STRUCTURE OF MICELLES OF SODIUM DODECYL SULPHATE IN WATER: AN X-RAY AND DYNAMIC LIGHT SCATTERING STUDY

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Abstract. Aqueous micellar solutions of sodium dodecyl sulphate (SDS) were investigated using X-ray scattering technique in the concentration range 0.008–0.1 M and analyzed by a model-independent approach. The obtained diameter of the spherical micelle (6.0 nm) with concentration 0.01 M is greater than that analyzed by direct modeling and by small-angle neutron scattering (4.4 nm). In the study of SDS solution of 0.01 M concentration by dynamic light scattering method, the following three hydrodynamic spheres were identified: SDS dimers and two micelles with water. The diffusion rate of these spheres decreases with the increase of their size. When adding 0.01 M of NaCl the dimers disappear, and the hydrodynamic spheres with diameter of 3.14 nm appear. The results are discussed in the framework of the concept of polyamorphous transition between ensembles of water clusters of low and high density levels. Polyamorphous transition accompanies the formation of dual structures of contact and separated by water micelles with different rates of diffusion.

Keywords: sodium dodecyl sulphate, micelle structure, small-angle X-ray scattering, wide-angle X-ray scattering, dynamic light scattering.

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Introduction

Surfactants in water form micelles at the critical concentration of micelle formation (CMC). This paper discusses the case, when the micelles are spherical, and the optimal properties in aqueous solution are achieved: detergency, wetting, adsorption, dispersion, catalytic, etc. For over a hundred years micelles are the objects of study, but their structure is still not completely understood [1]. Along with the Van der Waals attraction of the hydrocarbon groups of the surfactants and the electrostatic repulsion of the charged hydrophilic groups, the interactions of surfactant molecules with water take part in the formation of micelles. At 298 K, the enthalpy of micellization of sodium dodecyl sulphate (SDS) is equal to zero and the entropy of the water adds to the main contribution into the Gibbs energy of micelle formation. For example, it is possible to determine the formation of spherical SDS micelles analyzing vibrational properties and short-range order of water molecules [2,3].

Micellization accompanies the polyamorphous transition in ensembles of small systems of water with a low (LDL) and high density levels (HDL) [2-6]. In this case the following special properties of micelles appear: two relaxation times, bistability, duality of structure, hysteresis, significant fluctuations in extensive properties, oscillations, absence of supersaturation during the micellization.

Using static methods of small-angle X-ray scattering (SAXS) and of small-angle neutron scattering (SANS) the average number of molecules of 60-80 in the SDS micelle (without adding electrolyte) was determined [7,8]. The number of molecules in micelles measured using dynamic light scattering (DLS) methods and nuclear magnetic resonance 13C are equal to 27 and 20, respectively [9,10]. Thus, static and dynamic methods provide different sizes. Sizes of the micelles measured by DLS are in good agreement with the literature data obtained for surfactants solution with added inorganic electrolytes [9]. Unfortunately, the authors [8] approximated the correlation function only using the method of cumulants, they did not use the optimal automatic configuration of the device. Moreover, there is little evidence regarding the use of DLS to study the size of micelles and other ionic surfactants in the absence of NaCl [9]. The DLS method was used only to study the mutual
diffusion of SDS micelles and other ionic surfactants in the presence of NaCl [11-13]. The authors believed that in the absence of salt the diffuse part of the double electrical layer makes an ambiguous contribution to the value of the hydrodynamic diameter of the micelles’ spheres [11,13].

There are two fundamentally different methods of analysis of the SAXS spectra of micellar aqueous solutions: (i) an independent approach on micelle model and (ii) direct modelling. The first one was proposed by Zemb, T. and Charpin, P. [14]. Direct modelling starts with an assumed geometrical model of the classical micelles, then continues with the calculation of the SAXS intensity of the micellar solution in accordance with the model, and finalizes with the optimization of parameters of the micelle model by minimization of the functional error. The analysis of direct modelling is probably too “attached” to the existing model of micelles and restricts an independent study of micelles’ nature.

Most of the researchers involved in studying the structure of micelles by means of SAXS carried out a direct modelling using the classical model of micelle. This method was applied to the study of micellar solutions of SDS and sodium octanoate by means of SAXS and SANS simultaneously [15]. Eight combinations of 2% (0.067 M) of solutions of SDS, consisting of deuterated, protonated water and deuterated molecules of SDS were investigated using direct modelling. To describe the classical model of micelle, two different parameters were selected: the average number of aggregation and the average charge of the micelle. The authors of this classic study have assumed that the micelles can result from a fluctuation of the concentration of SDS. The average structure in a dense medium consisted of 74 SDS molecules and the standard deviation was 40%. In the distribution there were micelles with 30 molecules of SDS. As a result, the measured core diameter of the micelle was 3.6 nm and that of the core with shell was 4.4 nm. Using SAXS and the independent approach on the previously accepted model of the micelle, it was found that the outer diameter of SDS micelle equaled to 6.4 nm [16]. Another study performed using SAXS gave the same size of the micelles [17]. Thus, different methods of analysis of the SAXS data of micellar aqueous solutions lead to different values of the outer diameter of the micelles.

