $S(Q)$ for any shape other than spherical. This is because $S(Q)$ depends on the shape as well as on the orientation of the particles. To simplify this, prolate ellipsoidal micelles are assumed to be equivalently spherical. We have calculated $S(Q)$ as derived by Hayter and Penfold from the Ornstein–Zernike equation and using the mean spherical approximation.¹⁵ The micelle is assumed to be a rigid equivalent sphere of diameter $\sigma = 2(ab^2)^{1/3}$ interacting through a screened Coulomb potential.

Although micelles may produce polydisperse systems, we have assumed them to be monodisperse for the simplicity of the calculation and to limit the number of unknown parameters in the analysis. 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 ($\alpha = Z/N$, where Z is the micellar charge) 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, the corrections were made for instrumental smearing. For each instrumental setting the scattering profiles as given by eq 1 were smeared by the appropriate resolution function to compare with the measure data.¹⁶

Results and Discussion

Micelle Formation. Solubilization of the newly synthesized surfactants in water was achieved, depending on the number of

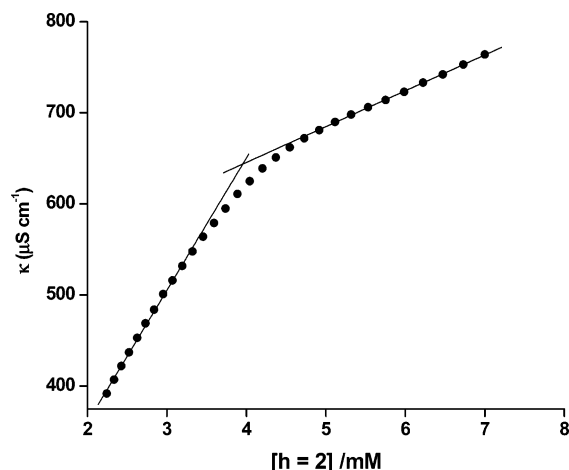


Figure 1. Specific conductance versus surfactant concentration for micellar solution of $h = 2$ at 312.5 K.

the headgroups that these surfactants had. Thus dissolving of single-headed surfactant ($h = 1$) in pure D₂O required heating, and the solution appeared translucent. Therefore all the experiments were performed at 40 °C or at higher temperature. Surfactants with $h = 2$ and $h = 3$ were, however, highly soluble in D₂O at ambient temperature, and solutions were transparent at any concentration from 25 to 100 mM. We believe that the facile solubilization in water was achieved because of the increasing hydrophilicity of the surfactant with the increase in the number of headgroups.

Critical Micellar Concentrations. The critical micellar concentrations for the surfactants were determined from electrical conductivity measurements at 40 °C by plotting the experimentally determined values of the specific conductivities (κ), as a function of surfactant concentrations. For an aqueous solution of each surfactant, a reproducible break was observed in κ vs [surfactant] plots, indicating the onset of micellization (Figure 1). In the case of surfactant with $h = 1$, clearly two inflections were observed at surfactant concentrations ~ 0.30 and ~ 0.89 mM. The cmc values obtained for surfactants $h = 2$ and $h = 3$ were 3.94 and 5.6 mM, respectively. The cmc value obtained for CPB (0.92 mM) using the same method was in good agreement with the cmc value reported for CPB in the literature.⁶ The slope of the linear region above the break was less than that below the break. This might be a consequence of the counterion binding to the pre-micellar or micellar interfaces. The cmc values were found to increase with each increase in the number of headgroups per surfactant molecule. Also, the absolute κ value increased dramatically with the increase in the number of surfactant headgroups. This is most likely due to greater headgroup repulsion in molecules bearing multiple headgroups, causing micelle formation to be less favorable. It may be noted that the cmc value is less in the case of $h = 1$ compared to that of CPB, which is also a single-headed surfactant. This can be attributed to the presence of an ester linkage in $h = 1$ between the headgroup and the hydrocarbon chain. Such a connection facilitates intermonomer association through water-mediated hydrogen bonding and dipolar interactions and therefore enhances its tendency to aggregate.

