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Effect of temperature and chain length of added primary amines on the sphere to rod transition of aqueous ionic micelles

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The importance of micelles as templates for nanomaterials is growing day by day. This resulted in an increasing interest for micelles in different sizes and shapes. Addition of n-amines to micellar solutions was found to bring change in the shape of the micelles from sphere to rod in aqueous ionic micellar solutions. The change in shape is qualitatively obtained from sudden change in the slope of pH versus amine concentration plots because the degree or protonation of n-alkylamines depends on the shape of micelles. In the present investigation, pH is measured at different temperatures to elucidate the influence of addition of n-amines on sphere-to-rod transition in aqueous micellar solutions. The surfactants employed in the present investigation are cetyltrimethyl ammonium bromide (CTAB), cetylpyridinium chloride (CPC), and sodium dodecyl sulphate (SDS). As the amine concentration is increased, the pH increases linearly at certain amine concentration and the slope of the resulting straight line changes on further addition of amine. It is noticed that increasing temperature requires more amine for structural transition of aqueous ionic micelles. It is also observed that the effectiveness of added amines leading to shape transition from sphere to rod is in the order of C_8NH_2>C_7NH_2> C_6NH_2.

Keywords: Aqueous ionic micelles, Critical micellar concentration, Micelle, Surfactant, Sphere-to-rod

The advent of nanotechnology broadened the spectrum of applications of micellar solutions from detergents to drugs and also being template for making nanomaterials and nanodevices[1,2]. The structure and concentration of the micelles play extremely significant role in these applications. The shapes of the micelles are generally spherical, cylindrical, conical, ellipsoidal, disc-like and lamellar. When the surfactant concentration is just above critical micellar concentration, the micelles assume spherical shape. As the concentration of the surfactant is increased, some of the spherical micelles coalesce together to take different shape. The variation in size and shape transition from one form to other are largely influenced by pressure, temperature[3], surfactant concentration[4] and nature and concentration of additives[5-8]. The shape transition is characterized by sharp change in viscosity and pH of micellarsolutions[8-11]. Formation of aggregates is significant due to the presence of aliphatic amines of higher carbon number in aqueous solutions and the aggregation is more pronounced in the presence of the salts of these amines[12].Kumar *et al*.[13] investigated the effect of addition of n-octylamine on structural transition in aqueous micellar solutions of SDS (sodium dodecyl sulfate) by viscosity and small angle neutron scattering (SANS) and they reported the corroboration of qualitative findings from viscosity with evidence obtained from SANS. Kabir-ud-Din *et al*.[14] studied the effect of addition of n-alkylamines on the structural changes of SDS micelles. They conducted experiments at 30°C and reported that the chain length of the added amine is an important parameter in micelle growth. They use both viscometry and SANS in their studies. To the best knowledge of authors, no systematic study has been reported on the effect of both temperature and chain length of added amines on the shape transition of micelles in aqueous media of cationic surfactants.For the present work two cationic surfactants *viz*., CTAB (cetyltrimethyl ammonium bromide) and CPC (cetylpyridinium chloride) are chosen.The amines selected for the present study are: C_6NH_2 (n-hexylamine), C_7NH_2 (n-heptylamine) andC_8NH_2 (n-octylamine), which are essentially insoluble in water. Experiments are conducted with SDS also which is

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well known anionic surfactant. Therefore, in the present study the effect of temperature and composition of n-amines on micellar structures of 0.3 M SDS, 0.1 M CTAB and 0.1M CPC in aqueous media have been investigated by pH measurements.