In the present study, the X-ray scattering technique with the independent approach on the accepted model of the micelle and DLS method were used to study the SDS micellar solutions in the concentration region between the critical concentration of formation of spherical micelles (CMC_1) and the critical concentration of formation of cylindrical micelles (CMC_2) to identify the cause of formation of micelles with large diameter and to improve the knowledge about micellization in the framework of the concept of coexistence of the polyamorphous transition in water and micelle formation.

**Experimental**

**Materials**

Sodium dodecyl sulphate (SDS) (Sigma) was recrystallized once from ethyl alcohol. The purity of SDS was confirmed by the absence of a minimum in the area of CMC_1 on the isotherm of surface tension of SDS aqueous solutions. The IR spectra of crystalline form of SDS before and after recrystallization were identical (data not shown).

SDS solutions were prepared in double distilled water. The purity of water was confirmed by the absence of its correlation function determined by dynamic light scattering. In the absence of dust particles, air bubbles, there is no dynamic light scattering in water. The intensity of scattering fluctuates at the level of the noise meaning that the relaxation time of the LDL↔HDL structures in water is less than the delay time in the analyzer Zetasizer Nano ZS 0.5 μs [6].

**Surface tension and electrical conductivity analysis**

The surface tension of SDS solutions in the region of CMC_1 was measured by Wilhelmy plate method (a platinum plate was used) with an error of ±0.1 mN/m at 25°C. Conductivity of SDS solutions was measured using the Milwaukee MW 301 conductivity meter with an accuracy of ±2% of full scale, at 25°C. CMC_1 and CMC_2 were determined using the dependence of conductivity on the concentration. The values of CMC_1 and CMC_2 measured by the conductometric method are equal to (8.0±0.2)-10^{-3} and (65±4)-10^{-3} M, respectively. These values coincide with the published data within the error of the experiment [18].

**X-ray scattering study**

The X-ray scattering measurements were carried out using the SAXSess mc² X-ray diffractometer (Anton Paar GmbH, Austria) in the mode of line collimation of the beam with cross-section 20×0.3 mm² (CuKα, λ = 0.154 nm). The power of X-ray generator ID3003 was
40 kV/50 mA. Aqueous solutions of SDS were placed in a fixed quartz capillary, the volume of the sample was 2 µL. The X-ray beam was directed to the centre of the capillary. The measurement was carried out for 5 minutes at sample temperature of 25°C, in the range of values of the modulus of the wave vector \( q \) of X-ray scattering from 0.03 to 28 nm\(^{-1}\). The modulus of the wave vector of X-ray scattering is defined as \( q = (4\pi/\lambda)\sin(\Theta/2) \), where \( \lambda \) is the wavelength of the incident X-ray radiation, \( \Theta \) is the scattering angle. Usually, the X-ray scattering at \( q > 10 \) nm\(^{-1}\) is considered wide-angle X-ray scattering (WAXS). The resolution of the system was set to 0.03 nm\(^{-1}\). The intensity of scattering was measured by a position-sensitive detector. Distilled water was used as a secondary standard. The intensity of SAXS of distilled water in the range \( q = 0.1-4 \) nm\(^{-1}\) depends mainly on its isothermal compressibility at given temperature and weakly depends on the scattering angle [19].

**Dynamic light scattering study**

The study of SDS aqueous solutions using dynamic light scattering (DLS) was performed on the Zetasizer Nano ZS analyzer (Malvern Instruments Ltd, UK). The linearly polarized (500:1) helium-neon laser with a wavelength of 632.8 nm was used as a light source of the spectrometer. The intensity of the incident beam was adjusted by an automatic attenuator (10 levels of attenuation), this allowed studying samples of different levels of scattering. As a detection system the avalanche photodiode was used. To exclude multiple scattering at high concentrations of particles/molecules and to optimize the signal from weakly scattering samples with low concentration of particles/molecules the technology of non-invasive backscattering (NIBS, technology patented by Malvern) was used. The NIBS technology provides optimization of the point of the scattering detection. For example, the position of the point from which scattering is detected, can be optimized to reduce sensitivity to scattering from the cuvette wall by measuring in the cuvette centre. At the same time, when concentrated samples are studied and multiple scattering is detected, the position of the point of measurement can be moved closer to the walls of the cuvette to reduce the effects of multiple scattering. Another advantage of NIBS is the possibility to identify dust or aggregates even under a single angle of scattering measurement, using a correlation function that allows accurate observation of the presence of any large size components.

