Effect of substitution on aniline in inducing growth of anionic micelles

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Abstract. Small-angle neutron scattering (SANS) measurements were carried out on sodium dodecyl sulfate (SDS) micelles in the presence of three different hydrophobic salts, i.e. aniline hydrochloride, *o*-toluidine hydrochloride and *m*-toluidine hydrochloride. All these salts induce a uniaxial growth of micelles to form prolate ellipsoidal structures. A progressive decrease in the surface charge of the micelles was observed with the addition of salts followed by a rapid growth of the micelles. The presence of a methyl substitution at the ortho position of aniline does not alter the growth behavior significantly. However, when the substitution is at meta position micellar growth is favored at lower salt concentration than that is observed for aniline. This can be explained in terms of the difference in the chemical environments of the substituents at the ortho and meta positions.

Keywords. Small-angle neutron scattering; micelle; hydrophobic salts.

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1. Introduction

Surfactant molecules can self-assemble in water to form a variety of structures such as globular micelles, rod-like micelles, lyotropic liquid crystalline phases and so on. The optimum geometry of the aggregates formed by the amphiphilic molecules is governed by interplay of different opposing forces. The main contribution, which favors the aggregation process, arises from the hydrophobic interaction while the repulsive interaction of the head groups opposes the aggregation. By changing the magnitude of these forces, the geometry of aggregates formed by surfactant molecules can be controlled. A decrease of the electrostatic repulsion of head groups in ionic micelles can lead to a change in the structure from globular to rod-like due to increase of the surfactant packing parameter [1]. The electrostatic repulsion of head groups in ionic micelles can be conveniently tuned with addition of electrolytes. Conventional electrolytes can change the ionic strength of the medium thereby changing the range of repulsive interactions [2]. However, hydrophobic counterions that adsorb on the surface of micelles can be used to alter the surface charge

density of the micelles [3]. This offers a convenient way to alter the electrostatics of surfactant head groups and thus tailor the aggregate geometry.

Formation of rod-like micelles in dilute solutions of cationic surfactants by the addition of hydrophobic counterions is well-documented [4]. However, analogous studies on anionic surfactants are still at its infancy. The present study aims at investigating the growth behavior of SDS micelles in the presence of aniline hydrochloride (AHC) and its ortho and meta substituents, i.e., *o*-toluidine hydrochloride (OTHC) and *m*-toluidine hydrochloride (MTHC) by small-angle neutron scattering (SANS). In acidic medium, aniline and its derivatives can exist as positively charged anilinium ions that can adsorb on the surface of anionic micelles due to its electrostatic and hydrophobic interactions.

2. Materials and methods

SDS (electrophoresis grade), *o*-toluidine and *m*-toluidine were obtained from Sisco Research Labs, India. AHC is obtained from Fluka. To prepare the salts, OTHC and MTHC, an ether solution of the corresponding amines were extracted with equimolar amount of dilute HCl and crystallized by slow evaporation of the solvent. SANS measurements were carried out on samples prepared in D_2O using the SANS facility at Dhruva reactor, Trombay. The incident wavelength was 5.2 Å with $\Delta\lambda/\lambda = 15\%$. The magnitude of the scattering vector was varied from 0.02 to 0.2 Å^{-1}.

3. Results and discussion

The variation of the SANS spectra for 50 mM SDS solutions at room temperature in the presence of different amounts of AHC is shown in figure 1. The concentration of AHC is depicted as the ratio of the molar concentrations of AHC to SDS, (x_{AHC}). In the absence of any salt the SANS spectra show the characteristic correlation peak indicating the presence of repulsive intermicellar interactions. With addition of AHC this correlation peak broadens as well as shifts to lower q values. The broadening of the correlation peak at constant volume fraction of the micelles is an indication of the decrease of the range of electrostatic interactions, which can be thought of a consequence of two factors. One is due to the decrease of the Debye screening length from an increase in ionic strength of the medium in a way similar to that observed by the addition of inorganic electrolytes. The second contribution is the decrease in the surface charge of the micelles due to adsorption of the hydrophobic counterions on micellar surface.

