Small-angle neutron scattering studies of sodium butyl benzene sulfonate aggregates in aqueous solution

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Abstract. The aggregation behaviour of a hydrotrope, sodium n-butyl benzene sulfonate (Na-NBBS), in aqueous solutions is investigated by small-angle neutron scattering (SANS). Nearly ellipsoidal aggregates of Na-NBBS at concentrations well above its minimum hydrotrope concentration were detected by SANS. The hydrotrope seems to form self-assemblies with aggregation number of 36–40 with a substantial charge on the aggregate. This aggregation number is weakly affected by the hydrotrope concentration.

Keywords. Hydrotrope; aggregation; sodium butyl benzene sulfonate; small-angle neutron scattering.

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1. Introduction

Hydrotropes, the amphiphilic and highly water-soluble organic salts, show an excellent property of dissolving other water-insoluble or sparingly soluble organic compounds in their aqueous solutions. The solubilization capacity of hydrotropes is far higher compared to the conventional surfactants and that has prompted their applications in detergents formulations [1], drug solubilization [2] and, in recent years, in formation of complex fluids with other surfactants bearing opposite ionic charges on their head groups [3–6]. Sodium salicylate is the most studied hydrotrope for the investigation of complex fluid formation with cationic surfactants such as cetyltrimethyl ammonium bromide (CTAB). Our own investigations [5] of three isomers of sodium butyl benzene sulfonate in combination with CTAB and cetylpyridinium chloride (CPC) have revealed the importance of the structure of the hydrotrope in determining the viscoelastic behaviour of hydrotrope and surfactant combinations in water.

Unlike surfactants, the aqueous solutions of hydrotropes have not received the attention they deserve. Because of their much smaller hydrophobic groups, usually

with C_3–C_4 alkyl chains, hydrotropes are considered to be poorly surface-active and in fact were treated as ionic salts in the early literature on hydrotropy [7,8]. However, due to a surge in interest in development of newer applications of hydrotropes in recent years [1,6,9], the characterization of hydrotrope solutions, with or without combination with conventional surfactants, is increasingly being attempted [5,10–13]. Although the self-aggregation tendency of hydrotropes has been hypothesized since long and it is also getting increasingly accepted, the aggregation parameters have not been investigated so far.

Analogous to critical micellar concentration (CMC) of a surfactant, hydrotrope molecules self-aggregate into loose assemblies, above a minimum hydrotrope concentration (MHC) which offer a microenvironment of a lower polarity and increased microviscosity that aids the solubilization of a water-insoluble solute [10]. Srinivas *et al* [11] have reported the crystal structures of several hydrotropes in solid phase by X-ray diffraction. These solid compounds showed open layer assemblies, reminiscent of lamellar liquid crystals of a surfactant, consisting of alternating hydrophobic clusterings of the non-polar regions adjacent to the ionic or polar regions that are knitted together in a two-dimensional network. Their studies did not, however, show the expected stacking of aromatic rings of the aromatic sulfonates as proposed earlier [13]. However, the aggregation behaviour of hydrotropes themselves in aqueous solutions is still uncertain. We have selected sodium *n*-butyl benzene sulfonate (Na-NBBS) as a model hydrotrope and used the SANS technique as a tool to understand its aggregation characteristic.

In this paper, the results of SANS experiments are reported, investigating the shape and size of the aggregates of sodium *n*-butyl benzene sulfonate in aqueous solutions. To the best of our knowledge this is the first SANS report on the aggregation behaviour of a hydrotrope in aqueous solutions.

2. Materials and methods

n-Butyl benzene, procured from Herdilia Chemicals, Mumbai, was sulfonated by concentrated sulphuric acid (98%) followed by neutralization with sodium hydroxide as reported earlier [5]. Sodium *n*-butyl benzene sulfonate (Na-NBBS) was purified by repeated crystallizations from methanol and dried at 80°C for 4–5 h. D_2O (99.4%) was supplied by Heavy Water Division, Bhabha Atomic Research Centre (BARC), Mumbai. The viscosity of aqueous solutions was determined using an Ostwald's glass viscometer at 30°C.

The sample solutions for SANS measurements were prepared by dissolving appropriate quantities of Na-NBBS in D_2O. For the SANS measurements the solutions were held in a quartz cell of 0.5 cm thickness with tight fitting teflon stoppers and all measurements were carried out at a temperature of 30 ($\pm$0.1°C).

The SANS experiments were performed using a SANS diffractometer at Dhruva reactor, BARC, Mumbai [24]. The data were recorded in the Q range of 0.02–0.25 Å^{-1}. The measured SANS distributions were corrected for the background and the solvent contributions and normalized to the cross-sectional units, using standard procedures [14].

