



Micelle formation in aqueous solutions of dodecylbenzene sulfonic acid studied by small-angle neutron scattering

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ABSTRACT

Structure and interaction parameters of micelles in solutions of dodecylbenzene sulfonic acid (DBSA) in deuterated water are studied by small-angle neutron scattering. The dependences of micellar aggregation number, fractional charge, charge per micelle and surface potential on surfactant concentration are analyzed. A typical increase in the micelle size with the growth in the acid content is found, which can be related to the transition from spherical to rod-like micelles. The obtained data are used for estimating surfactant micelle concentration in water-based ferrofluids stabilized with DBSA.

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1. Introduction

Dodecylbenzene sulfonic acid (DBSA), $\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{H}$, is a popular component of various colloidal solutions. Thus, the doping of the most promising conducting polymer polyaniline [1–5] with functional protonic acids such as DBSA improves its processibility and thermal stability. At the same time DBSA can form micelles, whose presence affects the size of the corresponding polymeric nanoparticles during polymerization. Again, DBSA plays an important role in improving the reaction rate and conversion of esterification for production of organic esters under relatively mild reaction conditions [6]. Also, DBSA is actively used in the double sterical stabilization of technical water-based ferrofluids [7–11], aqueous dispersions of magnetic (mostly magnetite) nanoparticles. The second surfactant layer at the surface of magnetite in such ferrofluids is formed due to physical adsorption in excess of the acid. The equilibrium of this process is strongly affected by free surfactant whose concentration is restricted by the critical micelle concentration. So, the micelle formation in this stabilization scheme should be considered among the factors, which determine stability of ferrofluids.

Despite the practical use of DBSA, the formation, structure and interaction of its micelles in aqueous solutions are poorly studied. The given work fills the deficiency of information on this question. Small-angle neutron scattering (SANS) is used to find out parameters of the structure and interaction of the DBSA micelles in deuterated water (d-water) as a function of the surfactant concentration in solution. Deuterated water is used to achieve a sufficient scattering contrast between the surfactant and liquid carrier and also for reduction of incoherent scattering background from hydrogen. The structure parameters of the micelles are compared with those obtained [10] for DBSA micelles formed in the above-mentioned water-based ferrofluids. The surfactant content in the bulk of ferrofluids is found.

2. Experimental

First, the critical micelle concentration (cmc) of DBSA in water was determined from the surface tension measurements performed with a Krüss Processor Tensiometer K100 using the ring method. Pure DBSA (c.p., Merck) was dissolved in bidistilled water (Millipore) with several concentrations within the range of 3×10^{-5} to 2.5×10^{-2} mol/l (0.001–0.8 vol.%). Surface tension was determined at 25 °C by recording ten data points per one concentration within a measuring interval of 300 s.

SANS experiments were performed with the Yellow Submarine small-angle instrument at the steady-state reactor of the

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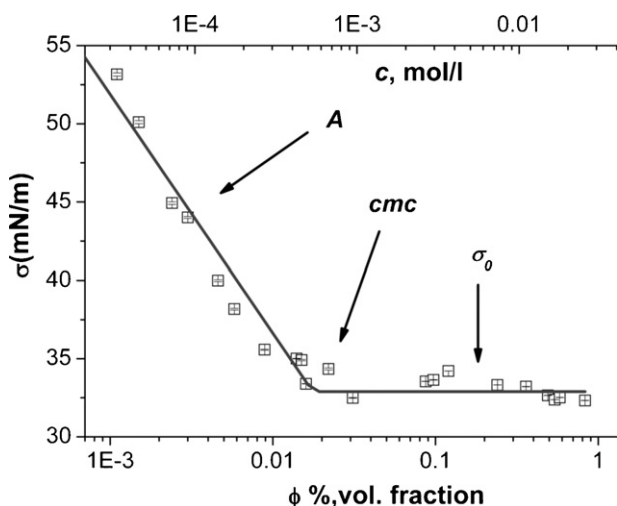


Fig. 1. Determination of the critical micelle concentration by surface tension vs. DBSA volume fraction (concentration). Solid line shows approximation according to (1).

Budapest Neutron Centre (BNC), Hungary. The differential cross-section per sample volume (hereafter referred to as scattered intensity) was obtained as a function of the scattering vector module, $q = (4\pi/\lambda) \sin(\theta/2)$, where λ is the incident neutron wavelength and θ is the scattering angle. The fixed wavelength of 0.386 nm (monochromatization $\Delta\lambda/\lambda = 20\%$) and sample-detector distances of 1.3 and 5.6 m (detector size 0.64 m) were used to cover the q -interval of 0.15–4.5 nm⁻¹. SANS measurements were performed at 25 °C. The calibration on 1-mm water sample was made after the background, buffer (D₂O) and empty cuvette corrections in a standard way [12]. Pure DBSA was dissolved in d-water (99.9%, Sigma–Aldrich) within a wide concentration interval 0.06–0.52 mol/l (2–17 vol.%).