Temperature control of the sample in the cuvette of the analyzer was carried out using an integrated Peltier element. The measurements were performed at the sample temperature of 25°C. Time of the thermostating after installation of the cuvette with the sample into the cell holder compartment was set to 5 minutes. The volume of each analysed sample was 2 mL.

Data processing: the autocorrelation function was carried out using the method of cumulants (parameters: average particle size Z and polydispersity index PDI) and the algorithm of soft NNLS (General Purpose – polydisperse model, regularization 0.01) to obtain the distribution. The calculations used the refractive index of water of 1.330 and the viscosity of 0.8872 cP.

**Results and discussion**

**X-ray scattering study**

Aqueous micellar solutions of SDS were investigated using X-ray scattering method (SAXS and WAXS). The obtained X-ray scattering curves of water and SDS solutions are presented in Figure 1. The concentration of SDS in solutions is greater than CMC. The range full range available for the SAXSess mc\(^2\) X-ray diffractometer is \( q = 0.03-28 \) nm\(^{-1}\).

The scattering profiles \( I(q) \) of water and the SDS solutions of 0.008, 0.01, 0.02, and 0.1 M have three peaks with the maxima positioned at \( q = 0.6, 1.5, \) and 19 nm\(^{-1}\) [4]. The first maximum corresponds to the distance between the micelles, the change in the profile of the scattering curve \( I(q) \) is more evident starting from the 0.03 M concentration. Therefore, it can be assumed that the concentration of micelles does not affect the scattering profile of the SDS solution of 0.01 M concentration at low-\( q \). The second peak is characteristic for the solutions of micelles; it is most clearly evident on the spectra at the concentration of SDS of 0.1 M. The intensity of X-ray scattering in this region of concentrations of SDS is the indicator of the structure of micelles. The third broad peak at 19 nm\(^{-1}\), identified in all scattering curves of water and SDS solutions, is the indicator of short-range order of water.

In the first approximation, the X-ray scattering curve can be represented as a sum of Bragg peaks, and the location of their maxima determines the distance \( d_{Bragg} \) between the particles in the ordered aggregates. According to the Bragg’s law, the distance \( d_{Bragg} \) can be described by Eq.(1).
\[ d_{\text{Bragg}} = a \frac{2\pi}{q_{\text{peak}}} \]  

where, the coefficient \( a \) is close to 1 even in the case of non-crystalline systems.

Using the Eq.(1) and the three values of \( q_{\text{peak}} \) the dimensions \( d_{\text{Bragg}} \) were calculated. The diameter of the micelles was ~4.2 nm, the average distance between the micelles was 10.5 nm and the distance O–O of a pair of molecules in the first coordination sphere of water was about 0.33 nm [4]. The O–O distance of the molecular pair in the first coordination sphere of water is changing. The mentioned distances are shown in Figure 2 in relative units \( I(q) \). This distance depends on the concentration of SDS [23]. According to estimates of different authors, the radial function of O–O distribution has a maximum in the region of 0.28–0.35 nm [24]. This band corresponds to the scattering from clusters of LDL and HDL of water and from clusters formed around SDS ions and micelles. The value of function \( I(q) \) depends on the square of the volume and scattering length density \( \Delta \rho^2 \), which is proportional to electron density \( \rho \). For water and clusters of LDL and HDL, \( \rho \) are equal to 9.53·10^{-6}, 8.96·10^{-6} and 11.16·10^{-6} Å^{-2}, respectively. If the function \( I(q) \) in the area of CMC₁ depended only on water concentration, then it would have been observed a gradual decrease of \( I(q) \) when the concentration of water decreased, same as for SDS solutions of 0.02, 0.03 and 0.1 M concentrations. Indeed, with increasing concentration of SDS the concentration of water decreases. However, the values of \( I(q) \) for solutions of SDS with concentrations of 0.008 and 0.01 M are larger than those for water without SDS (Figures 1 and 2). Therefore, in the area of CMC₁ the electron density of water clusters is changed. It increases because HDL appears around the micelles. The appearance of HDL around the micelles is proved by the method of molecular dynamics [25].

The obtained feature of the scattering curve for SDS solutions at \( q = 19 \) nm⁻¹ in the area of CMC₁ (Figure 2) can be explained by the shift of equilibrium LDL ↔ HDL in the process of the polymorphous transition in comparison with the same equilibrium in water. For concentrations of SDS greater than 0.02 M, the increase in the content of HDL around the micelles already does not compensate the reduction of \( I(q) \) due to reduction of water content in solution (Figure 2). As can be seen from Figure 2, CMC₁ can be determined by the peculiarities in the behaviour of the scattering cross section of clusters depending on the concentration of SDS.