Materials and Methods

Sodium dodecyl sulphate (SDS) and Cetyltrimethylammonium bromide (CTAB) were obtained from Sigma-Aldrich of AR grade with ≥99% purity were recrystallized twice from ethanol-water mixture and acetone respectively. Both the surfactants were dried at 40°C under moderate vacuum. AR grade Cetylpyridinium Chloride (CPC) obtained from Sigma-Aldrich was used as supplied. The purity of surfactants was ascertained from the absence of minimum in the surface tension versus logarithm of concentration plots. At 25°C the critical micellar concentrations of SDS, CTAB and CPC were 8.1×10^{-3} M, 9.2×10^{-4} M and 9.0×10^{-4} M, respectively.

n-Hexylamine, n-heptylamine, n-octylamine were obtained from Fluka, "Purum" grade were dried on KOH and distilled. The amines were stored in a dry chamber. Every possible care was taken to protect the amines from exposure to atmosphere and no moisture was allowed to enter the containers. Ordinary water was first demineralized by passing through an ion-exchange column. It was distilled twice in presence of alkaline potassium permanganate in all quick fit pyrex glass assembly. 0.3 M SDS, 0.1 M CTAB and 0.1 M CPC aqueous solutions were prepared in three volumetric flasks by weighing requisite amount of surfactants and were used as mixed solvents to study the effect of n-amines on its properties. The concentration of mixed solvent was fixed throughout work. Different solutions of amines were prepared in each of surfactant solution (0.3 M SDS/0.1 M CTAB/0.1 M CPC) and the concentrations of amines were calculated as moles per kg surfactant solution. Surfactant solutions in the presence of higher amines (heptylamine and octylamine) were thoroughly shaken for 2-3 h after addition.

The pH of surfactant solutions were measured by Elico Digital pH Meter (Model No.LI120). To make measurements at constant temperature, prepared solutions were immersed in a thermostatted water bath for at least 20 minutes before measurements. The pH measurements were made at 25, 30, 35 and 40°C. The temperature of the bath was controlled to an accuracy of ±0.1°C.

Results and Discussion

Variation of pH values of surfactant solutions as a function of added amines at various temperatures are shown in (Fig. 1) for SDS, (Fig. 2) for CTAB and (Fig. 3) for CPC micellar solutions. At low molalities of amine, pH is seen to increase linearly with gradual addition of amine in very small amounts. By continuing the addition of amine, there is a sudden change in slope of straight line and with further addition of the amine the p^H varied linearly. It is clearly seen from all the plots of (Figs 1-3), that the variation of pH with concentration of added amines to micellar solution gives two straight lines with intersection. The sharp change in slope of straight line with the addition of amine is attributed to sharp transition in the shape of aggregates. It may also be seen from (Figs 1-3) that for ionic micellar systems, the effectiveness of amines leading to shape transition is in the order C_8NH_2> C_7NH_2> C_6NH_2. However shape transitions of cationic micelles (CTAB and CPC) were observed to occur at higher molalities of octylamine, heptylamine and hexylamines, in comparison with anionic micelles (SDS). The concentration of amines at which the shape transition occurred for SDS micellar systems in the present work using pH measurements as noticed from (Fig. 1) is in consistent with the results of Kumar *et al.*[13] and Kabir-ud-Din *et al.*[14].

The shape of micelle is determined essentially due to balance between two opposing forces operating at micelle's interfacial region. These are (i) electrostatic repulsive force that acts between the head groups which tends to maximize the interfacial area per molecule, and (ii) the hydrocarbon-water surface energy that favours the aggregation leading to tight packing of head groups that results in rods or discs. An increase in ionic strength in micellar solution causes a reduction in electrostatic repulsion thus favouring the aggregation. Increase in ionic strength can be brought by addition of an electrolyte or by increasing the concentration of ionic surfactant. Addition of a surface active substance such as an amine get solubilized at the surface of the micelle, promoting sphere-to-rod transition yielding mixed micelles with ionic surfactants. It is understood that the solubilization of amine in micelles of ionic surfactants is made possible by electrostatic and hydrophobic forces. The amino group gets assembled on the surface of the micelle and the solubilized amines thus tend to form mixed micelles with ionic surfactants effectively

