PRAMANA — journal of physics
© Indian Academy of Sciences
Vol. 71, No. 5
November 2008
pp. 997–1002

Tuning intermicellar potential of Triton X-100–anthranilic acid mixed micelles

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Abstract. Structural parameters of micelles formed by Triton X-100 in the presence of solubilized anthranilic acid at different pH values was investigated using light scattering and small angle neutron scattering. Analysis of the SANS data indicate that micelles are oblate ellipsoidal in nature with little variation in the dimensions, in the investigated pH range (from 0.5 to 6.0). The interaction potential of the micelles shows a minimum closer to the isoelectric point of anthranilic acid. A similar variation is observed in the cloud point of the micelles with pH. The observed variation in the interaction potential with pH of the micellar solution can be explained in terms of the reversal of charge on anthranilic acid due to shift in the acid–base equilibrium. The variation in interaction potential and cloud point with pH is modelled using Coulombic repulsion of charged molecules at the micelle interface.

Keywords. Complex fluids; surfactants; colloids.

PACS Nos 47.57.E; 82.70.Uv; 82.70.Dd

1. Introduction

Micellar systems are of immense technological importance. The effectiveness of a surfactant for such applications depends on the structure as well as their effect on solution properties. Nonionic surfactants represent an important class of amphiphiles, which find extensive applications in industrial and pharmaceutical formulations. In many practical applications regarding nonionic surfactants often an electrolyte is present in the medium, which plays an important role in the modification of both intermicellar and intramicellar interactions. The growth behaviour of Triton X-100 micelles in the presence of alkali metal chloride salts such as LiCl, NaBr, KCl, etc. have been studied using various techniques [1,2]. However, the structural changes of nonionic micelles in the presence of hydrophobic salts or hydrotropes that are adsorbed on the surface of micelles have not been studied extensively. The effect of salicylic acid on the structure of Triton X-100 micelles has been investigated by

SANS [3,4]. The aim of this study is to show the pH-induced changes in the surface charge of nonionic micelles. Amino acids are an important class of compounds that are susceptible to pH-induced charge reversal because they carry specific ionizable carboxyl and amine groups. In the present study, we studied the behaviour of Triton X-100 micelles (8% or 127 mM) in the presence of the hydrophobic amino acid, anthranilic acid (50 mM) at varying pH using light scattering, small angle neutron scattering (SANS) and cloud point measurements.

2. Materials and methods

Triton X-100 (isooctylphenoxy polyethoxy ethanol) was obtained from Sisco Research Laboratories, Mumbai, India and anthranilic acid was obtained from Spectrochem, Mumbai, India. SANS experiments were carried out on samples prepared in D_2O using the SANS diffractometer built at Dhruva reactor, BARC, Trombay, India. The mean wavelength of incident radiation was 5.2 Å and the measured Q (magnitude of scattering vector) range was from 0.02 to 0.3 $Å^{-1}$. Light scattering measurements were performed using a Malvern 4800 Autosizer employing a 7132 digital correlator. The light source was an Ar-ion laser operated at 514.5 nm with maximum power output of 2 W. The cloud points of micellar solution at various pH were determined visually by noting the temperature at which the thermally equilibrated solution becomes turbid. The pH of the solutions was varied by the addition of different concentrations of hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions. The concentration of Triton X-100 (8%) and anthranilic acid (50 mM) was kept constant for all the measurements.

3. Light scattering results

The variation of scattered intensity (counts) for Triton X-100 (8%) solutions in the presence of 50 mM anthranilic acid at various pH values at a scattering angle of 90° is shown in figure 1. The intensity of the scattered light is the highest at pH 3.2, which corresponds to the natural pH value of Triton X-100 (8%) and 50 mM anthranilic acid solution, and drops noticeably as pH is either increased or decreased by the addition of an acid or a base. At this low value of Q the scattering intensity depends on the volume of the scatterers, which in turn depends on the nature and strength of intermicellar interactions. Thus the observed changes in the scattered intensity can be due to the change in the net volume of the individual micelles and/or changes in the intermicellar interaction. In order to differentiate and analyse the above two effects, SANS measurements were carried out on Triton X-100 (8%) in the presence of 50 mM anthranilic acid.