Neutron Scattering. Role of the Number of Headgroups. Figure 2 shows the SANS data from aqueous solution of single-, double-, and triple-headed surfactants along with that of CPB at fixed surfactant concentration (25 mM) at 40 °C. SANS data of double- and triple-headed surfactants and CPB show a correlation peak expected from the suspension of charged particles such as cationic micelles. However, in the case of

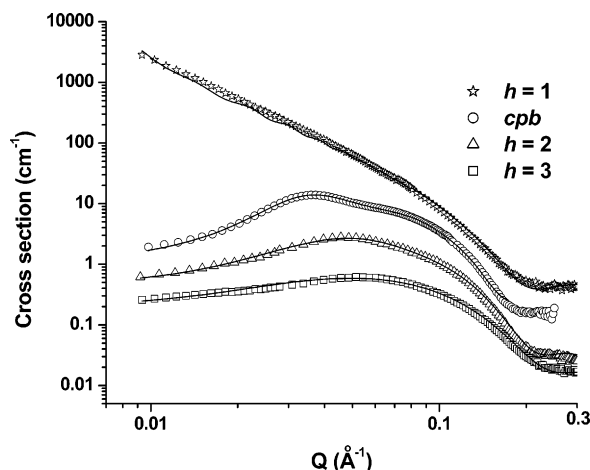


Figure 2. SANS distributions from micellar solutions of single- ($h = 1$), double- ($h = 2$), triple-headed ($h = 3$) pyridinium surfactants and CPB at 25 mM at 40 °C. The lines shown are theoretical fits, and the open symbols are experimentally determined data points.

TABLE 2: Effect of Increasing the Number of Headgroups (h) in the Surfactants on the Q -Value^a

| surfactant | N | α | $b = c$ (Å) | a (Å) | a/b |
|------------|-----|----------|-------------|---------|-------|
| CPB | 122 | 0.18 | 24.0 | 29.9 | 1.25 |
| $h = 2$ | 55 | 0.19 | 19.0 | 34.2 | 1.80 |
| $h = 3$ | 32 | 0.20 | 16.5 | 32.1 | 1.95 |

^a All the SANS spectra were taken at 40 °C using 25 mM micellar solution of each surfactant.

single-headed surfactant ($h = 1$), the characteristic of SANS data does not suggest that this system also contains the micelles. In the case of micellar solutions the SANS peak occurs at $Q_m \approx 2/\pi d$, where d is the average distance between micelles. Since Q_m was found to vary with the number of headgroups (h), one can conclude that the intermicelle distance and hence the number density (n) of the micelles is different from CPB to double-, to triple-headed surfactant solutions even when they have identical surfactant concentration. This suggests that the aggregation number (N) of the micelle varies with h . The detailed analysis further confirms that micelles are indeed formed from CPB and double- and triple-headed surfactants irrespective of h . It is found that N decreases from 122 (for CPB) to 55 (for $h = 2$) to 32 (for $h = 3$) with an increase in the number of headgroups per single hydrocarbon chain (Table 2). This is not surprising as larger headgroup sizes and enhanced electrostatic repulsion, as in the case with $h = 2$ and $h = 3$, will require greater micellar surface and would only be able to accommodate fewer number of surfactant molecules to pack into a single micellar aggregate (Figure 3). The fractional charge (α) on the micelle increases from 0.18 (CPB) to 0.20 ($h = 3$) with the number of headgroups on the surfactant. As the number of headgroups increases, the dissociation of counterions of the micelles increases and also, with an increase in charge, the headgroup hydration increases, facilitating greater ionization. Both the semimajor (a) and semiminor axes ($b = c$) decrease with increases in the number of headgroups. This is expected because with every increase in the number of cationic headgroups the charge repulsion at the headgroup level among the proximal surfactant molecule becomes more and more pronounced. To alleviate these unfavorable electrostatic repulsions, the hydrocarbon chains in the micelles of multiple-headed surfactants most likely adopt folded conformations, leading to the formation of an increasingly “disorderly” collection of surfactant molecules in the resulting micellar aggregate (Figure 3). In such less orderly aggregates,

