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Temperature dependent small-angle neutron scattering of CTABr–magnetic fluid emulsion

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Abstract. Small-angle neutron scattering studies have been carried out to check the structural integrity of citryltrimethylammonium bromide (CTABr) micelles in a magnetic fluid for different magnetic fluid concentrations at two different temperatures 303 and 333 K. It is found that the CTABr micelles grow with increasing magnetic fluid concentration and there is a decrease in the micellar size with increase in temperature.

Keywords. Magnetic fluids; micellar solutions; small-angle neutron scattering.

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1. Introduction

Neutron scattering experiments on randomly oriented scattering particles in solution yield spherically averaged data and such data can only provide information on general shape and boundaries of the scattering particles. If the particles are partially oriented by being given a definite orientation, the resulting scattering data contain more detailed structural information. Magnetic fluids, a stable colloidal dispersion of nanomagnetic particles in a magnetically passive liquid, have been used successfully to orient biological assemblies such as tobacco rattle viruses (TRV) [1]. In this technique, magnetic forces cause the moments or spins of the magnetic particles to align along the direction of magnetic field and their alignment, in turn, causes alignment of the dispersed assemblies. It is to be mentioned here that such assemblies, which are to be aligned, have intrinsic diamagnetic moments and therefore can be aligned along the field direction in the absence of magnetic particles but a very strong magnetic field is required. In contrast, the magnetic fluid alignment technique requires no intrinsic magnetic properties of the dispersed assemblies and only moderate field is required.

The preliminary aim of this work is to examine the possibility of this new alignment technique to align micelles in micellar solutions and to find whether the structural integrity of the micelles in a micellar solution is disturbed due to the presence of magnetic fluid. Micelles are aggregates of surfactant molecules and these aggregates are usually formed in different shapes of spherical, cylindrical, ellipsoidal, disc-like etc. The size and shapes of these micelles are studied using small-angle neutron scattering (SANS) [2]. A preparation of stable emulsion of magnetic fluid with micelles will be of great interest, as this will give rise to the additional characteristic of magnetic behavior to the micellar solutions. The magnetic behavior of the micellar solutions will allow controlling the properties of micellar solutions in the presence of magnetic field if the micelles can be aligned. These studies are of importance as the micellar solutions are widely used in household, industrial and research applications [3].

Cetyltrimethylammonium bromide (CTABr), being a cationic surfactant, ionizes in water. CTABr micelles are thus essentially aggregates of CTA^+ ions and micelle is positively charged. The Br^- ion, referred to as counter-ion, tend to stay near the surface of the micelle. Micellar solution of CTABr is isotropic at temperatures above 301 K in the concentration range of 0.001 M to 0.72 M. CTABr micelles are spherical at low concentration but become prolate shaped at higher concentration. In 0.1 M solution of CTABr, micelles are ellipsoidal ($a \neq b = c$) and a/b ratio is 2.2 (where a is semimajor axis and $b = c$ is semiminor axis) [2]. It is also known that spherical CTABr micelles grow to ellipsoidal micelles by the addition of salt such as NaSal, KBr etc. [4–8]. Several CTABr–magnetic fluid emulsions with varying magnetic fluid concentration were prepared. Here we report the results of SANS studies of these emulsions for different concentration of magnetic fluids at 303 and 333 K.

2. Experimental

Based on the work reported by Shimoizaka *et al* [9] and Wooding *et al* [10], we have produced aqueous magnetic fluids containing Fe_3O_4 particle using two-step processes [11]. The magnetic particles were characterized by X-ray diffraction and magnetization techniques. The X-ray diffraction pattern shows single phase cubic spinel structure. The particle radius obtained from X-ray and magnetization measurements are 55 and 51 Å, respectively. In this method magnetic fluid is stabilized by bilayers of two surfactants. A primary surfactant (oleic acid in the present case) which is chemi-adsorbed to Fe_3O_4 particle through their carboxylic head group stabilizes the precipitates. The secondary surfactant (in the present case also oleic acid) then coated on primary surfactant stabilized magnetic particle with the head groups of secondary surfactant providing a hydrophilic outer shell exposed to the surrounding polar solvent. This results in a stable aqueous magnetic fluid. Similar procedure was adopted for D_2O-based fluid.

CTABr powder weighing 0.182 g was dissolved in 5 ml of water/D_2O to get 0.1 M CTABr solution. This solution is stirred and heated to 333 K. 0.1 M CTABr–magnetic fluid emulsions were prepared for 5, 10 and 15% magnetic fluid concentration (Cm) by the following way. For example, for preparing 0.1 M CTABr + 10% MF, 0.182 g CTABr powder was first dissolved in 3 ml of water and then 0.5 ml magnetic fluid was added. After proper stirring the solution was brought to 5 ml total volume and then heated to 333 K. The aim behind this procedure was to keep

CTABr concentration same for all magnetic fluid concentrations. Stability of these emulsions was checked visually (stable for long time, > 1 year).