4. SANS results

The evolution of the SANS spectra for Triton X-100 (8%) in the presence of 50 mM anthranilic acid at various pH is shown in figure 2. The intensity of scattered neutrons in the low Q limit $I_{(Q\to 0)}$ is maximum for pH = 3.2 and drops with any change in pH. The SANS data were analysed using core–shell oblate ellipsoid [5]

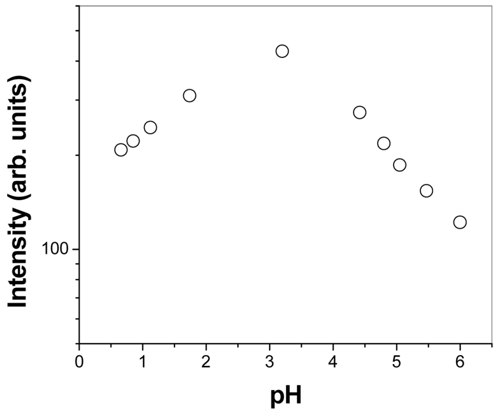

Figure 1. Variation of scattered intensity of light from Triton X-100 (8%) and 50 mM anthranilic acid micelles at different pH values.

structures for form factor ($F(Q)$). The major and minor axis of the ellipsoids were used as fitting parameters in $F(Q)$, while the thickness of the hydrophilic shell was kept constant at 13.0 Å. Triton X-100 micelles are known to contain a significant amount of water in their hydrophilic region and hence the scattering length density of the shell was calculated taking into account the degree of hydration. For calculating $S(Q)$, particles were replaced by a sphere of equal volume of diameter $\sigma = 2(a_2^2 c_2)^{1/3}$ and Baxter's sticky hard-sphere model of attractive interactions for $S(Q)$ were employed [6]. The magnitude of the attractive interaction can be described in terms of a dimensionless parameter called stickiness parameter (τ) that is related to the potential parameters (u_0, Δ, σ) and temperature T via

$$\tau = \frac{\sigma + \Delta}{12\Delta} \exp(u_0/k_{\mathrm{B}}T), \tag{1}$$

where k_{B} is the Boltzmann constant. The width (Δ) of the attractive potential was taken as a fixed parameter (3 Å), while the magnitude of the potential (u_0) was varied to quantify the changes in the interaction between the micelles. Data analysis based on the above procedure shows that the micelle dimensions do not change much with pH. Hence the variation in the SANS spectra is likely to be due to changes in $S(Q)$. The stickiness parameter (τ), which is related to the interaction potential, was found to increase on changing the pH from 3.2 (figure 3). At pH = 3.2, $\tau \sim 0.2$ and the corresponding $u_0 \sim -2.3\ k_{\mathrm{B}}T$ indicates a weak attractive interaction between the micelles. With increase in τ, u_0 becomes increasingly less negative and the attractive interaction between the micelles diminishes. The interaction potential between Triton X-100 micelles can be thought of as the sum of the attractive van der Walls interaction and Coulombic repulsion due to charged anthranilic molecules on the surface of the micelles. Assuming a Yukawa form of the potential for the Coulombic repulsion, one can approximate the interaction potential as

$$u(r) = u_1 + \frac{n^2 z_{\mathrm{AA}}^2 e^2}{\varepsilon\left(1 + \frac{\kappa\sigma}{2}\right)^2} \exp^{-\frac{\kappa(r-\sigma)}{r}}; \quad u_0 = u(r) \text{ at } r = \sigma, \tag{2}$$

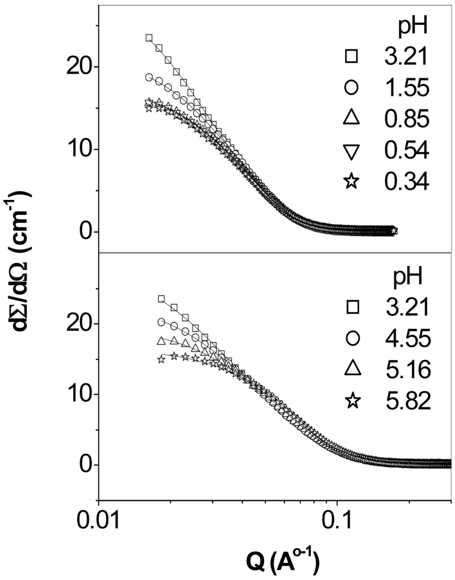

Figure 2. SANS data from Triton X-100 (8%) and 50 mM anthranilic acid micellar solutions with varying pH at 30°C.

where u_1 is the net potential of interaction that is independent of the charge on the micelles, z_{AA} is the net charge on anthranilic acid, n is the number of anthranilic acid molecules per micelle, κ is the inverse Debye screening length and ε is the dielectric constant. By substituting u_0 in eq. (1) and taking the natural logarithm, we get the expression

$$\ln(\tau) = A_1 + B_1 z_{\mathrm{AA}}^2, \tag{3}$$

where A_1 and B_1 are two pH-independent constants.