The size of micelles can be calculated from the pair distribution function \( p(r) \) in a solution of SDS with concentration of 0.01 M (Figure 3) using SAXSess mc² software. This solution is less dependent on the structure factor \( S(q) \) when the repulsion of the micelles from each other is taken into account [20]. Based on the profile of \( p(r) \), one can imagine a small sphere with a diameter of 2 nm with statistics of the pair distribution of the scatters, which is invested in a large sphere with a diameter of 4.2 nm.

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**Figure 1.** The X-ray scattering curves of micellar solution of SDS and water, \( q = 0.03-28 \) nm⁻¹. SDS concentrations (top down): 0.01, 0.008, water, 0.02, 0.1 M.

**Figure 2.** The dependence of the scattering cross section of the scatters (of the ensemble of HDL and LDL clusters) or the dependence of \( I(q) \) at \( q = 19 \) nm⁻¹ on the concentration of SDS [21]. The dashed line shows the evaluation of the function without influence of \( \rho \) of HDL, LDL.
Thus, the micelle may consist of contact with HDL and hydrated with LDL structures of SDS at different times, and that they are in equilibrium with each other and with the monomers (Figure 4). The scattering cross section of the contact micelles can be superimposed on the scattering cross section of the hydrated micelles. Superimposed average diameters of their spheres are visible from the radial distribution functions of electron density: 2.8 and 6.0 nm (Figure 5). The radius of a small sphere of 1.4 nm is slightly less than the length of the alkyl group SDS of 1.67 nm.

The parameters of the pair distribution function $p(r)$ for a series of surfactants are presented in Table 1. These data were obtained in this study and in other studies using the same SAXSess m$^2$ diffractometer model and with the same processing of the SAXS data [26,27].

The width of peaks in the $p(r)$ profile provides the information about the degree of disorder of atoms, included in a pair of distribution. The relationship of the width of the second peak to the width of the first shows that the disorder of atoms in the micelles of ionic surfactants is always greater. This fact does not correspond to the concept of a classical micelle of ionic surfactants. Their second peak should show a small-sized layer of hydrophilic groups and of ions with opposite sign of charge. The disorder in this layer should be less than the disorder of the hydrocarbon part of micelle, because this layer is smaller and contains an adsorption layer of ions. As can be seen from Figure 4, the second sphere of the micelle is formed from superimposition of HDL, the contact micelle, LDL, alkyl groups, and $\text{SO}_4^-$, $\text{Na}^+$ of the hydrated micelle; in this sphere of the obtained micelles the disorder is greater.

Figure 3. The pair distribution function $p(r)$ of the micellar structure of SDS with a concentration of 0.01 M at temperature of 298 K.

Figure 4. Two possible superposition of dual micelle of SDS according to results of SAXS: the contact micelle (a), the hydrated micelle (b).
Table 1

| Solutions of surfactants                     | The ratio of the width of the second peak to the width of the first peak | The outer diameter of the micelle, nm | The ratio of the area under the second peak to the area under the first peak |
|---------------------------------------------|------------------------------------------------------------------------|----------------------------------------|-----------------------------------------------------------------------------|
| SDS, 0.01 M, 25°C                           | 1.64                                                                  | 6.4                                    | 4.0                                                                         |
| Sodium octanoate, 0.7 M, 10°C               | 2.3                                                                   | 4.75                                   | 8.9                                                                        |
| Sodium octanoate, 0.7 M, 40°C               | 2.6                                                                   | 4.75                                   | 7.0                                                                        |
| TWEEN 40, 0.01 the weight fraction, 25°C    | 1.2                                                                   | 3.3                                    | 3.0                                                                        |
| TWEEN 40, 0.25 the weight fraction, 5°C     | 1.4                                                                   | 2.5                                    | 1.8                                                                        |

Figure 5. The profile of electron density of the SDS micelle structure of 0.01 M at temperature of 298 K.

Figure 6. Functions of interactions:
1 – the potential of average force $w(r)$;
2 – the pair distribution function $p(r)$.

The comparative analysis of the relationship of the widths of the two peaks observed in the $p(r)$ function profile of each surfactant (Table 1) showed that the disorder in micelles of sodium octanoate is greater than that in SDS micelles. The area under the peaks of functions $p(r)$ provides the information about the number of pairs of scatterers. The ratio of the area under the peaks shows that the SDS micelle has less pairs of scatterers, than octanoate sodium, because the latter is more hydrated. Sizes of smaller and larger spheres of the micelles correlate with the structure of the surfactant. The outer diameter and the number of scatters in anionic surfactants are significantly higher than that in non-ionic TWEEN 40 [27]. This result can be explained only by the presence of water in forming micelles of ionogenic surfactants. So, a hydrocarbon group of TWEEN 40 contains 16 carbon atoms. The hydrophilic group consists of 20 oxyethylene groups, acetate group, pyran ring, and the outer diameter of the micelles of TWEEN 40 is less than that of the micelles of sodium octanoate. For comparison, a hydrocarbon group of sodium octanoate contains 8 carbon atoms and the hydrophilic group consists of carboxyl and sodium ions.