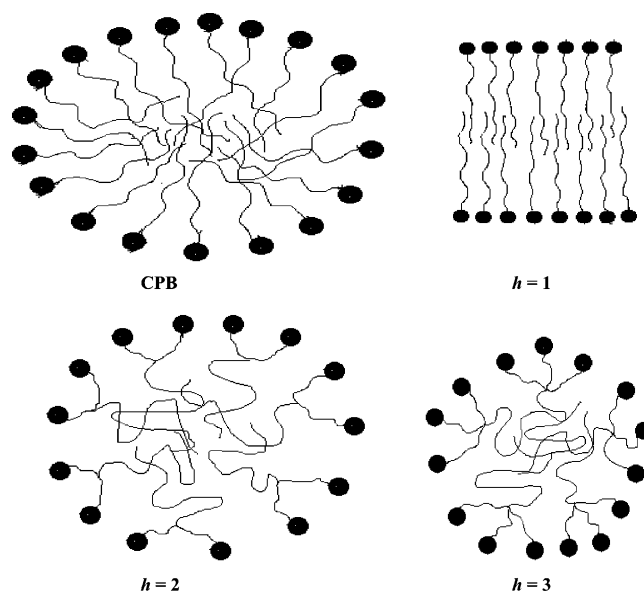


Figure 3. Schematic representation of aggregation of multiheaded surfactants where CPB, $h = 2$, and $h = 3$ form micelles but $h = 1$ forms lamellar structures.

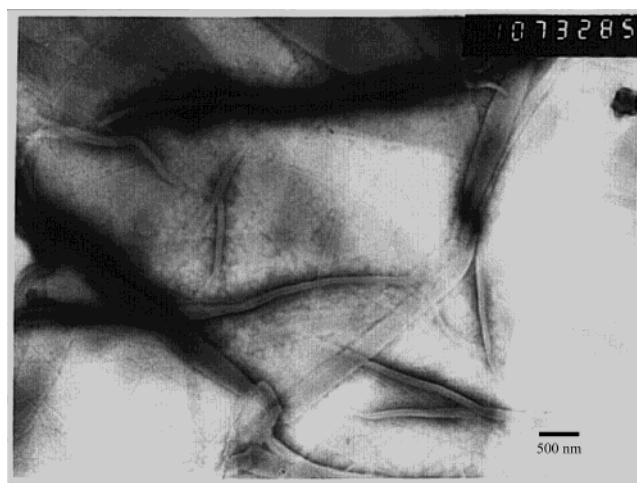


Figure 4. Negative-stain transmission electron micrograph of aqueous suspension of $h = 1$ (5 mM).

the hydrophobic core of micelle experiences significantly more exposure to the aqueous environment.

The higher scattering intensity and the nonexistence of a correlation peak in the case of $h = 1$ indicate the formation of a large structure with this system. It is found that the scattering intensity in the low- Q region ($<0.08 \text{ Å}^{-1}$) decreases as $1/Q^2$ in almost a straight line, and this suggests the formation of either lamellar or vesicular structure for $h = 1$. At higher Q values ($>0.08 \text{ Å}^{-1}$), there is an increase in the drop of the intensity and a minimum is observed. Transmission electron microscopy on this sample confirms the presence of lamellar structures (Figure 4) of widths ranging from 40 to 100 nm and length of $\sim 2 \mu\text{m}$. Formation of such ribbonlike structures indicates strong intermolecular association in such aggregates. It is possible that the presence of ester linkages and aromatic headgroups in $h = 1$ might help superposition of individual lamellae in the aggregates. We have, therefore, fitted the data for $h = 1$ assuming the lamellar structure, where the intensity varies as $1/Q^2$ in the low- Q region and the large- Q data give the thickness of the lamellar structure. The fitted value of thickness is about 30 Å. Under the same conditions, aqueous solutions of either

