

Temperature and Concentration Effects of Aqueous Solution of Sodium Octanoate on Micelle Formation Measured by Small angle X-ray Scattering

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Characteristic sizes of sodium octanoate micelles have been determined (by nucleus radius) with the use of small angle X-ray scattering technique at various molar concentrations, which are for a spherical shape 1 and nonspherical 1.2 nm, respectively. The value of the critical concentration for micelle formation (CMC₂) has been also found equal to 0.7 M.

Keywords: Small-angle X-ray scattering, Sodium octanoate, Micelles, Spherical and nonspherical structures.

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1. INTRODUCTION

Among some special features of “soft” nanostructures such as micelles in contrast to solid structures is exchange of monomeric molecules between micelles and water, two relaxation times, absence of supersaturation, hysteresis of properties, which dictates their wide practical application. Capability of micelles to include metals, including rear-earth metals, is applied for isolation and purification of metals, and which is critically important, for deposition of thin metal and oxide coatings by using gas-phase thermolysis and layered sedimentation [1]. Despite the fact that these structures are intensively studied by scientists of various fields, there is no, unfortunately, complete understanding of interrelation between form and electronic structures of these formations, also for the reason of limitations of hardware possibilities [2].

2. EXPERIMENTAL SECTION

This work studies micelle solutions of sodium octanoate by small angle X-ray scattering (SAXS) technique in characteristic ranges of critical micelle formation concentration (CMC): CMC₁ – the formation stage, CMC₂ – crossover of spherical micelles to nonspherical. Solutions of sodium octanoate (Fluka) with concentration of 0.4-1.00 mol/l between CMC₁ and CMC₂ were studied.

SAXS was studied with small angle X-ray diffractometer SAXSess mc² (Anton Paar, Austria) in a linear collimation mode (Cu K_α with a wavelength of 0.154 nm). Resolution of the system was 0.03 nm⁻¹. Measurements were conducted in the range from 0.03 to 28 nm⁻¹, which corresponds to the objects with sizes from 0.12 to 100 nm. Thermocell (with range of – 30 to 120 °C) made it possible to conduct temperature measurements at 10, 25 and 40 °C.

3. RESULTS AND DISCUSSION

With small angle X-ray scatterings spectra pair-distance distribution functions (1) were constructed both in treating with indirect Fourier transformation (IFT) and also with the help of its expansion, namely, generalized indirect Fourier transformation (GIFT) [3, 4].

$$p(r) = \frac{1}{2\pi^2} \int_0^\infty I(q)(qr) \sin(qr) dq \quad (1)$$

These functions are Fourier-transformation of scattering function

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr \quad (2)$$

where q – scattering vector determined as $q = (4\pi/\lambda)\sin(\theta/2)$, λ – wavelength of X-ray beam, θ – scattering angle between incident and scattered radiation, r – distance between two scattering centers inside a particle.

For diluted disperse systems the IFT method is applied, in which the particle interaction is ignored. For high concentrations the particle interaction influences heavily on the scattering intensity $I(q)$, which is considered in the GIFT method. The method is predicated on the assumption that the scattering intensity is determined by the production of contributions $P(q)$ – form-factor and $S(q)$ – structural factor, where the latter includes interparticle interaction [3, 4]:

$$I(q) = n P(q) S(q), \quad (3)$$

$$S(q) = 1 + 4\pi n \int_0^\infty h(r)r^2 \frac{\sin(qr)}{qr} dr \quad (4)$$

where n – the particle density, $h(r) = g(r) - 1$ – common correlation function, $g(r)$ – radial distribution function.

For spherical monodisperse isotropic systems equation (3) gives the exact solution. Nevertheless, as was shown with many examples [3], introduction of “averaged structural factor” S_{ave} or more exact “effective structural factor” $S_{eff}(q)$ provides good results for polydisperse spheres and inhomogeneous particles.

In this work polydisperse system of solid spheres was chosen for model computations. Typical curves of SAXS obtained for micelle structures of NaCs with various concentrations: 0.4, 0.5, 0.7 and 1 M are given in Fig.1. Noticeable ordering is observed which is due to the increase of molar concentration of NaCs solution, which is illustrated by the approximating curve obtained according to calculation with IFT and GIFT and superimposed on the spectral distribution. However,

more detailed conclusions about possible structural formations of micelles of NaCs may be derived from analysis of pair-distance distribution functions and electron density distributions.

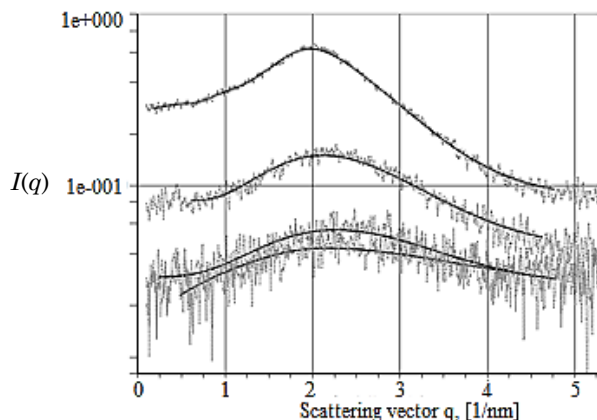


Fig. 1 – Spectra of small angle X-ray scattering on micelle structure of sodium octanoate at concentrations of 0.4, 0.5, 0.7, and 1 M (from bottom to top, respectively)

It should be noted that as physical object micelle structures are highly sensitive to form-factor and interparticle interactions, which must be considered in the structural factor of their interactions [3, 4]. In real-world conditions, by the SAXS spectra pair-distance distribution functions – $p(r)$ can be constructed for all changing parameters – temperature and concentration. Characteristic view of $p(r)$ for the object studied with a concentration of 1 M at a temperature of 25 °C is shown in Fig. 2, which is in accord with conclusions in [2, 5]. Such kind of distribution does not allow one to establish unambiguously enough of which form the structure of NaCs micelle is – spherical or not. This is indicated by the change, with respect to zero, of a relationship between two first peaks of dependence $p(r)$, and also by its sign variability at great values of the wave vector.