The profile of the radial electron density $\Delta \rho(r)$ of SDS micelle is presented in Figure 5. Function $\Delta \rho(r)$ shows the difference in values of $\rho$ in different parts of the micelle in relation to $\rho_{H2O}$, which corresponds to the zero value on the curve $\Delta \rho(r)$. In SAXS, the electron density less than that of water refers to the electron density of the hydrocarbon core of classic micelle. Hydrocarbon groups, for example, a methylene group, has $\rho_{CH2}= 6.5 \cdot 10^{-6}$ Å$^2$, i.e. less than $\rho_{H2O}$. Their size obtained at the intersection of $\Delta \rho(r)$ with zero values of 1.4 nm, is less than the size of the hydrocarbon part of the classic micelle of 1.67 nm. The radius of the whole micelle is 3.0 nm. It differs significantly from the radius obtained by the methods of SANS [14] and by light scattering [28]. According to the obtained data in the present study, the size of the shell thickness is 1.6 nm; which is too large for sulphonate ester groups and sodium ions in the model of a classical micelle. That is obvious, so to
confirm this conclusion there is no need to present comparative calculations of the obtained shell volume of the micelle from hydrophilic groups.

There are some contradictions between the methods of measurement of the micelles size SAXS and SANS. It is known that the formation of micelles in aqueous solution is explained by the hydrophobic interactions. The fundamental approach to hydrophobic interactions is based on consideration of the potential of average force \( w(r) \). It is shown that \( w(r) \) and \( p(r) \) are inverse functions [29]. The potential of average force between particles in water has two minima: at their contact and at the distance of the diameter of a water molecule. The concept of \( w(r) \) explains the existence of the contact (the first minimum of \( w(r) \), Figure 6) and the separated by water molecules hydrophobic interaction (the second minimum of the \( w(r) \), Figure 6), which is confirmed experimentally [30]. The functions \( w(r) \) and \( p(r) \) associate the energy of interaction between ions of the surfactant with the structure of the micelles. The maximum of \( p(r) \) correlates with a negative value \( w(r) \) or attraction (Figure 6). Conversely, the minimum of \( p(r) \) corresponds to a positive value \( w(r) \), i.e. repulsion.

Each of the two structures of the micelles is formed as a result of the transition order-disorder in the ensemble of HDL and LDL nano-systems, which oscillate between the states of an order (A) and disorder (B). These oscillations of small systems of water are accompanied by the oscillations of the two structures of the bistable micelle. Sometimes there is a contact micelle surrounded by HDL. Then there is the micelle, in which the SDS ions are separated from the other SDS ions by LDL (Figure 4). This interpretation of dual micelle is consistent with the concept of the potential of average force and the formation of the dual micelles during the polymorphous transition [4].

Two possible superpositions of SDS micelles in contact and separated by water molecules (hydrated) are shown in Figure 4. The SAXS and SANS methods allow visualization of the superposition of the cross sections of the two superimposed structures. When concentrations of SDS exceed CMC, the content of HDL around the contact micelle prevails [4], and so the diameter of SDS micelles obtained by SAXS method is 6.0 nm. The qualitative analysis of \( \Delta p(r) \) for the structure of the proposed model of micelle coincides with the model obtained in the experiment. For the quantitative analysis the material and the time balance of the two structures of micelle is not yet known.

Other researchers have also observed the duality of ionic micelles. So, using the method of \(^1\)H NMR the presence of 33% of premicelles, 27% of the micelles and 40% of the monomers were identified in solutions of SDS in the area of CMC [35]. The method of \(^1\)H NMR allows to follow the fast processes, but it cannot answer the question about the structure and size of aggregates. Therefore, the results of study of SDS solutions obtained using \(^1\)H NMR method can be explained with the help of our hypothesis. In our concept, the micelle and premicelle correspond to contact and hydrated micelles [35]. The contact micelle is not dissociated and the hydrated micelle has a long diffuse part of the electrical double layer. Therefore, in our concept, the classical formula is used to calculate the Gibbs energy of micelle formation, including the degree of dissociation of the micelles [4]. Due to the cooperatively processes of solubilisation the hydrophobic molecules (hydrocarbons) shift the equilibrium to the side of the contact micelle, and hydrophilic molecules (citric acid) shift that to the side of the hydrated micelle. In the hydrated micelle the synthesis of metal nanoparticles is possible. The new view at the structure of the micelle allows creating a new complex technology of obtaining nanomaterials from poor ores and wastes [36].