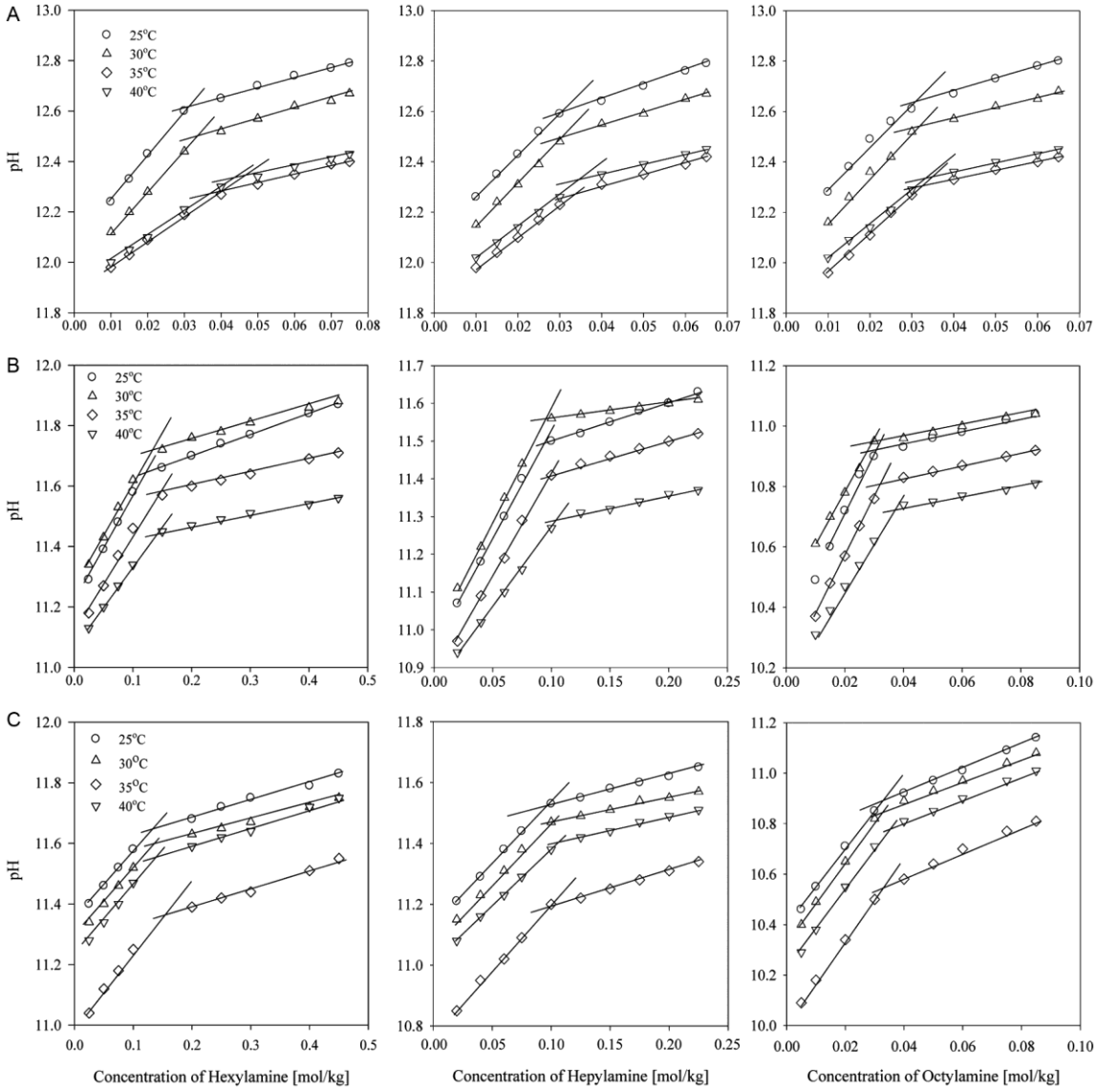

Fig. 1 — Variation of pH values of (A) 0.3 M SDS; (B) 0.1 M CTAB; and (C) 0.1 M CPC solutions as a function of added amines

causing sphere-to-rod transition[5,12-15]. The observations made from (Figs 1-3) are also in accordance of this mechanism.

Another observation that can be made by a close examination of (Fig. 1) is that at any given temperature the pH value increases slightly with increase in amine chain length. The reason for this behavior can be attributed to the solubility of amines in water. Hydrolyzation of amine takes place according to:

$$R\text{-}NH_2 + H_2O \leftrightarrow R\text{-}NH_3^+ + OH^- \quad ... \quad (1)$$

Solubilization of the amine increases because more and more protonated amines are attracted towards the negatively charged surface of the SDS micelle. This leads to reduction in the electrostatic repulsive force between the head groups, thus rendering the hydrocarbon-water surface energy more stronger thus favouring the shape transition from sphere-to-rod even at lower amine concentration. Therefore, a slight increase in pH is seen in case of SDS micellar solutions with increasing chain length of amines.

