Journal of Nano- and Electronic Physics
Vol. **10** No 6, 06013(5pp) (2018)

Журнал нано- та електронної фізики
Том **10** № 6, 06013(5cc) (2018)

Ultrasound Effect on Molecules of Sodium Dodecyl Sulphate as Systems of Nanoparticles

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(Received 25 August 2018; revised manuscript received 07 December 2018; published online 18 December 2018)

The article studies ultrasound effect on molecules of sodium dodecyl sulphate (SDS) and on critical micelle concentration (CMC). Ultrasound had no effect on degradation and decomposition of water molecules. Small-angle X-ray scattering was applied to study miscellar solutions of SDS before and after sonication. X-ray spectra were analyzed with an approach which does not take the micelle model into consideration. On ultrasonic treatment, diameter of SDS micelle nucleus decreased from 2.6 to 2.4 nm and of the whole micelle from 6.0 to 4.6 nm. Obtained results were explained on the basis of a hypothesis of micelle dual properties. Ultrasound increases presence of high density liquid (HDL) in a micelle at the cost of low density liquid (LDL).

Keywords: Ultrasound, Sodium dodecyl sulphate, Micelles, Small-angle X-ray scattering, Water structure.

DOI: 10.21272/jnep.10(6).06013 PACS number: 81.16.Be

1. PROBLEM STATEMENT

Ultrasonication of miscellar aqueous solutions of surfactant is applied for metal nanoparticles synthesis [1], stabilization of sensibilizers solubilized in surfactant micelles on photodynamic therapy of cancer [2], decontamination in electronic industry [3]. In the miscellar aqueous solutions exposed to ultrasonication, air bubbles of almost the same size are formed [4]. As ultrasound power and sonication time increase, size of the bubbles increases, as power decreases, size decreases, as well. Thus, size, size distribution, electrokinetic potential of the bubbles can be adjusted by applying ultrasound and modifying the structure of surfactant micelles.

Measuring the speed of sound with infinitely small amplitude is used to determine CMC surfactant [5]. Speed of ultrasound, like other properties, varies in different ways before and after CMC, as surfactant concentration grows. Experimental points of ultrasonic velocity as a function of SDS concentration lie on two lines of different inclination. At the intersection of the lines, CMC of DDS is identified. Inclination change is associated with change of fluctuation in water density around monomeric surfactants during micelle formation.

Fluctuations of HDL and LDL near 1 nm in size in water are explained by tendency of water to increase entropy and to decrease enthalpy [6]. When a surfactant appears in a solution, content of LDL or small systems increases. Micelle formation is accompanied with liquid polyamorphous transition in an ensemble of small systems of water LDL ↔ HDL near the surfactant molecules [7, 8]. This is evident due to s-changes of ultrasound speed in the DDS concentration area 0.004-0.01 M [9], maximum of valence band of OH-groups of water in spectra of combination scattering [7], intensity of X-rays scattering at $q = 19$ nm^{-1} [8]. In accordance with the hypothesis of mutual interaction of polyamorphous transition and micelle formation, the micelle is of double nature. It is a superposition of two structures: 1. the contact one surrounded with water structure with HDL and 2. the hydrated one saturated with water with LDL [8].

Micelles structure is studied with small-angle X-ray scattering (SAXS). There are two essentially different techniques used to analyze SAXS spectra of micellar aqueous solutions: an approach which does not consider the micelle model and the direct modeling. The first one proposed by Glatter [10] consists in Fourier transformation of SAXS spectrum data in order to obtain autocorrelation function which is average over the ensemble, and in deconvolution procedure for this function in order to get a profile of radial electron density of micelles. Direct modeling starts from a suggested geometrical "nucleus/shell" micelle model, calculation of SAXS intensity of micellar solutions according to the model and optimization of the micelle model parameters through the least square method applied.

The majority of researchers used direct modeling to define the micelles structure with SAXS. Thus, the DDS micelles nucleus diameter was 3.6 nm and 4.4 nm with the shell [11]. Two adjustable parameters – mean aggregation number and average micelle charge – were taken for approximation of a classical model. External diameter of DDS micelles of 6.4 nm was defined by the approach which does not consider a pre-arranged micelle model [12]. In our works [8] the large scale of DDS spherical micelles obtained with SAXS is explained by a layer of HDL which surrounds a contacting micelle and LDL, which, in its turn, separates DDS ions in a hydration micelle. After a micelle has been formed, number of HDL with higher electron density prevails over LDL, thus micelles of large size are observed with SAXS method. Higher density of water around the micelles is confirmed by the methods of molecular dynamics in a number of works [13]. Our article is focused on determination of ultrasound effect on the micellar solutions since new visions on the micelle structure have occurred.