Recently, the kinetics of hydrocarbon groups in SDS micelles by quasi-elastic small-angle scattering of neutrons was observed [37]. It was established the existence of two local spheres in micelles, inside which the hydrogen atoms of the conformers of hydrocarbon groups with different diffusion coefficients move. The small local sphere has a radius of 0.10±0.04 nm, the hydrogen atoms in it move with the diffusion coefficient \((0.20±0.08)\cdot10^{-5}\) cm\(^2\)/s. In the large sphere with the radius of 0.29±0.09 nm, the hydrogen atoms move with the diffusion coefficient \((1.7±0.1)\cdot10^{-5}\) cm\(^2\)/s. The different diffusion of the hydrogen atoms along the chain of one molecule of SDS is explained using the classical micelle model [37]. When the hydrogen atoms of the chain are closer to the centre of the micelle core, they move slower. When the hydrogen atoms of the chain are closer to the surface of the micelle, they move faster. On the other side, the hydrocarbon groups of contact micelle have a smaller diffusion coefficient, because they are compressed by HDL. The hydrocarbon groups of hydrated superposition of micelles have a larger diffusion coefficient, because they are located in the micelle with the more “loose” water molecules of LDL.
**Dynamic light scattering study**

Micelles form and decay very quickly, the relaxation time of the processes of micellisation established using various methods for aqueous solutions of different surfactants varies from 1 to $10^9$ s. The values of relaxation time measured by the short-term methods, such as the method of pressure jump and the method of temperature jump are in the interval from $10^{-2}$ s to $10^5$ s. As a result of measurements by stationary methods such as NMR, EPR, the ultrasound absorption, the values of the relaxation were found smaller than $10^{-5}$ s [38]. It is assumed that the obtained relaxation time values correspond to the processes of association/dissociation of monomer–micelle, of association/dissociation of opposite ions of the micelle, of formation/decay of the micelle into ions, of the formation/decay of the micelles into submicelles. In the study of the kinetics of micelle formation in solution with SDS concentration of 0.01 M at 20°C, two values of relaxation time were obtained: 15 μs and 1.8 ms [39]. It is assumed that the time of 15 μs refers to the process of exchange of SDS ions with micelles and the time of 1.8 ms refers to the process of decay and formation of micelles. It should be noted that in the study of the kinetics of micelle formation the identification of the particles involved in the relaxation processes were not performed [37]. The effect of the changes in the water structure on the kinetics of micelle formation was not taken into account either. In “rigid” methods of classical studies of the kinetics of micelle formation such as the pressure jump, temperature jump and the ultrasound absorption, their effect on the process of micelle formation is not taken into account either.

Meanwhile, using the “soft” method of static light scattering it was shown that in aqueous solutions of ionic surfactants at concentrations near CMC, in the area of micellization, water heterogeneous structures with high anisotropy are formed in small amounts [38]. The law of attenuation of the intensity of argon laser radiation with wavelength 514.5 nm polarized parallel to the scattering plane from the incident light which is polarized perpendicularly to the scattering plane and observed at an angle of 90° was studied [40]. With time, the intensity is attenuated exponentially with a certain time constant. The time constant remained constant for water during the whole observation time. The effect of temperature on the inverse value of the constant allowed determining the activation energy of formation of heterogeneous anisotropic structures. It was equal to the enthalpy of the hydrogen bonds breaking between water molecules - 25.1 kJ/mol [41]. A periodic change of the scattering intensity of the SDS aqueous solution with a concentration of 0.032 M was observed. Oscillations of the scattering intensity continued for a few days of observations for the same solution. As a result of this study, in aqueous solutions of SDS and other ionic surfactants, the rotation of the plane of polarization of the polarized monochromatic beam in the same region of surfactant concentration was observed [42]. With increasing SDS concentration up to CMC, the rotation angle of the polarization plane gradually increased, and after reaching CMC it gradually decreased.

In the present study, the SDS solutions of 0.01 and 0.02 M concentrations were studied in the presence and absence of the same concentration of NaCl, using the DLS method. The DLS device detects the total intensity of the polarized monochromatic light scattering from particles during 1-2 minutes with 0.5 μs intervals, *i.e.* in the entire range of change of the relaxation time of the processes of SDS micelle formation from 15 μs up to 1.8 ms. The parameters of measurements, the obtained average diameters of the particles ($d$) and their standard deviations from the average are shown in Table 2; the average diameters obtained from the distribution of the number of scatterers over their size are given in parentheses.