3. Results and discussion

The SANS distribution has been analysed by the Hayter–Penfold analysis for the colloidal solutions [15]. The coherent scattering cross-section, $d\Sigma/d\Omega$, for a system of monodispersed interacting aggregates is given as

$$\frac{d\Sigma}{d\Omega} = n_{\mathrm{m}} V_{\mathrm{m}}^2 (\rho_{\mathrm{m}} - \rho_{\mathrm{s}})^2 \{ \langle F^2(Q) \rangle + \langle F(Q) \rangle^2 (S(Q) - 1) \}, \tag{1}$$

where n_{m} denotes the number density of the particle (aggregate), ρ_{m} and ρ_{s} are the scattered length densities of particle and solvent (D_2O), respectively, $V_{\mathrm{m}} (= 4\pi a^2 b/3)$ is the solvent excluded volume of an ellipsoidal particle where a and b are the semiminor and semimajor axes of the ellipsoid, respectively.

For the SANS data analysis, the semiminor axis a was fixed at 10.7 Å, i.e. length of a Na-NBBS monomer. The volume of Na-NBBS was taken to be 238.6 Å^3 for the calculation of scattering length density. Its volume was calculated from the density measurements of aqueous solutions of Na-NBBS. Although the structure of hydrotrope aggregates is not established yet, it is believed to be like surfactant micelles and it could be a polydisperse system. But to avoid the complexity of calculations we assumed them as monodispersed in this preliminary report. The dimensions of the aggregates (a, b), aggregation number (N_{a}) and the fractional charge (α) have been determined from the analysis.

The small-angle neutron scattering measurements covered the Na-NBBS concentration range from 0.12 (just above its MHC) to 1.5 mol·dm^{-3} and the SANS distributions are shown in figure 1. At concentration 0.12 and 0.4 mol·dm^{-3}, the scattered intensity is extremely low and the data show no evidence of aggregates in the solution. It must be noted that other experimental techniques such as surface tension and solubilization studies, indicated the MHC of Na-NBBS to be 0.1 mol·dm^{-3}, i.e., Na-NBBS aggregates above this concentration [5]. The SANS, however, could not detect the aggregation, if any, at these concentrations which indicates that the hydrotrope remains either as loose aggregates or the aggregate concentration is not enough to give appreciable scattering. However, at higher concentrations, i.e. at and above 0.8 mol·dm^{-3}, the interaction peak with typical intermicellar interaction appears. With the increase in concentration from 0.8 to 1.5 mol·dm^{-3}, the interaction peak shifts to higher Q continuously and the peak height increases, indicating increase in the number density of the particles. These results indicate very small aggregates in the concentration range from MHC of Na-NBBS to 0.8 mol·dm^{-3} which must grow during this concentration range. This behaviour of Na-NBBS is similar to the behaviour of surfactant solutions such as sodium dodecyl sulfate (SDS), which also shows detectable aggregates well above its CMC [16]. The SANS, therefore, indicate a possible stepwise growth and possibility of strong polydispersity in the solution. Beyond 0.8 mol·dm^{-3}, the SANS spectra indicate further increase in the number density of particles and poor growth of the aggregates. Although the data are limited, SANS behaviour is a clear indication of charged aggregates in the solution. However, the way these molecules aggregate is a point of debate. Hydrotropes such as Na-NBBS with sufficiently longer alkyl group, may show an aggregation of only the butyl chains forming a small hydrophobic region while the aromatic rings with sulfonate group keeps a substantial
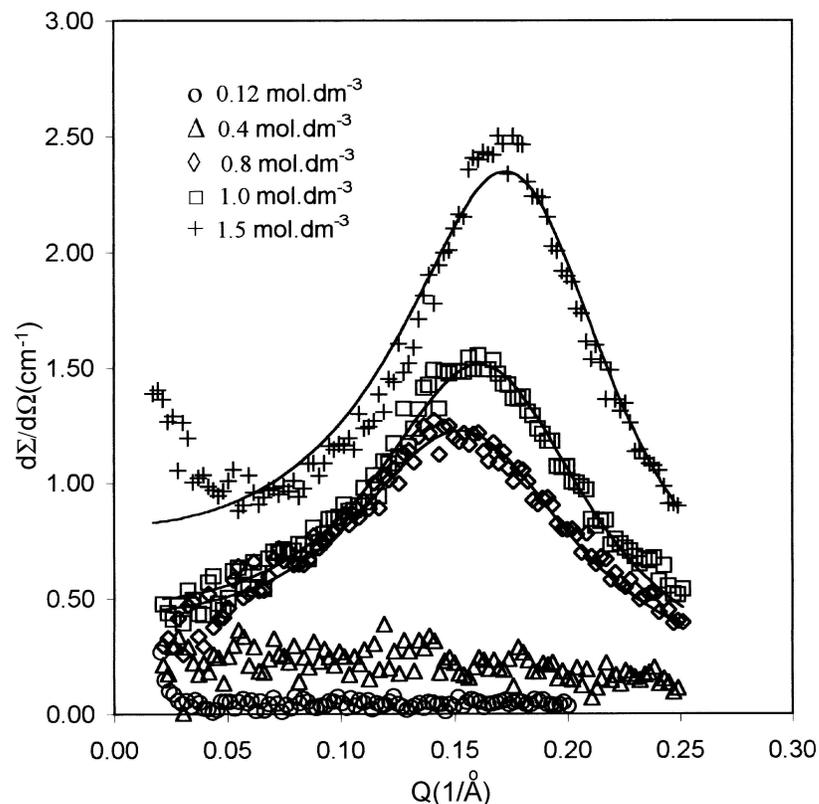
Figure 1. SANS distribution of aqueous Na-NBBS solutions as a function of concentration.