In case of CTAB/CPC systems, as revealed from (Figs 2 and 3), pH is found to decrease with increase in chain length of amine. Since these are cationic micelles, the ionization of the amines is greatly reduced so that only very small number of protonated

amine molecules could reach close to the micelles. The observed pH values of CTAB and CPC are found to be lower than that of SDS micellar solutions. The decrease in p^H values of CTAB/CPC micellar solution with increase in chain length of added amine, is due to the predominance of hydrophobic interactions than electrostatic parameter[15].

Since electrostatic repulsions are large in CTAB/CPC micellar systems than in SDS micellar system, the shape transition of CTAB / CPC micelles occurs at higher amine concentrations in comparison with SDS micelles. The concentrations of amines observed for shape transition of ionic micelles from sphere-to-rod at various temperatures are also obtained. The variation of concentration of amine for shape transition of surfactant-amine micelles as a function of temperature are shown in (Fig. 4A for SDS, Fig. 4B for CTAB and Fig. 4C) for CPC micellar systems. From (Fig. 4), it can be seen that the concentration of amine required for micellar shape transition decreases with increasing chain length of added amine for all surfactants and increases linearly with increasing temperature. However, the effect of temperature is very significant in case of SDS system, slightly significant in case of CTAB system and very marginal in case of CPC system.

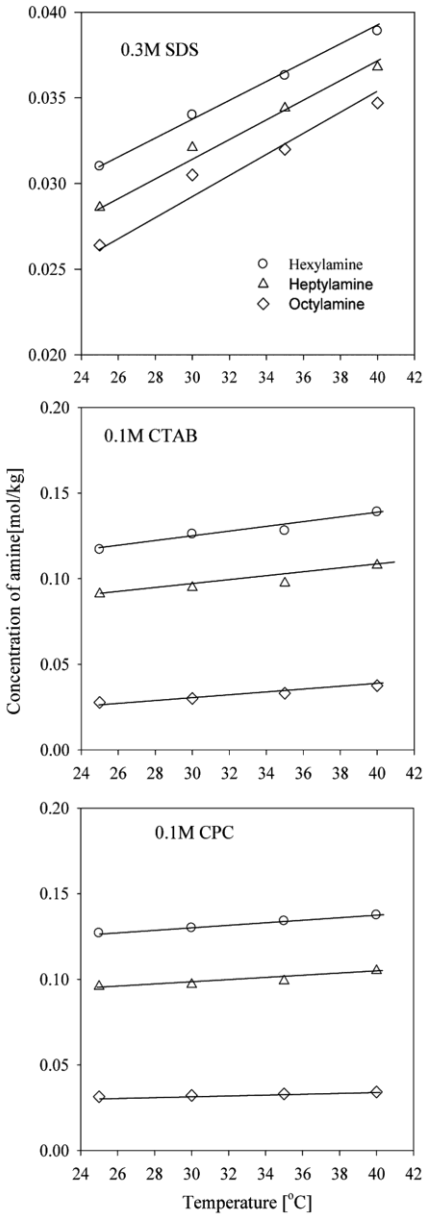

Fig. 2 — Concentration of n-alkylamine for shape transition of micelles as a function of temperature

Conclusion

In the present work, p^H measurements were used successfully as a tool for studying shape transitions of ionic surfactant and amine mixed micellar systems. For SDS, CTAB and CPC micellar systems, the effectiveness of added amines leading to shape transition from sphere-to-rod is in the order $C_8NH_2 > C_7NH_2 > C_6NH_2$. However shape transitions of cationic micelles (CTAB and CPC) occur at higher amine concentrations compared with anionic micelles (SDS). Increasing temperature increases the concentration of amine required for shape transition.

Conflict of interest

All authors declare no conflict of interest.

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