The average hydrodynamic size of the particles was calculated using the Zetasizer Nano ZS instrument software according to the obtained correlation functions. The average diameters calculated according to the intensity of scattered light and to the number of scatterers (presented in parentheses in Table 2), are different. So, for a solution of a 0.01 M SDS concentration the result of the calculation according to the intensity of the scattered light corresponds to three types of spheres with diameters 1.28, 185, 602.9 nm, and the result of the calculation, according to the number of scatterers, gives only one type of spherical particles with an average diameter of 0.98 nm and standard deviation of 0.22 nm. The reasons for this difference are described in the user manual of the device [43]. The appearance of hydrodynamic spheres with diameter values of 185 and 602.9 nm can be attributed to the appearance of microemulsion, air bubbles, but not fluctuations. Therefore, first of all, the validity of our measurements will be discussed.
Table 2

The parameters of measurements and the obtained average diameters of the particles in aqueous SDS micellar solutions in the presence and absence of NaCl, at 298 K.

| Samples of SDS and SDS+NaCl, M | PdI    | y      | d, nm | I, % | Standard deviation of d, nm |
|--------------------------------|--------|--------|-------|------|----------------------------|
| 0.01                           | 0.412  | 0.879  | 1.28  | 23.2 | 0.21                       |
|                                | (0.98) |        |       | (0.22) |                             |
|                                | 185    | 61.6   | 49.78 |      |                             |
|                                | 602.9  | 15.2   | 168.1 |      |                             |
| 0.01+0.01                      | 0.316  | 0.923  | 3.56  | 73.7 | 0.78                       |
|                                | (2.82) |        |       | (0.59) |                             |
|                                | 209.3  | 23.4   | 68.29 |      |                             |
|                                | 5019   | 2.9    | 612.6 |      |                             |
| 0.02                           | 0.591  | 0.842  | 0.98  | 29.0 | 0.2                        |
|                                | (0.80) |        |       | (0.16) |                             |
|                                | 320.3  | 68.3   | 184.1 |      |                             |
|                                | 5395.5 | 3.6    | 312.6 |      |                             |
| 0.02+0.02                      | 0.278  | 0.897  | 3.5   | 71.3 | 0.78                       |
|                                | (2.69) |        |       | (0.59) |                             |
|                                | 226.5  | 26.4   | 74.21 |      |                             |
|                                | 5067   | 2.3    | 608.0 |      |                             |

PdI- is the polydispersity index or the average distribution of spheres;
y- is the section on the ordinate axis (y) of the correlogram;
d- shows the hydrodynamic sizes of three particles with different respective rates of diffusion, the average diameters obtained from the distribution of the number of scatters over their size are given in parentheses;
I- is the intensity of scattering by particles.

The purity of the SDS compound and its solutions was checked by the absence of minimum on the isotherm of surface tension of the solutions. The IR spectrum of the crystal of SDS obtained after its recrystallization from ethyl alcohol, coincided with the original IR spectrum (data not shown). The air bubbles were visually absent after settling the solution during the measurements. The solution was filtered through 0.45 µm membrane filter before pouring into the cell of the instrument.

The settings parameters, which are selected by the device automatic system, are the important criterion of reliability of measurements. In the present study, the setting parameters of the measurements were set in the following ranges: time of the measurement 50-80 s, the count rate 181.8-549.6 of kilophotones per second (kp/s), the segments on the ordinate axis (y) of the correlogram 0.842-0.923, the index of polydispersity (PdI) from 0.278 up to 0.591. These values were optimal for the equipment. The decrease in count rate during the measurement indicates the loss of particles in the monitoring area due to sedimentation. The value of the segment y, which is used to estimate the ratio of signal/noise of light scattered by studied sample, is optimal in the range 0.6-1.0. If it is greater than 1, it means that there are very large fluctuations of the particles in a dispersed system, the sample absorbs light or fluoresces. The values of the PdI index were optimal also. When PdI< 0.05 the system is monodispersed, and when PdI> 7 the system contains particles with very broad size distribution. In this case the DLS method cannot be applied to study the system. The baseline for all correlation functions was zero; another its position means that there are very large fluctuations in the system (the presence of air bubbles). When the particles move free, the correlation function is always damped. The correlation function for large particles has a flatter slope than that for small particles. Analysis of the correlation function using the software provides the average particle size (Z) and the index of polydispersity (PdI). After confirming the reliability of our measurements, the hydrodynamic spheres can be identified.