Thus one would expect that $\ln\tau$ should vary as z_{AA}^2 with a minimum at the isoelectric point of the anthranilic acid. Variation of z_{AA} with pH can be calculated using Henderson–Hasselbalch equation from the known pKa (2.14 for COOH and 4.92 for NH_2) value of the anthranilic acid. The solid line in figure 3 is a fit to the measured $\ln\tau$ value using eq. (3). Amino acid molecules that are solubilized on the surface of the micelles change the surface charge of the micelles with change in pH. Close to the isoelectric point of anthranilic acid (~3.4), the micelles are neutral and exhibit attractive interactions. With the development of any charge on the amino acid molecules due to change in pH the net attractive interaction between the micelles decreases, and this is clearly captured in the SANS pattern.

5. Cloud point results

Micellar solutions of nonionic surfactants exhibit phase separation when the temperature is raised above the so-called cloud point temperature. The cloud point

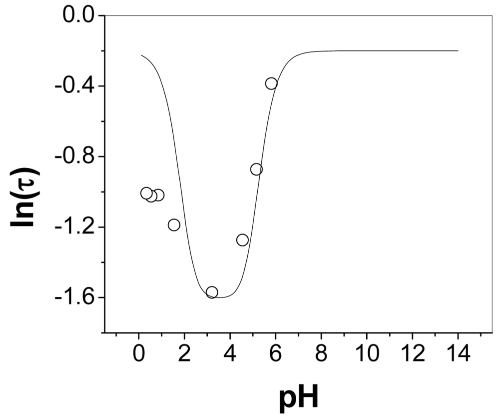

Figure 3. Variation of the sticky parameter (τ) determined from $S(Q)$ fitting as a function of pH for Triton X-100 (8%) micelles in the presence of 50 mM anthranilic acid.

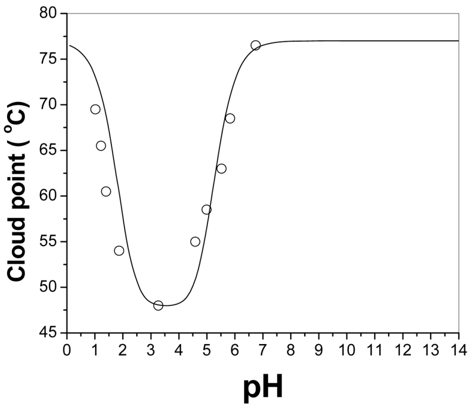

Figure 4. Variation of the cloud point (°C) of Triton X-100 (8%) micelles in the presence of 50 mM anthranilic acid as a function of pH.

temperature varies with the concentration of surfactant and the presence of salt and other additives. Figure 4 shows the variation of cloud point of Triton X-100 and anthranilic acid micelles as a function of pH. It shows a minimum at pH 3.2 and increases upon moving away from this pH similar to stickiness parameter. The cloud point T_c of a charged micelle can be thought of as the temperature at which $u(\sigma) \sim k_B T_c$. Based on this argument given for the variation of ln τ with pH, one can approximate the variation in cloud point as

$$T_c = T_0 + B_2 z_{AA}^2, \quad (4)$$

where T_0 is the cloud point of Triton X-100 (8%) and anthranilic acid (50 mM) micelles at pH = 3.2 and B_2 is constant that is independent of pH. The solid line in figure 4 is the fit to the cloud point curve using eq. (4). It is observed that both ln τ and the cloud point varies as z_{AA}^2 with a change in pH. This further confirms the fact that anthranilic acid molecules are adsorbed on the surface of the micelles and induces a reversal of charge of Triton X-100 micelles with change in pH.

6. Conclusions

The present paper demonstrates the transition from nonionic to ionic micelles from both the experimental and theoretical point of view. A micellar system with anthranilic acid adsorbed on Triton X-100 micelles is investigated by small angle neutron scattering and cloud point measurements. It has been demonstrated that the attractive intermicellar potential decreases by the adsorption of the molecules on micelle surfaces by both SANS as well as cloud point measurements. The decrease in the attractive potential with change in pH can be explained in terms of the reversal of charge on anthranilic acid due to shift in the acid–base equilibrium. Thus pH can be used to control the intermicellar interactions between the micelles in properly designed system.

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