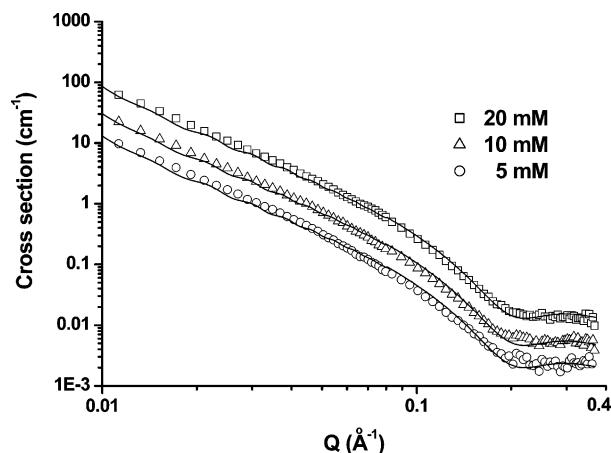


Figure 5. SANS distributions from aqueous solution of single-headed pyridinium surfactant ($h = 1$) at different concentrations: 5, 10, and 20 mM at 40 °C.

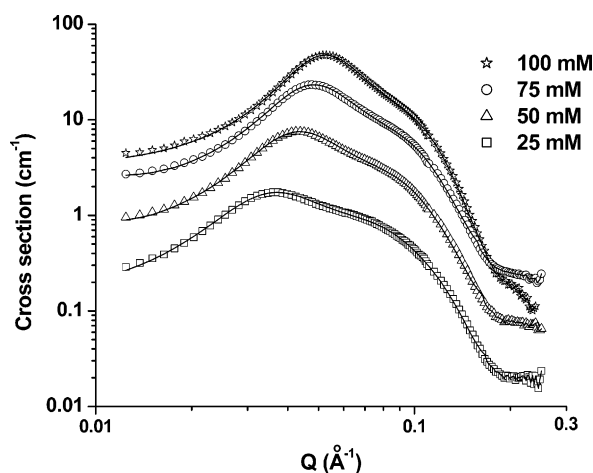


Figure 6. SANS distributions from a micellar solution of cetylpyridinium bromide at different concentrations: 25, 50, 75, and 100 mM at 40 °C.

CPB or $h = 2$ or $h = 3$ did not show existence of any lamellar or other microscopic structures.

While CPB forms a micellar aggregate in water, $h = 1$ forms a lamellar structure even though both have a single headgroup per hydrocarbon chain. It is possible that surfactant $h = 1$ is more tightly associated in the aggregate because of the presence of an ester linkage $[-OC(O)-]$ between the pyridinium headgroup and the hydrocarbon chain. The presence of this linkage facilitates intermonomer association through dipole-induced-dipole interactions. These ester linkages are located near the “Stern layer” region¹⁷ of the micelles; strong hydrogen bonding interactions among the surfactant molecules can occur through interfacially associated water molecules.¹⁸ Furthermore, unlike surfactants with trimethylammonium headgroups, surfactants with pyridinium headgroups should have additional aromatic $\pi-\pi$ interactions between the headgroups and that might also bring the surfactant monomers together resulting in the formation of the lamellar structures.

Role of Surfactant Concentration. The effect of concentration variation on the aggregation properties of all the surfactants has been examined. SANS distributions at various surfactant concentration for $h = 1$ and CPB at 40 °C are shown in Figures 5 and 6, respectively. In the case of $h = 2$ and $h = 3$, observations similar to that of CPB have been observed (not shown). The concentration variation range examined was from 5 to 25 mM for the single-headed surfactant and 25 to 100 mM

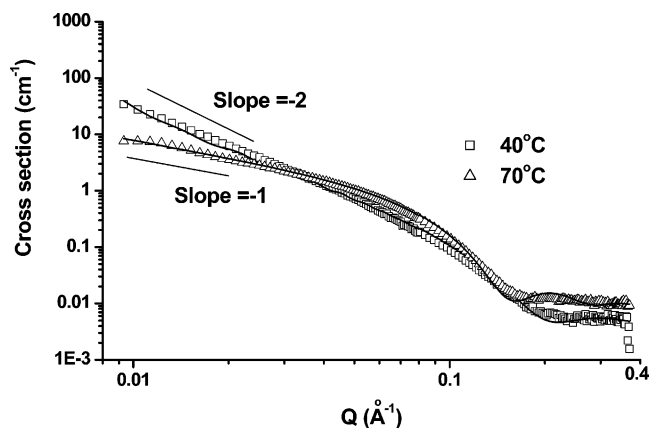


Figure 7. SANS distributions from a 10 mM aqueous solution of single-headed pyridinium surfactant ($h = 1$) at various temperatures: 40 and 70 °C.