The position of the correlation peak shifts slightly to lower q values as x_{AHC} increases, suggesting an increase of the average intermicellar distance, which would correspond to an increase in the aggregation number of the micelles. The position of the correlation peak (q_{max}) can be approximated to the average intermicellar distance (d) by the relation, $q_{max} = 2\pi/d$. The correlation peak disappears at higher salt concentrations indicating a decrease of interparticle interaction and/or increase of the micellar dimension. The SANS spectra at the high q region merge for all salt concentrations indicating that the smallest dimension of the micelles remains approximately the same. Thus the merging of SANS spectra at high q region for all
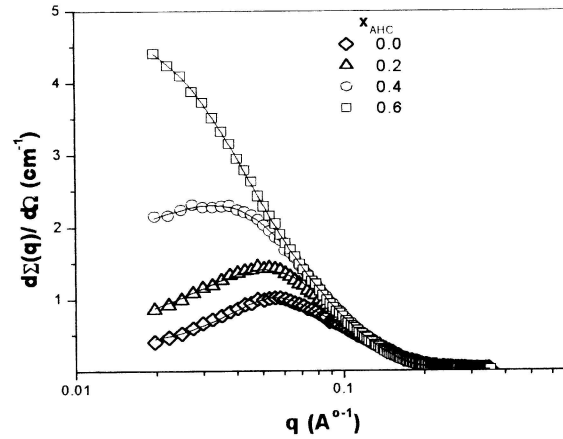
Figure 1. Scattering intensity as a function of scattering vector q for 50 mM SDS with various amounts of added AHC salt. The molar ratio of salt to surfactant is indicated as x_{AHC}.

salt concentrations suggest that the micelles are growing uniaxially. One possibility of uniaxial growth of spherical micelles is prolate ellipsoidal structure to the micelles. Such prolate ellipsoidal growth of the micelles with addition of similar hydrophobic salts has already been reported in cationic micelles [4]. Moreover, it is expected that a prolate ellipsoidal growth of the micelles could lead to a drastic increase in the relative viscosity of the solution due to the formation of entangled network of micelles. In fact, here a large increase in viscosity of the solution is observed with the addition of salt thereby suggesting a prolate ellipsoidal structure to the micelles. A quantitative estimate of the micellar parameters could be obtained by model fitting the SANS data using an appropriate form for the structure and interaction of the micelles.

The differential scattering cross-section per unit volume for a system of monodisperse interacting particles can be written as [5]

$$\mathrm{d}\Sigma(q)/\mathrm{d}\Omega = NP(q)S'(q) + B, \tag{1}$$

where N is the number density of the micelles, $P(q)$ is the particle structure factor, $S'(q)$ is the orientationally averaged structure factor and B is the constant (incoherent) background. The single particle structure factor, $P(q)$, has been calculated by assuming the micelles are monodisperse ellipsoids. For an ellipsoidal micelle with major radius a and minor radius b, $P(q)$ is [5]

$$P(q) = \int_0^1 |F(q,\mu)|^2 \, \mathrm{d}\mu, \tag{2}$$

$$F(q,\mu) = v(\rho_{\mathrm{m}} - \rho_{\mathrm{s}})\frac{3j_1(u)}{u}, \tag{3}$$
$$u = q[a^2\mu^2 + b^2(1-\mu^2)]^{0.5},$$

where v is the volume of the micelle, ρ_{m} and ρ_{s} are the coherent scattering length

densities of the micelle and solvent respectively and $j_1(u)$ is the first-order spherical Bessel function.

The interparticle structure factor $S(q)$ specifies the correlation between the centers of different particles. $S(q)$ has been evaluated analytically for charged spherical particles using the mean spherical approximation by Hayter and Penfold [6]. Later, these results have been extended to dilute charged colloidal dispersions by a rescaled mean spherical approximation (RMSA) procedure [7]. For anisotropic particles, the orientationally averaged structure factor $(S'(q))$ can be calculated using the decoupling approximation [5].