2. EXPERIMENTAL TECHNIQUE

DDS («Sigma») was re-crystallized from ethanol. Pu-

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rity of a surfactant was proven by absence of minimum in the area of CMC on an isotherma of superficial tension of its aqueous solutions. DDS CMC, which is defined with a conductometric method, is $8.0 \pm 0.2 \cdot 10^{-3}$ M. CMC within the experimental error coincides with CMC obtained in the work [14] and with concentration defined by superficial tension. CMC coincides with average concentration of polyamorphous transition defined by speed of ultrasound in DDS aqueous solutions [5]. The DDS solutions were prepared by weighing and dissolution in distilled water which was obtained with potassium permanent added. The water was taken after double distillation. First distillation was performed with potassium permanent in order to oxidize possible organic impurities. Superficial tension of the solutions was measured with the platinum plate technique with accuracy of ± 0.1 μN/m at 25 °C, conductivity was measured with a conductivity meter Milwaukee MW 301 with full scale accuracy of ± 2 % at 25 °C. CMC was defined out of relationship between conductivity and concentration.

The DDS solutions were ultrasonicated in an ultrasound processor VCX-130 (Sonics & Materials, Inc). This process depends on intensity of sonic flow of energy of 130 W, ultrasonic wave frequency of 30 kHz, temperature and time of a solution sonication, in particular. These parameters are expected to increase possibility of water molecules decomposition into H·and ·OH free radicals. OH radical may oxidize DDS hydrocarbon radical to carboxylic acid [15]. In acid environment, DDS may hydrolyze and form dodecyl alcohol, therefore it is required to find the appropriate conditions for solutions ultrasonication that provide water and DDS sustainability to carboxylic acids [15].

In three tests a 10 ml 0.01 M DDS solution was ultrasonicated (130 W, 30 kHz) for 2 minutes at 25 °C. Then DDS concentration was defined with a standard spectrophotometric method with methylene blue dye used. DDS concentration in three tests was shown to remain unchanged during a 2 min ultrasonication. Minimum of surface tension was absent after the 2 min ultrasonication near CMC, CMC was slightly reduced to 7.7×10^{-3} M. Therefore, CMC confirms that surfactant impurities did not occur in the solution but the micelle structure has changed. Solution temperature did not increase and water did not evaporate. SAXS method was then applied to study the 0.01 M DDS solutions that were and were not ultrasonicated for 2 minutes.

SAXS [10, 11] was studied at an X-ray diffractometer SAXSess mc² (Anton Paar GmbH, Austria) in a mode of linear collimation of the beam with cross-section of 20 × 0.3 mm² (CuK_α, $\lambda = 0.154$ nm).

X-ray generator ID3003 was used in the experiment. Power was 40 kV / 50 mA. DDS aqueous solutions were inserted into a quartz capillary rigidly fixed with a holder TCS120. X-ray beam was directed to the center of the capillary for 5 minutes at 25 °C. The measurements were carried out in range of values of magnitude of X-ray propagation vector q from 0.03 to 28 nm^{-1}, which was defined $q = \left(\frac{4\pi}{\lambda}\right)\sin\left(\frac{\Theta}{2}\right)$, where λ is wave length of impinging X-rays, Θ is a scattering angle. It is generally believed that wide-angle x-ray scattering starts at $q > 10$ nm^{-1}. The resolution of the system was 0.03 nm^{-1}. Scattering intensity was measured with a position-sensitive detector and obtained data were processed with the software in order to define DDS micellar structure.