TABLE 3: Effect of Concentration on the Q Value for CPB and Double- ($h = 2$) and Triple-Headed ($h = 3$) Surfactant Systems at 40 °C^a

| surfactant | C (mM) | N | α | $b = c$ (Å) | a (Å) | a/b |
|------------|----------|-----|----------|-------------|---------|-------|
| CPB | 25 | 122 | 0.18 | 24.0 | 29.9 | 1.25 |
| | 50 | 136 | 0.19 | 24.0 | 33.2 | 1.38 |
| | 75 | 145 | 0.19 | 24.0 | 35.0 | 1.46 |
| | 100 | 148 | 0.21 | 24.0 | 36.1 | 1.50 |
| $h = 2$ | 25 | 55 | 0.19 | 19.0 | 34.2 | 1.80 |
| | 50 | 61 | 0.20 | 19.0 | 37.4 | 1.97 |
| | 75 | 64 | 0.21 | 19.0 | 39.4 | 2.07 |
| | 100 | 66 | 0.21 | 19.0 | 40.6 | 2.14 |
| $h = 3$ | 25 | 32 | 0.20 | 16.5 | 32.1 | 1.95 |
| | 50 | 34 | 0.25 | 16.5 | 33.6 | 2.04 |
| | 75 | 36 | 0.31 | 16.5 | 35.8 | 2.17 |
| | 100 | 38 | 0.36 | 16.5 | 39.7 | 2.41 |

for CPB, double-, and triple-headed surfactants. Figure 5 shows the SANS data for $h = 1$ at the concentrations of 5, 10, and 20 mM. It is found that the data at different concentrations are similar and can be scaled by the factor of concentration. This suggests that lamellar structure remains approximately the same when the concentration is varied for $h = 1$.

For other surfactants, which form the micelles, it is observed that, with an increase in concentration, the interparticle distance decreases and the peak shifts to higher Q values. The micellar parameters for these systems are given in Table 3. It is observed that micelle size increases with the increase in the surfactant concentration. The aggregation number for CPB increases from 122 to 148 when the concentration is increased from 25 to 100 mM. This corresponds to the change in the axial ratio from $a/b = 1.25$ to $a/b = 1.5$ upon an increase in concentration. In the case of $h = 2$ and $h = 3$, N changes from 55 to 66 and from 32 to 38, respectively, and a/b changes from 1.8 to 2.14 for $h = 2$ and 1.95 to 2.41 for $h = 3$ with an increase in concentration from 25 to 100 mM.

Effect of Temperature. Keeping the surfactant concentration fixed, the SANS experiments have been performed at different temperatures from 40 to 70 °C. Figure 7 shows the variation of neutron cross-section for the aggregates of surfactants, $h = 1$ at 10 mM when the temperature is increased from 40 to 70 °C. We also see changes in slope of the curve from -2 to -1 . This indicates the lamellar to rodlike micelles with a radius of about 25 Å. A similar transition has also been observed earlier in the literature.¹⁹

The temperature dependence of the SANS cross-section for CPB at 50 mM is shown in Figure 8. Similar experiments were performed with the micellar solutions of $h = 2$ and $h = 3$ (both