Semimajor axis of the ellipsoid and the surface charge of the micelles were used as the variables to fit the data. The micelle number density can be calculated from the concentration of micelles and the volume occupied by one surfactant monomer, assuming no volume change on mixing. The surfactant monomer volume has been estimated by Tanford formula [8]. With the addition of hydrophobic salt a change in the volume fraction of the micelle is expected as the salt is solubilized into the micelle surface. The volume occupied by the salt molecules is included in the volume fraction of the micelles, assuming that all the salt molecules are solubilized in the micelles. Because of the penetration of water molecules into the headgroup region of the micelles, the scattering length density of the headgroup region is not significantly different from that of solvent. Thus the semiminor axis (b) of the ellipsoid is taken as the length of the hydrocarbon chain (16.7 Å). The interparticle structure factor $S(q)$ is governed by the volume fraction and surface charge of the micelles and the ionic strength of the medium. The ionic strength is fixed by the concentration of unassociated surfactant molecules and counterions arising from added hydrophobic molecules. No accounting of the polydispersity of the micelles was taken, as this will introduce additional parameters in the fit. The solid lines in figure 1 shows the fit to the data and in all cases the value of the reduced chi-square is close to unity confirming the validity of the model. The parameters of the fit are summarized in table 1.

The aggregation number of the micelle is estimated from the volume of the ellipsoid and the volume occupied by surfactant and hydrophobic salt molecules. The fractional charge is estimated from the ratio of surface charge of the micelles to the aggregation number. The aggregation number observed for SDS micelles in the absence of any added salt is in good agreement with those reported earlier [2]. The micelle aggregation number increases upon addition of AHC and the fractional charge on the micelle initially decreases quickly and then reaches a steady value.

Table 1. Micellar parameters obtained from 50 mM SDS with varying concentration of AHC salt.

x_{AHC}	Aggregation number (N_{agg})	Fractional charge (α)	Semiminor axis, b (Å)	Semimajor axis, a (Å)
0	75	0.21	16.7	22.5
0.2	106	0.07	16.7	35.6
0.4	133	0.03	16.7	49.7
0.6	207	0.01	16.7	84.9

Effect of substitution on aniline in inducing growth of anionic micelles

Table 2. Micellar parameters obtained from 50 mM SDS with 20 mM concentration of AHC, OTHC and MTHC salts ($x_{\mathrm{salt}} = 0.4$).

$x_{\mathrm{salt}} = 0.4$	Aggregation number (N_{agg})	Fractional charge (α)	Semiminor axis, b (Å)	Semimajor axis, a (Å)
x_{AHC}	133	0.03	16.7	49.7
x_{OTHC}	131	0.03	16.7	50.0
x_{MTHC}	197	0.02	16.7	75.1

SANS studies on SDS micelles in the presence of substituted aniline hydrochloride, i.e. OTHC and MTHC also showed prolate ellipsoidal growth of the micelles. In the presence of OTHC, the growth behavior of SDS micelles was found to be similar to that of AHC. However, when the substitution is at meta position, micellar growth is favored even at lower salt concentration than that is observed for AHC. A comparative data of the micellar parameters for $x_{\mathrm{salt}} = 0.4$ is given in table 2, which clearly suggests the enhanced growth of the anionic SDS micelles in the presence of the *m*-toluidine hydrochloride (MTHC) in comparison with that of *o*-toluidine hydrochloride (OTHC).

The difference in the growth of SDS micelles in the presence of OTHC and MTHC may be explained in terms of the difference in the chemical environments of the substituents on the counterions at the SDS micellar surface. The salt molecules reside on the surface of the micelles in such a way that the NH_2 group and the ortho protons experience hydrophilic environment while the meta and para protons experience hydrophobic environment. Since ortho group is directed towards the hydrophilic part, the presence of methyl group at ortho position of aniline hydrochloride does not alter the growth behavior of SDS micelles. However, a substitution at the meta position of aniline hydrochloride influences the growth behavior significantly due to the fact that the substituent is directed towards the hydrophobic core of the micelles thereby increasing its ability to adsorb on the surface of the micelles.

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