If the studied sample consists of one nanoparticle, total SAXS intensity of the particle $I_1(q)$ will be calculated as follows:

$$I_1(q) = I_0 p_1^2 V_1^2 P(q), \quad (1)$$

where I_0 is an apparatus constant, ρ_1 is a scattering length density which proportional to electron density for X-ray scattering, V_1 is a volume of a particle. $P(q)$ is a normalized form factor quadrate, or scattering intensity of a particle of a pre-set shape with a unit volume and average density. Moreover, $P(q)$ has information on internal structure of a particle, on distribution of scattering centers, or scatterers. For instance, with electron density of HDL and LDL clusters, the ensemble of N scatterers produces the intensity

$$I_1(q) = I_0 N p_1^2 V_1^2 P(q), \quad (2)$$

If a micelle of electron density ρ_1 is embedded into a matrix (water) which electron density is $\overline{\rho_2}$, particle scattering intensity will be

$$\Delta I_1(q) = I_0 \Delta\rho^2 V_1^2 P(q), \quad (3)$$

where $\Delta\rho = \rho_1 - \bar{\rho}_2$ (a so-called "contrast") since electron density of the matrix is always subtracted. An ensemble of N particles produces the intensity

$$\Delta I(q) = N \Delta I_1(q) S(q). \quad (4)$$

If the micelles concentration increases and distances between the micelles approach to their size, interference of amplitudes of scattered waves from different particles starts having an impact on the curve of scattering intensity for an isolated particle, that is represented in the expression (4) with a structure factor $S(q)$.

The expressions (2) and (3) may be combined into the expression (5):

$$\Delta I(q) = kP(q)S(q), \quad (5)$$

where all constant values (volume of particles, particle concentration, contrast of electron density) are joined into a coefficient k. In spherical coordinates, scattering intensity for a spherically symmetric particle of radius R and density set by a radial function $\rho(r)$ is defined as

$$I(q) = \left[4\pi \int_0^R r^2 \rho(r) \frac{\sin(qr)}{qr} dr \right]^2, \quad (6)$$

where r is radial distance; random object scattering intensity is related to direct space via the expression

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr, \quad (7)$$

where r is distance between two centers of scatterers inside a micelle, $p(r)$ is the pair-distance distribution function (PDDF) between the scatterers, that is related to a correlation function $\gamma(r)$ via ratio $p(r) = r^2\gamma(r)$.

Magnitude of X-ray propagation vector has dimensions which are reciprocal to nm^{-1}. In the present work, SAXS spectra of DDS micellar solutions were analyzed with the Glatter method before and after sonication. PDDF were calculated from the expression (5) with Indirect Fourier Transformation (IFT) implemented in the software complex GIFT applied here:

$$p(r) = \frac{1}{2\pi^2}\int_0^\infty I(q)\frac{\sin qr}{qr}dq. \quad (8)$$

Then PDDF were converted into a profile of radial electron density of micelles $\Delta\rho(r)$ in DECON programme. It is worth mentioning that scattering intensity is measured by number of photons scattered per a unit of time. Photons were corrected for a steradian unit and a cross-section unit of the scatterer. The steradian unit conversion calculation into the units of real density of the scatterers requires high-accuracy measurements of the standard samples. As rule, such "real" units of intensity are not marked in the SAXS spectrum because the shape of the intensity curve is all that matters for structural data interpretation, measurement units of the curve are of no importance.

3. RESULTS AND DISCUSSION

The SAXS spectrum of the DDS solutions in range from 0.03 to 28 nm^{-1} without sonication is shown in the work [7]. The solution functions $I(q)$ have three peaks with maxima at $q = 0.6$; 1.5 and 19 nm^{-1}. The first maximum corresponds to a distance between the micelles and is visually absent for $I(q)$ to 0.03 M. Intermicellar interaction, therefore, may be considered to have no effect on a diffraction pattern in a 0.01 M solution. The second maximum indicates the micelles presence in the solutions. The micelle structure is identified from the diffraction near $q = 1.5$ nm^{-1}. The third wide maximum near 20 nm^{-1} represents short-range order of water. It may be observed in functions $I(q)$ for water and solutions.

SAXS spectrum shows (Fig. 1) that the first maximum on $I(q)$ is absent, too, after a 0.01 M DDS solution was ultrasonicated. Therefore, micellar interaction may be concluded to have no effect upon the micelle structure after ultrasonication. Radial function of pair distances between scatterers of DDS micelle cross-section is calculated from SAXS spectra with GIFT software (Fig. 2).