3. Results and discussion

The experimental values of surface tension $\sigma(\varphi)$ against the logarithm of the concentration (φ , vol. fraction and c , mol/l) are plotted in Fig. 1. This dependence has a typical shape for micelle formation solutions described well by the expression:

$$\sigma(c) = -A(\ln(\text{cmc}) - \ln(c))g(c) + \sigma_0, \quad (1)$$

$$\text{with } g(c) = \begin{cases} 1 & \text{for } c \leq \text{cmc} \\ 0 & \text{for } c > \text{cmc}, \end{cases}$$

where σ_0 is the surface tension at surfactant concentrations higher than cmc and $A = \partial\sigma/\partial\ln(c)$ (the slope) corresponds to the alteration in the surface tension as a function of the natural logarithm of the surfactant concentration, c . The curve in Fig. 1 is fitted to the function (1) with the varied cmc, σ_0 and A , which gives $\text{cmc} = (5.51 \pm 0.03) \times 10^{-4}$ mol/l = $(1.8 \pm 0.01) \times 10^{-2}$ vol.%, $A = 6.62 \pm 0.02$ mN/m and $\sigma_0 = 32.9 \pm 0.1$ mN/m. The obtained value of cmc for DBSA is comparable with those for surfactants of the same (C₁₂) alkyl chain length, e.g. sodium p-dodecylbenzene sulfonate ($\text{cmc} = 1.2 \times 10^{-3}$ mol/l) or CH₃(CH₂)₁₁(OCH₂CH₂)₆OH ($\text{cmc} = 8.7 \times 10^{-5}$ mol/l).

The excess surface concentration Γ can be calculated as [13]:

$$\Gamma = \frac{-A}{kRT}, \quad (2)$$

where R is the gas constant, T is the temperature. For DBSA as an ionic surfactant the counterions are taken into account by setting

$k = 2$ [13]. From the excess surface concentration (Γ) the minimum area per molecule at the air/water interface (S^*) can be found [14]:

$$S^* = (\Gamma \cdot N_A)^{-1}, \quad (3)$$

where N_A is the Avogadro's number. Calculations in accordance with (2) and (3) give $\Gamma = 1.34 \times 10^{-6}$ mol/m² and $S^* = 1.24$ nm².

The obtained experimental SANS curves from micellar solutions are given in Fig. 2. They are divided into three groups corresponding conventionally to low ($\varphi < 5$ vol.% or $c < 0.15$ mol/l), intermediate ($5 \leq \varphi < 10$ vol.% or $0.15 \leq c < 0.3$ mol/l) and high ($10 \text{ vol.\%} \leq \varphi$ or $0.3 \text{ mol/l} \leq c$) concentration of DBSA. The peaks in the experimental SANS curves at $q < 1 \text{ nm}^{-1}$ reflect the interaction between micelles. The position of the interference maximum shifts to a larger q -value with an increase in the surfactant concentration, which points to a decrease in the characteristic intermicellar distances in the solution.

Assuming that micelles are monodisperse spheres one can write the scattered intensity in the standard form as

$$I(q) = n(\Delta\rho)^2 V^2 F^2(q) S(q), \quad (4)$$

where n is number particle density; $\Delta\rho = \rho - \rho_s$ is the contrast, the difference between the scattering length densities of the particle, ρ , and solvent, ρ_s ; V is the micelle volume; $F^2(q)$ is the squared form-factor of a single particle (defined in a way that $F^2(0) = 1$); and $S(q)$ is the structure-factor describing the interaction between micelles. For non-spherical micelles the well-known decoupling approximation [15,16], which assumes that there is no correlation between position and size/orientation of particles can be used, where

$$I(q) = n(\Delta\rho)^2 V^2 \langle |F(q)|^2 \rangle (1 + \beta(q)[S(q) - 1]). \quad (5)$$

Here, $\beta(q) = \langle |F(q)|^2 \rangle / \langle |F(q)|^2 \rangle$ is a q -dependent anisotropy factor with $\langle \dots \rangle$ denoting the averaging over all possible micelle orientations. To model $S(q)$, we apply the rescaled mean spherical approximation for dilute charged colloidal dispersions developed by Hansen and Hayter [17]. Since the studied micelles consist of ionic surfactant molecules, the screened Coulomb potential is used in the model:

$$U(r) = \pi\epsilon_0\epsilon D^2\psi_0^2 \frac{e^{-(r-D)/k_d}}{r}, \quad \text{for } r > D, \quad (6)$$

where $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the vacuum permittivity; $\epsilon = 78.5$ is the dielectric constant of the solvent medium (water) for 25 °C; D is the particle diameter; $\psi_0 = z/[\epsilon_0\epsilon D_0(2 + k_d D_0)]$ is the surface potential, which is related to the charge on the micelle, z ; k_d is the usual Debye–Huckel inverse screening length. In addition, the resolution function of the SANS set-up with pin-hole geometry [18] is taken into account when calculating the model curves.

The results of the fits are shown as solid lines in Fig. 2. The varied parameters are the aggregation number (N_{agg}), degree of ionization (α), axial ratio (γ) and residual background. They are used for calculating the average size (D_0) and charge (z) of micelles, as well as the inverse screening length (k_d) and surface potential (ψ_0). Both types of the resulting parameters are gathered in Table 1. One can see that the micelle axial ratio grows with the surfactant concentration within the interval of 1.4–2.65 thus showing a transition towards elongated (rod-like) particles. This is accompanied by an increase in the mean micelle size. The obtained fractional charge of the micelles (below 0.2) is in agreement with the well-known fact that in micellar systems of ionic surfactants only a fraction of 0.15–0.3 of counterions are dissociated, the rest of them are effectively bound to the micellar surface [19].

A more detailed analysis of the change in the micelle parameters with the DBSA concentration in solution is given in Fig. 3. Thus, one can see (Fig. 3a) that the corresponding dependence for the aggregation number has two slopes. We associate this observation

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