

Small angle neutron scattering studies of mixed micelles of sodium cumene sulphonate with cetyl trimethylammonium bromide and sodium dodecyl sulphate

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Abstract. The aqueous solutions of sodium cumene sulphonate (NaCS) and its mixtures with each of cetyl trimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS) are characterized by small angle neutron scattering (SANS). NaCS when added to CTAB solution leads to the formation of long rod-shaped micelles with a dramatic increase in the CTAB aggregation number. Its addition to SDS on the other hand results in the formation of smaller mixed micelles where part of SDS molecules in the micelle is replaced by NaCS molecules.

Keywords. Mixed micelle; small angle neutron scattering; hydrotrope; sodium cumene sulphonate.

PACS Nos 28.20.Cz; 28.20.Fc; 61.05.Fd; 78.70.Nx; 83.35.Jn

1. Introduction

Hydrotropes are mild surface active amphiphilic organic salts with hydrophobic part comparatively smaller than that of a conventional surfactant. Hydrotropes exhibit a higher and often more selective ability to solubilize guest molecules. The self-aggregation of the hydrotropes has been considered to be a pre-requisite for a number of applications in various fields such as drug solubilization [1], chemical reactions [2], separation of organic compounds [3], etc. The hydrotropic phenomenon has been used recently for the extraction of curcuminoids from turmeric [4], piperine from *Piper nigrum* [5] and boswellic acids from *Boswellia serrata* resins [6]. The studies carried out on individual hydrotropes or surfactant-hydrotrope mixtures support the fact that hydrotropes are capable of forming self-aggregates in the aqueous solutions above a certain minimum concentration known as minimum hydrotrope concentration (MHC), analogous to critical micellar concentration (CMC) for surfactants [7,8].

Pal *et al* [9] had characterized the CTAB + BBS mixed system by SANS indicating sphere-to-rod transition of CTAB micelles with the addition of small amounts (~ 10 mole%) of BBS and a sharp increase in the viscosity of the solution. Sodium cumene sulphonate (NaCS) is another hydrotrope found useful in a number of applications such as extraction of natural products [4], chemical reactions [10], etc. The hydrophilic headgroup of NaCS and *n*-butyl benzene sulphonate (NBBS) is the same but they differ in their hydrophobic part. The aim of the present work is two-fold. An attempt is made to compare the solution properties of NaCS–CTAB mixture with that of NBBS–CTAB mixed system. Also, the difference in the behaviour of NaCS when oppositely charged CTAB is replaced by similarly charged sodium dodecyl sulfate (SDS) is demonstrated using small angle neutron scattering (SANS).

2. Materials and methods

Sodium dodecyl sulfate (SDS (99%)) was obtained from Fluka and was used as such. Cetyl trimethylammonium bromide (CTAB) of 99% purity was obtained from Spectrochem and was recrystallized with methanol + acetone (1:1) mixture before use. Sodium cumene sulphonate (NaCS) was obtained from Navdeep Chemicals Ltd., Mumbai, India. The impurities, such as inorganic salts, were removed from the hydrotrope by its repeated re-crystallization from methanol. D₂O (99.4% purity) was supplied by the Heavy Water Division, BARC, Mumbai, India. All other reagents and solvents were of the highest grade available.

The SANS experiments were performed on a SANS diffractometer at the Dhruva reactor, BARC, Mumbai [11]. All the solutions used in the neutron scattering experiments were prepared in D₂O in order to have a good contrast between the micelles and the solvent. The temperature was maintained at $30 \pm 1^\circ\text{C}$, unless stated otherwise. The expression for the differential cross-section $d\Sigma/d\Omega$ for a collection of polydispersed colloidal particles is given by

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

where ρ_m and ρ_s are the scattering length densities of the mixed micelle and the solvent, respectively; $n(a)$ and $V(a)$ are the number density and volume of the mixed micelles having semi-major axis (a), $f(a)$ gives the length distribution of the micelles and Q is the scattering vector. The polydispersity is assumed to be present only in the semi-major axis (a) of the micelle. Schultz distribution was used for the calculation of polydispersity of the mixed micelles. Semi-major axis (a), semi-minor axis (b) and the fractional charge were the fitted parameters in the analysis. These parameters were optimized by means of least square analysis and the error was calculated by standard methods [12].