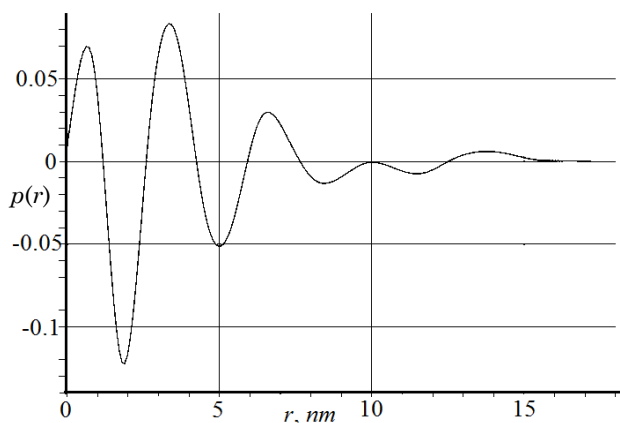


Fig. 2 – Pair-distance distribution functions of micelle structure of sodium octanoate with a concentration of 1 M at a temperature of 25 °C

At the same time, the electron density profiles $\rho(r)$ constructed with $p(r)$ for concentrations of micelle solutions equal to 0.5 and 1 M (Fig. 3a, b) make it possible to establish the micelles form unambiguously enough. Pattern of dependence of $\rho(r)$ for the concentration of 0.5 M is typical

for micelles of spherical shape (Fig. 3a), whereas for the concentration of 1 M (Fig. 3b) – for nonspherical shape with a nucleus radius of ~ 1.1 and ~ 1.2 nm respectively.

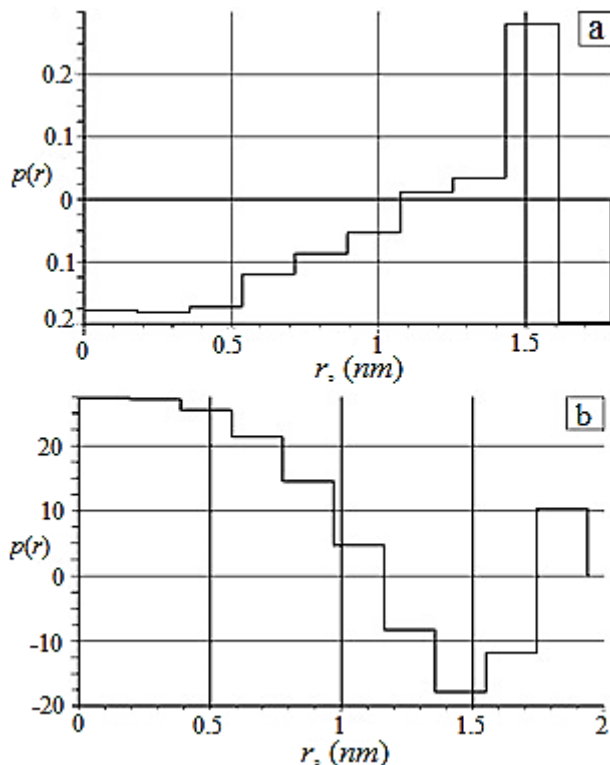


Fig. 3 – Electron density profiles of micelle structure of sodium octanoate at a temperature of 25 °C with a concentration of: a – 0.5 M, b – 1 M

SAXS on micelles in quartz capillary at temperature variations from 10 to 40 °C with the use of pair-distance distribution function $p(r)$ made it possible to find concentration and temperature distinction (Fig. 4). For example, $p(r)$ for solution of NaCs with a concentration of 0.7 M at temperatures of 10, 25, and 40 °C distribution is observed close to lamellar structure with a size of around 5 nm, which is indicative of the transition from spherical micelles to nonspherical ones, i.e. corresponds to CMC₂.

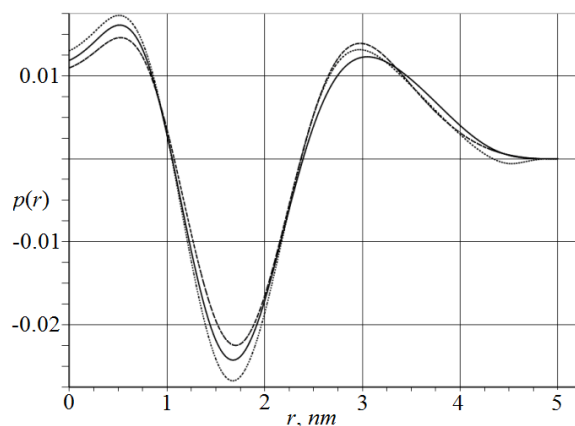


Fig. 4 – Temperature effect on micelle structure of sodium octanoate determined by pair-distance distribution function: --- at 10 °C, — at 25 °C, at 40 °C

4. CONCLUSIONS

Thus, the investigation results of SAXS on micelle solutions of sodium octanoate at various molar concentra-

tions and temperatures make it possible to characterize both possible shapes of the micelles with variations from spherical to nonspherical, by analogy with [6], and their sizes and also CMC_2

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