Small-angle neutron scattering measurements for CTABr–magnetic fluid emulsion were carried out using SANS diffractometer at Dhruva reactor, Trombay, Mumbai [12]. The mean wavelength λ of the incident neutron beam is 5.2 Å with a wavelength resolution of ∼15%. The scattered neutrons are detected in an angular range of 0.5–15° using a linear position sensitive detector (PSD). The accessible wave vector transfer Q ($= (4\pi/\lambda)\sin\theta/2$, where θ is the scattering angle) range of instrument is 0.018–0.30 Å^{-1}. The measured data have been corrected and normalized to a cross-section unit, using standard procedure.

3. Results and discussion

In small-angle neutron scattering one measures the differential scattering cross-section per unit volume, $\mathrm{d}\Sigma/\mathrm{d}\Omega$, as a function of scattering vector Q. For a colloidal solution, $\mathrm{d}\Sigma/\mathrm{d}\Omega$ can be expressed as

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q) = nV^2\left(\rho_{\mathrm{p}} - \rho_{\mathrm{s}}\right)^2 P(Q)S(Q), \tag{1}$$

where n is the number density of the micelles, ρ_{p} and ρ_{s}, are respectively, the scattering length densities of the particle and the solvent and V is the volume of the micelle. $P(Q)$ is the intraparticle structure factor and depends on the shape and size of the particle. $S(Q)$ is the interparticle structure factor and is decided by the interparticle distance and the particle interactions.

In the case of a D_2O-based magnetic fluid, there is poor contrast between the core (Fe_3O_4) of the particle and the solvent. However, there is a very good contrast between the surfactant coating (outer shell) and the solvent. Under this condition the scattering from D_2O-based magnetic fluid is mainly decided by the surfactant coating. Therefore, the SANS data was analysed using the core shell model. The bilayer thickness (34 Å) obtained from the fit to the scattering pattern is substantially less than the total length for an all-trans extended conformation of primary and secondary surfactants (40 Å). The difference of 6 Å is probably due to the inter-penetration between hydrocarbon chains of the surfactants. Similar behavior was also observed by Lifen *et al* [13]. It may be mentioned that the size parameters of the core (magnetic particles) were used as determined from H_2O-based magnetic fluid as in this case the contrast for surfactant coating is negligible and the scattering is mainly from the magnetic particles. It was found that the data fit to the log-normal distribution of the particles with median radius $R_{\mathrm{m}} = 50.6$ Å and polydispersity $\sigma = 0.5$.

Figures 1 and 2 show the SANS data of MF–CTABr emulsions in D_2O for varying magnetic fluid concentration at 303 and 333 K, respectively. It is observed that at 303 K, correlation peak starts disappearing and there is an increase in the scattering signal in the low Q region as the magnetic fluid concentration is increased. This may be due to the large scattering contribution of the magnetic particles in the MF–CTABr emulsions. The fact that the concentration of magnetic particles is two order of magnitudes smaller than that of the micelles in emulsions, the scattering from the two components (magnetic particles and micelles) may be considered as simple additive. This gives rise to the scattering contribution only from micelles in MF–CTABr emulsions by subtracting the corresponding contribution of magnetic particles. Figures 3 and 4 show the deduced scattering signals for micelles in MF–CTABr emulsions.

It is observed from figures 3 and 4 that the scattering cross-section from micelles increases and the correlation peak shifts to the low Q values as the magnetic fluid concentration increases in the MF–CTABr emulsions. This is an indication of the formation of larger micelles with the increase in the concentration of magnetic fluid. The data have been analysed in terms of eq. (1). The intraparticle structure factor $P(Q)$ has been calculated by treating the micelle as prolate ellipsoidal. For such an ellipsoidal micelle,

$$P(Q) = \int_0^1 \left[F(Q,\mu)^2 \mathrm{d}\mu\right], \tag{2}$$

$$F(Q,\mu) = \frac{3(\sin x - x\cos x)}{x^3}, \tag{3}$$

$$x = Q\left[a^2\mu^2 + b^2(1-\mu^2)\right]^{1/2}, \tag{4}$$

where a and b are, respectively, the semimajor and semiminor axes of the ellipsoidal micelle and μ is the cosine of the angle between the directions of a and the wave vector transfer Q.

The interparticle structure factor $S(Q)$ for charged micelles has been calculated as derived by Hayter and Penfold [14] from the Ornstein–Zernike equation and using the rescaled mean spherical approximation [15]. The micelle is assumed to be a rigid equivalent sphere of diameter $\sigma = 2(ab^2)^{1/3}$ interacting through a screened Coulomb potential.