As one can see from Table 2, in solutions of SDS in the absence of NaCl, three hydrodynamic spheres are identified. These spheres can be denoted by numbers as their diameters increase. If for SDS solutions of 0.01 and 0.02 M concentrations without addition of salt 4 values of the diameter of the first sphere to average (Table 2), than the average diameter of the first sphere will be equal to 1.01 nm. Then the volume of the first sphere is equal to 0.540 nm³. The volume of a molecule of SDS is equal to 0.352 nm³ [44]. Therefore, in the solution of SDS
the monomers or dimers with the largest diffusion rate from the three spheres existing in the SDS solution are identified. The second and the third spheres without added salt are the joint fluctuations of water density and SDS concentration. The diffusion rate of the second sphere is greater than that of the third sphere. The density of LDL is less than that of HDL. Therefore, the second sphere consists of LDL+SDS, and the third sphere consists of HDL+SDS. The DLS software identifies these unusual particles by hydrodynamic spheres. In fact, the fluctuations of water density are anisotropic. The properties of these water structures are different in various directions. Their anisotropic structure is not yet known. It can be in the form of a spiral, sandwich, planes, etc. As the experiment shows, the structure has an optical activity. It is arguing that both structures exist longer than the time delay of the DLS instrument, i.e. 0.5 μs. This is logical as the hydrocarbons and hydrocarbon groups of SDS increase the life time of water clusters (density fluctuations). In micellar solution of SDS, these structures oscillate. One can predict the existence of two structures based on the theory of Hill, T. and of polyamorphous transition in water in a concentration region of the micelle formation [45].

Using the SAXS method, the cross section of two superimposed structures and monomers is observed. According to the SAXS measurements, the size of the sphere, which has SDS molecules, is limited by the diameter 6-6.4 nm. Thus, as it is described in detail [4], the spherical micelles of SDS represent a bistable oscillating system which is accompanied by polyamorphous transition in the ensemble of small systems of water.

When NaCl is added to the solution, the SDS molecules leave their joint with water clusters and form classical micelle. The electrostatic field of the salt ions destroys the fluctuations of water density. The average hydrodynamic diameter of the first sphere of micelle with addition of NaCl is 3.14 nm (see Table 2). This approximately coincides with the diameter of contact micelle 2.8 nm according to SAXS data. With increasing concentration of NaCl, the diameter of the micelle increases and reaches its highest value at the concentration of 0.45 M NaCl. The intensity of light scattered by micelles increases up to 71.3-73.7 %, and the intensity of light scattered by clusters of micelles together with water decreases as compared to that in the absence of NaCl in solution (see Table 2). In the presence of NaCl, the SDS monomers are included in the micelles or, probably, partially they are “hiding” in the remaining joint clusters of micelles and water. In the presence of NaCl, the hydrodynamic spheres with a size of 3.14 nm move faster than their hydrated counterparts. The spheres already are not “wrapped” by anisotropic structures of the water molecules. Bistable structures are in equilibrium with them, but these structures are much fewer than without added salt.

The DLS method can be used to obtain the information about the heterogeneous dynamics in SDS solution or about the fluctuations in space and time [46]. In this case, the diffusion coefficient and the diameter of the hydrodynamic sphere can be calculated using the data of the decay constant of the correlation function Γ. The picture of Brownian motion of crystalline nanoparticles, for example, gold, obtained by DLS is clearer. The hydrodynamic sphere is the hydrated solid particle. For micelles, it was obtained the summary information about the fluctuations of SDS concentration, about the fluctuations of density, entropy, anisotropy of water. In this case, the software of the device that uses the mathematical model of Einstein-Smoluchowski “considers” these fluctuations as the Brownian motion of solid particles. In other words, the dynamics of processes in a solution of SDS in a concentration region of micelle formation, where the SAXS method detects “blobs” of electron density (lower or higher than that in usual water), is described in the theory of DLS by Brownian motion of hydrodynamic spheres.

Conclusions

The processes of sodium dodecyl sulphate (SDS) micelles formation in aqueous solutions were studied using the X-ray scattering method (SAXS and WAXS) and dynamic light scattering (DLS).

The obtained results showed that the analysis of the X-ray scattering profile using the two approaches (i) independent on micelle model and (ii) direct modelling, differ considerably. As a result of the first approach for SDS aqueous solution with a concentration of 0.01 M, the calculated diameter of the micelle core was 2.8 nm, the calculated diameter of the micelle with a shell was 6.0 nm. As a result of the second approach, the calculated parameters using literature data, were 3.6 and 4.4 nm, respectively.

The obtained results of the study of SDS 0.01 M solutions using DLS method showed the presence of three hydrodynamic spheres with diameters of 1.0 nm (SDS monomers),
185 nm (joint fluctuations of SDS+LDL), 603 nm (joint fluctuations of SDS+HDL). When adding 0.01 M NaCl in SDS solution the monomers of SDS disappear, instead, the hydrodynamic spheres with a diameter of 3.14 nm (71-73 %) form. These spheres have the diffusion coefficient approximately equalled to the monomers diffusion coefficient. The number of the hydrodynamic spheres of SDS+SDS and LDL+HDL is greatly reduced.

The obtained results and their hypothetical contradiction with classical ideas about the structure of micelles of ionic surfactants are explained in the framework of coexistence of polyamorphous transition in water and micellization or, in other words, of coexistence of fluctuations of the SDS concentration and of fluctuations of water density.

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