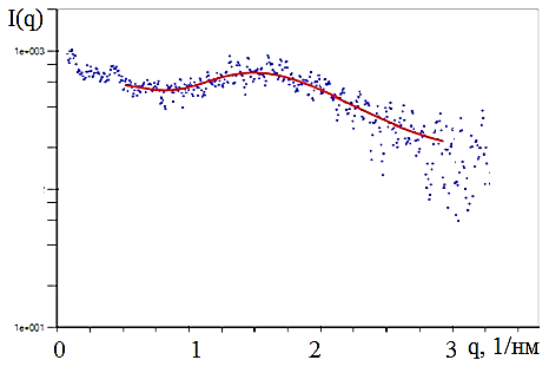

Fig. 1 – Averaged function $I(q)$ for sodium dodecyl sulphate micellar structure at concentration of 0.01 M after ultrasonication

As may be seen on Fig. 2, $p(r)$ represents a statistics of scatterers distribution (DDS, H_2O) in two different spheres. Width of each peak $p(r)$ with a maximum informs on a disorder in a distribution pair. For two $p(r)$, scattering intensity is nonstandardized but from $p(r)$ a ratio of two peaks width may be obtained and compared. Peaks width ratio of the second big one and of first small one is 1,63, which means that a disorder in the micelle remains unchanged prior and after the ultrasonication.

Areas under the peaks $p(r)$ report the number of scatterers in two different spheres. After ultrasonication, ratio of areas under the second peak to an area under the first one increases from 4 without ultrasonication to 5 sec. with it. Therefore, number of scatterer pairs of the external micellar shell increases after ultrasonication. In other words, electron density of the external shell of the DDS micelle becomes more solid.

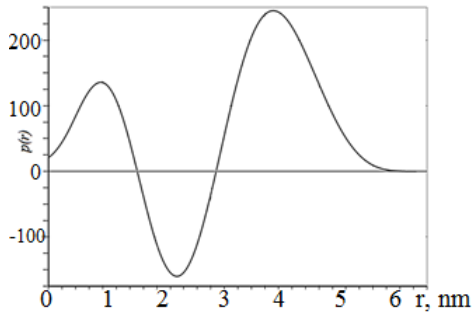

Fig. 2 – Radial function of pair distances $p(r)$ for scatterers in DDS micelles at concentration of 0.01 M at 5 °C with ultrasonication

Hydration of DDS and TWEEN micelles was observed for comparison. In order to discuss the experimental data for sound speed with small amplitude in the DDS aqueous solutions, DDS speed ratio is required [5]

$$[U] = (U - U_o)/(U_o C),$$

where U_0 is sound speed in water, C is DDS concentration. At low DDS concentration, $[U]$ is a constant value corresponding to a DDS monomer structure. At higher DDS concentration, $[U]$ ratio decreases due to micelle formation. The speed ratio comprises an instant part $[U]_{inst.}$ caused by intermolecular interaction, a relaxation part $[U]_{rel}$ caused by sound energy dissipation and reconfiguration of the structure of the solution as a result of sound pressure effect, $[U] = [U]_{inst.} + [U]_{rel.}$ The factors like an absorbtion and scattering of ultrasound waves influence on the relaxation part $[U]_{rel.}$ measurement. Shift in HDL ↔ LDL to HDL and formation of DDS micelles result in $\Delta[U]$ decrease between a monomer and micellar solutions state. For ion DDS, $\Delta[U] = 0.633$ ml / g, for non-ion TWEEN, the acoustic effect $\Delta[U] = 0.259$ ml / g. SAXS and acoustic method, therefore, provide the same results concerning difference in ion and non-ion surfactant hydration.

Following the procedure of SAXSess software mc², $p(r)$ was converted by the DECON programme into a profile of radial electron density of micelles or, if in other measuring units, into scattering length density. In Fig. 3 they are presented in the device software in proportional units. The nomograme function $\Delta p(r)$ shows the differ-

ence in ρ for various parts of a micelle with respect to ρ_{H_2O} which equals zero at $\Delta p(r)$. Hydrocarbon groups, like methylene group, have scattering length density of $\rho_{CH_2} = 6.5 \cdot 10^{-6} \text{Å}^{-2}$, LDL $8{,}96 \cdot 10^{-6} \text{Å}^{-2}$ that is lower than $\rho_{water} = 9{,}54 \cdot 10^{-6} A^{-2}$. Radii $r = 1.3$ and 1.2 nm obtained at intersection of $\Delta p(r)$ and zero are believed to be equal to radii of internal hydrocarbon part of a classical micelle with and without ultrasonication.

Thus, diameters of the whole micelle are 6.0 and 4.6. External micellar shell becomes more inhomogeneous, "torn" after ultrasonication. Electron density, for example, after having been ultrasonicated at radii 2.1-2.3 nm grows and at radii 1.8-2.1 nm decreases. The micelle diameters obtained in experiments before sonication are bigger than the diameters obtained via spectrum analysis through simulation. After sonication the diameters are almost the same.