The analysis of data using the above method gives the dimensions of the micelle, aggregation number and the fractional charge on the micelle. The semimajor axis

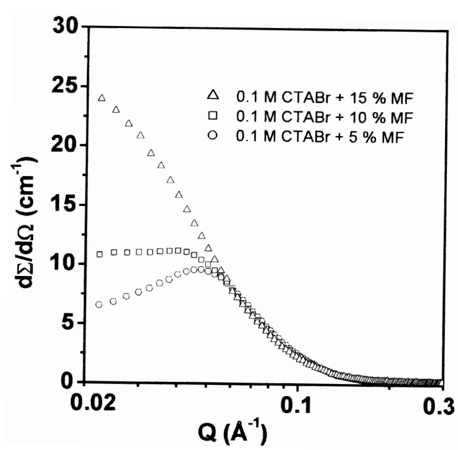

Figure 1. SANS pattern at 303 K.

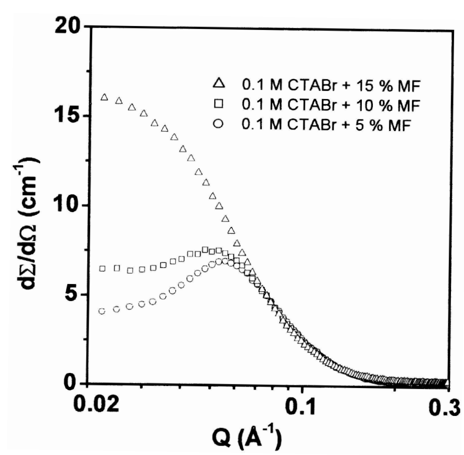

Figure 2. SANS pattern at 333 K.

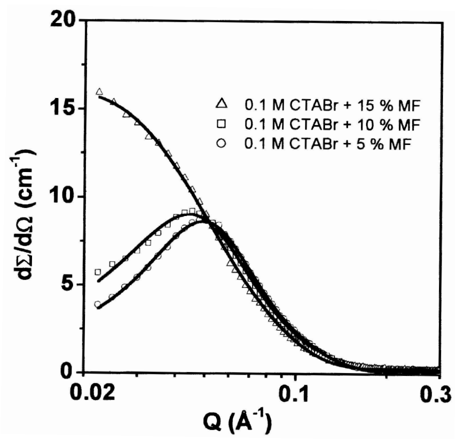

Figure 3. Deduced scattering pattern at 303 K.

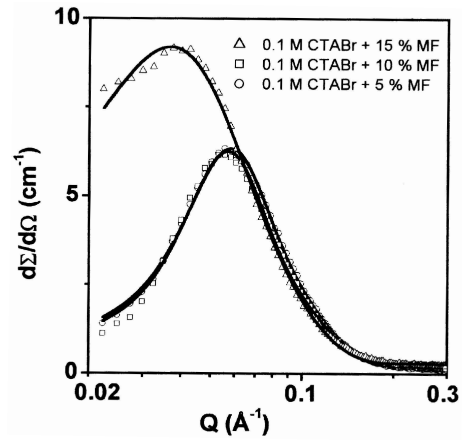

Figure 4. Deduced scattering pattern at 333 K.

(a), semiminor axis ($b = c$) and the fractional charge ($\alpha = Z/N$, where Z is the micellar charge) are the fitted parameters in analysing the SANS data. The aggregation number is calculated by the relation $N = 4\pi ab^2/3v$, where v is the volume of the surfactant monomer. It is that CTABr micelles are prolate ellipsoidal with semimajor and semiminor axes as $a = 47.0$ Å, $b = c = 21.4$ Å, respectively. These micelles have the aggregation number of 161 and the fractional charge is 0.13.

The micellar parameters in these systems are given in table 1. It is seen that the aggregation number increases and the fractional charge on the micelles decreases with the increase in the concentration of magnetic fluid. Most interestingly, the axial ratio of the micelles increases with the increase in the magnetic fluid concentration in the MF–CTABr emulsions. This is consistent with the rheological studies [16] where viscosity increases when the magnetic fluid concentration in the emulsions is increased and in the presence of magnetic field an increase in axial ratio is responsible for higher viscosity. Similar trends in change in micellar size have also been observed at higher temperatures (see figure 4 and table 1). The only difference is that by increasing temperature, the micellar sizes become smaller and hence there is decrease in the corresponding measured viscosity.

Table 1. The micelle parameters obtained from neutron scattering fit for MF–CTABr emulsion at $T = 303$ and 333 K.

	$T = 303$ K				$T = 333$ K			
MF (%)	N	α	$b = c$ (Å)	a (Å)	N	α	$b = c$ (Å)	a (Å)
5	166	0.08	21.4	48.6	109	0.17	20.1	36.1
10	198	0.05	21.6	56.6	117	0.18	20.2	38.2
15	304	0.01	21.6	87.2	235	0.03	20.2	77.0

4. Conclusion

Stable CTABr–magnetic fluid emulsions with varying magnetic fluid concentrations have been prepared. SANS measurements show that the aggregation number and the axial ratio of CTABr ellipsoidal micelles increase with the increase in the magnetic fluid concentration and this effect is suppressed by increasing the temperature.

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