contact with water and hence probably retain the strong electrolyte nature. Since the viscosity increase for the hydrotrope solutions is also not very large, the size of the hydrotrope aggregates also is not expected to be very big. The clustering of few hydrotrope molecules is thus expected and hence the structure will resemble a small rod or, at the most, ellipsoid to accommodate the aromatic rings, and at the same time to avoid large specific surface area by making the cluster spherical. We, therefore, analyzed the SANS distribution data assuming an ellipsoid geometry of the aggregates of Na-NBBS. Figure 1 shows the solid lines indicating the theoretical fit.

The parameters obtained from the fit are given in table 1. With the increase in concentration from 0.8 to 1.5 mol·dm^{-3}, there is a marginal increase in the aggregation number from 36 to 42. The axial ratio of the particle changed from 1.69 to 1.96 at the same time, which indicates that the shape of the Na-NBBS aggregate is of a prolate ellipsoid. The fractional charge of the Na-NBBS aggregate is about 0.4 and is comparatively higher than that on anionic surfactant SDS [16] micelles at approximately the same concentration and it decreased with increase in the hydrotrope concentration. With the increase in the hydrotrope concentration,

Table 1. Aggregation parameters for Na-NBBS by Hayter–Penfold analysis of the SANS data.

Na-NBBS conc. $(\text{mol}\cdot\text{dm}^{-3})$	Aggregation number (N_a)	Fractional charge, α	Semiminor axis, a (Å)	Semimajor axis, b (Å)
0.8	36	0.45	10.7	18.1
1.0	38	0.42	10.7	18.9
1.5	42	0.33	10.7	21.0

the relative viscosity (viscosity with respect to water) of Na-NBBS solutions also increases (figure 2). At high concentrations, the distance between the hydrotrope aggregates become comparable to the aggregate size and the counterions stay in the vicinity of the hydrotrope aggregates neutralizing the charge of the aggregate more effectively which results in the decrease of fractional charge α. In highly dense and colloidal systems, the counterions are more tightly bound in order to reduce the repulsion between the charged heads on the aggregate surface. The SANS results show that the hydrotrope Na-NBBS does form aggregates in aqueous solutions but of a smaller size as compared to the surfactant SDS.

4. Conclusions

The microstructures of Na-NBBS aggregates in aqueous solutions as investigated by SANS show ellipsoidal aggregates in the concentration range of 0.8 to 1.5 $\text{mol}\cdot\text{dm}^{-3}$.
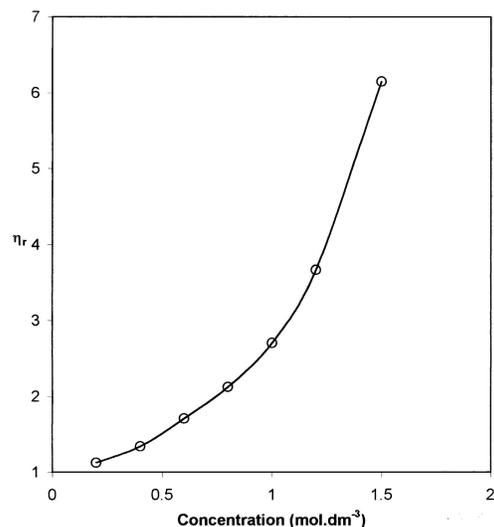

Figure 2. Relative viscosity (η_r) of aqueous Na-NBBS solutions as a function of concentration.

Na-NBBS exhibits co-operative aggregation, albeit loose at low concentrations, forming self-assembly analogous to micelles of an anionic surfactant. Increase in the concentration also leads to a decrease in fractional charge on the aggregates because of the counterion binding. The SANS measurements can be used to determine the geometry and interaction of hydrotrope aggregates.

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