New dimensions of the micelle as compared to that of direct simulation and their causes are noteworthy.

In our model, a bistable DDS micelle may have a HDL contact structure ($11.6 \cdot 10^{-6} \text{Å}^{-2}$) and a hydrated LDL structure $8{,}96 \cdot 10^{-6} \text{Å}^{-2}$). In the contacting micelle, the hydrocarbon groups contact with each other and are surrounded by HDL. In the hydrated micelle, each DDS molecule is surrounded by LDL. Their cross sections obtained with SAXS superimpose and provide quite other dimensions as compared to that of the classical micelle. The obtained results and their hypothetical contradiction to classical concepts on the structure of ion surfactant micelles are explained within the frames of coexistence of polyamorphous transition in water and micelle formation or, in other words, of coexistence of DDS and water density fluctuations [6].

Superimposed average diameters of their spheres found from the function of radial electron density of micelles are 2.8 and 6.0 nm (Fig. 2).

Radius of the small sphere of 1.4 nm is little less than length of the DDS alkyl groups of 1.67 nm and external radius of the micelles of 3.0 nm is bigger than that of 2.2 nm obtained through direct simulation. Their difference in 0.8 nm is too significant for placing the adsorbed sodium ions of the classical micelle model and thus our dual micelle model may be adopted. Influence of ultrasound expands over water that surrounds the micelle. Disorder in the micelle with scatterer number increased and nucleus dia and micelle dia decreased may be explained by shift in HDL ↔ LDL to HDL and the contacting micelle. Increase of HDL molecules at cost of LDL and DDS contacting molecules reduces the dimensions of the micelle. Number of

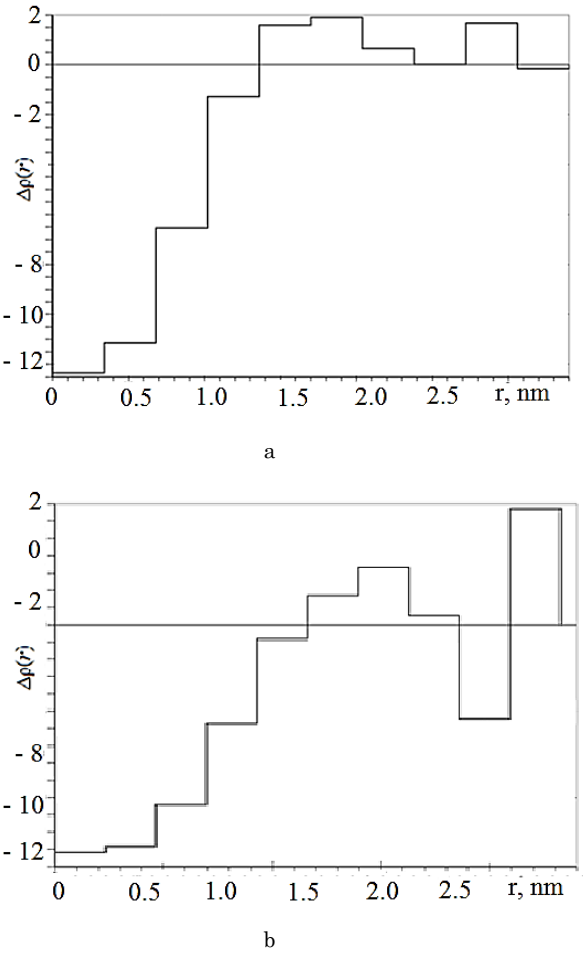

Fig. 3 – X-ray scattering length density of DDS micelles with 0.01 M concentration at 250 C: a) without ultrasonication, b) with ultrasonication

scatterers increases. Disorder in the micelleremains the same as LDL molecules with lower entropy are substituted with HDL molecules with higher entropy and higher disorder in the contacting micelle.

Thus, ultrasonication of the micellar solutions has no effect upon DDS molecules degradation but causes changes in hydration of the solution micelles. SAXS analysis of X-ray spectra with no regard for the micelle models suggests presence of HDL and LDL clusters (fluctuation in water density) in the micelles and change in their number. During ultrasonication of the DDS micellar solutions, nucleus diameter and micelle diameter decrease and the number of scatterers grows. Thus it may be concluded that quantity of HDL around the micelle increases.

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