For the calculation of the composition of the mixed micelles, Rubingh's regular solution theory was used which accounts for the non-ideality of the mixtures in terms of the components' activity coefficients [13].

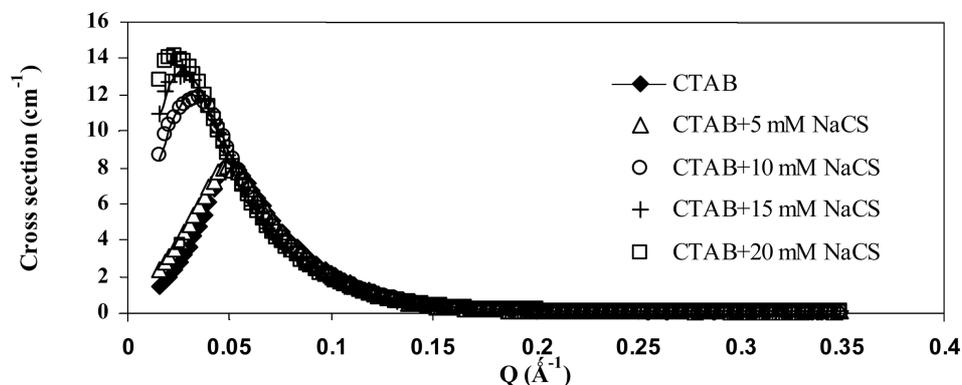


Figure 1. SANS distribution of 100 mM CTAB with NaCS of different concentrations.

3. Results and discussion

Figure 1 shows the SANS spectra of 100 mmol/dm³ CTAB in the presence and in the absence of NaCS. With the addition of NaCS from 5 mmol/dm³ to 20 mmol/dm³, the Q_{\max} was shifted to lower Q (from 0.0494 Å⁻¹ to 0.0231 Å⁻¹). It was a clear indication of the growth of CTAB micelles in the presence of oppositely charged NaCS molecules. These results were similar to those obtained by Pal *et al* [9] for the addition of NBBS to 100 mmol/dm³ CTAB solution. There was sphere-to-rod transition of the CTAB micelles when oppositely charged NBBS was added to it. Even though the peak shifted to lower Q with increasing concentration of NaCS, the large Q data (>0.04 Å⁻¹) was independent of the hydrotrope concentration suggesting that one dimension of the micelles (i.e. semi-minor axis) was not affected significantly.

CTAB (100 mmol/dm³) forms ellipsoidal micelles with semi-major axis 48.6 ± 2.4 Å and semi-minor axis 20.6 ± 0.4 with an aggregation number 156 ± 14 (table 1). The addition of NaCS to CTAB solution led to the dramatic growth of the CTAB micelles. The semi-minor axis was almost constant whereas the semi-major axis increased from 49 Å to 167 Å with the addition of 15% NaCS to the CTAB solution.

The quantitative results for CTAB + 20 mmol/dm³ NaCS could not be obtained due to the limitations of the SANS instrument to provide data at still lower Q range. The comparison of the quantitative results for CTAB-NBBS [9] and CTAB-NaCS mixed systems indicates that the structural changes in the CTAB micelles with the addition of oppositely charged hydrotrope were dominated by the electrostatic effect between the head groups and the effect due to the differences in the length of the hydrotrope were insignificant.

Similar to CTAB micelles, SDS micelles were also charged and showed significant intermicellar interaction (figure 2). NaCS solution at 1000 mmol/dm³ concentration showed very broad interaction peak at 0.214 Å⁻¹ with minimum intensity. Without NaCS, SDS spectra showed Q_{\max} at 0.0661 Å⁻¹ which was shifted to 0.059 Å⁻¹ with the addition of 200 mmol/dm³ NaCS. When the concentration of NaCS was further increased, the peak was shifted to higher Q indicating formation of smaller mixed

Table 1. Characteristics of CTAB–NaCS and SDS–NaCS mixed system with respect to the concentration of NaCS (P: polydispersity).