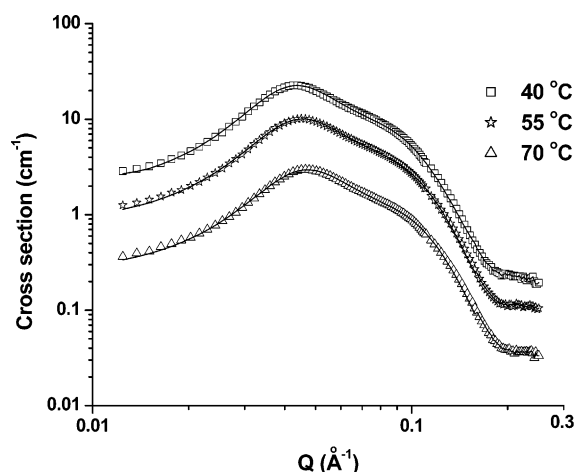


Figure 8. SANS distributions from a 50 mM micellar solution of cetylpyridinium bromide at various temperatures: 40, 55, and 70 °C.

TABLE 4: Effect of Temperature on the Q Value for CPB and Double- ($h = 2$) and Triple-Headed ($h = 3$) Surfactant Systems at 50 mM Concentration^a

| surfactant | T (°C) | N | α | $b = c$ (Å) | a (Å) | a/b |
|------------|----------|-----|----------|-------------|---------|-------|
| CPB | 40 | 136 | 0.19 | 24.0 | 33.2 | 1.38 |
| | 55 | 120 | 0.20 | 24.0 | 29.4 | 1.23 |
| | 70 | 109 | 0.22 | 24.0 | 26.5 | 1.10 |
| $h = 2$ | 40 | 61 | 0.20 | 19.0 | 37.4 | 1.97 |
| | 55 | 55 | 0.21 | 19.0 | 34.2 | 1.80 |
| | 70 | 48 | 0.22 | 19.0 | 29.9 | 1.57 |
| $h = 3$ | 40 | 34 | 0.25 | 16.5 | 33.6 | 2.04 |
| | 55 | 29 | 0.27 | 16.5 | 30.3 | 1.84 |
| | 70 | 26 | 0.27 | 16.5 | 26.8 | 1.41 |

^a The volumes of the individual surfactant and the corresponding semiminor axis ($b = c$) have been kept fixed in the fitting procedures.

at 50 mM) at different temperatures (not shown). The scattering cross-section decreases and the peak shifts to higher Q values as the temperature is increased for all the surfactant solutions. The micellar parameters from these systems are given in Table 4. The degree of counterion dissociation increases with every increase in temperature, which also leads to the increase in the effective headgroup area of the surfactant in the micelle. This in turn results in a decrease in N with the increase in the temperature. For CPB, the aggregation number decreases from 136 to 109 and α per monomer increases from 0.19 to 0.22 with an increase in temperature from 40 to 70 °C. a and a/b also decrease from 33.2 to 26.5 Å and 1.38 to 1.1, respectively, with the same increase in temperature. N decreases from 61 to 48 for $h = 2$, and for $h = 3$ it changes from 34 to 16. α also increases from 0.2 to 0.22 and from 0.25 to 0.27 for the surfactants $h = 2$ and $h = 3$, respectively. The above results indicate that micelles from CPB and multiheaded pyridinium surfactants become more spherical with the increase in temperature.

Conclusions

Aggregation behavior of three new cationic pyridinium surfactants that vary in terms of the number of headgroups and cetylpyridinium bromide (CPB) has been investigated. The critical micellar concentration increases with the increase in the number of headgroups. From small-angle neutron scattering experiments, it is shown that surfactants with double and triple headgroups and CPB form micellar aggregates in water, whereas the aqueous solution of single-headed surfactant ($h = 1$) forms lamellar aggregates. SANS analysis further indicates that the micelles become progressively smaller in size as the number

of headgroups in the surfactant increases. The aggregation number (N) is dramatically decreased and the fractional charge (α) is increased with the rise in the number of headgroups. The semimajor axis (a) and semiminor axis ($b = c$) decrease with an increase in the number of headgroups in the surfactant. With an increase in concentration, the aggregation number and the size of the micelles increase and the micelles become progressively smaller in size with an increase in the temperature. The aggregation number decreases and the fractional charge increases with an increase in temperature. These results suggest that surfactants can be successfully engineered to control the extent of formation and the structure of the aggregated species.

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References and Notes

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