System	N_{NaCS}	$N_{\text{surfactant}}$	Semi-major axis, a (Å)	Semi-minor axis, b (Å)	P (%)	Fractional charge, α
100 mM CTAB (A)	0	156±14	48.6±2.4	20.6±0.4	20	0.13
A + 5 mM NaCS	8±1	167±17	51.4±3.2	21.1±0.4	20	0.08
A + 10 mM NaCS	37±5	365±48	107.0±11.0	21.8±0.3	32	0.03
A + 15 mM NaCS	76±13	506±83	148.0±19.0	22.1±0.4	40	0.02
100 mM SDS (B)	0	77±5	27.8±0.9	15.2±0.2	15	0.21
B + 100 mM NaCS	49±4	56±5	32.3±1.5	14.8±0.3	20	0.09
B + 200 mM NaCS	70±8	39±5	39.2±3.0	13.1±0.3	22	0.09
B + 300 mM NaCS	79±9	29±4	42.5±3.1	12.1±0.3	25	0.08
B + 400 mM NaCS	84±12	23±3	48.4±4.2	11.0±0.3	28	0.08

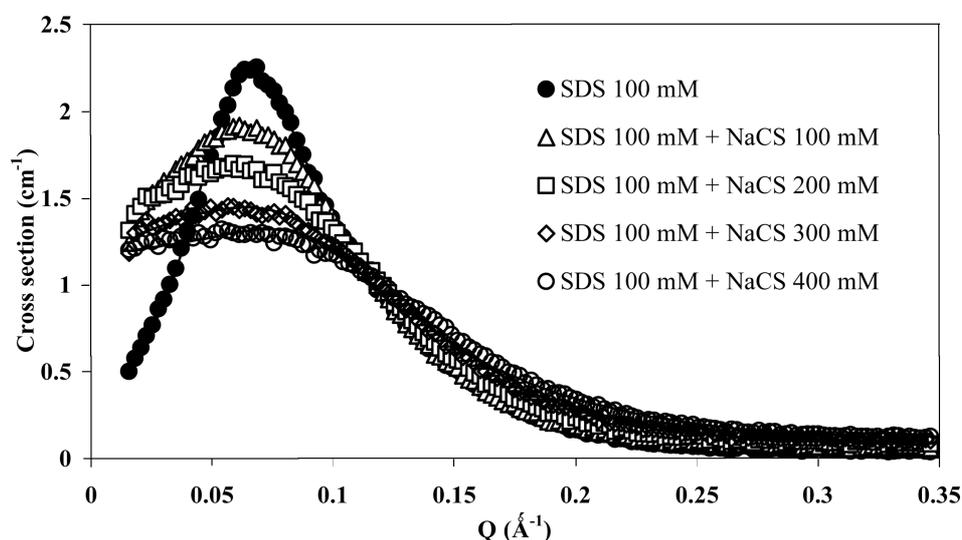


Figure 2. SANS distribution of 100 mM SDS with NaCS of different concentrations.

micelles. The intensity of the spectra decreased continuously with the addition of NaCS to the SDS solution.

When compared with CTAB, SDS formed smaller ellipsoidal micelles with semi-major axis 27.8 ± 0.9 Å, semi-minor axis 15.2 ± 0.2 Å and aggregation number 77 ± 5 (table 1). Addition of NaCS to SDS solution led to the formation of elongated micelles with increased aggregation number. Since the hydrophobic part of NaCS is very small compared to SDS, the mixed micelles preferred rod-shaped geometry with ordering of SDS tails in such a way that the smaller NaCS molecules can be accommodated in the mixed micelle. This behaviour was totally opposite to that observed in CTAB–NaCS mixed micelles where addition of NaCS to CTAB led to the formation of elongated rod-shaped micelles with increased number of

CTAB molecules. With the addition of 400 mmol/dm³ NaCS, the semi-minor axis decreased from 15.2±0.2 Å to 11.0±0.3 Å which requires folding of SDS tails inside the micelle. Semi-major axis on the other hand showed opposite trend.

4. Summary

Addition of NaCS to CTAB solution led to the dramatic increase in the CTAB aggregation number with sphere-to-rod transition of the CTAB micelles. There was growth of CTAB micelles along the semi-major axis whereas the semi-minor axis was not affected significantly. The NaCS–SDS mixed system on the other hand formed smaller micelles with elongated ellipsoidal geometry. Both, semi-major and semi-minor axes of the SDS micelles were modified with the addition of NaCS.

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