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Q1 Raman spectroscopy of micellization-induced liquid–liquid fluctuations 2 in sodium dodecyl sulfate aqueous solutions

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ABSTRACT

This study is devoted to the investigation of the influence of micellization on structure properties of water and to 18 micellization-induced liquid–liquid fluctuations in sodium dodecyl sulfate aqueous solutions. The dependence of 19 Raman spectra of SDS aqueous solutions on surfactant concentration has been studied. Significant changes in the 20 dependences of water valence band characteristics at the moment of micellization have been observed. Precision 21 analysis of valence bands with the multivariate curve resolution–alternate least squares (MCR–ALS) method has 22 confirmed these results. The observed structural changes in water are interpreted as significant fluctuations of 23 the sizes of populations of LDL-rich and HDL-rich clusters of water. 24

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1. Introduction

Amphiphilic substances play an important role in the processes 31 of life activity of biological systems, and they find wide practical applica- 32 tions in technology processes [1–4]. Micelles are widely used for 33 concentration and separation of metals [5], surfactants [6], and biologi- 34 cally active substances [7]. Overall interactions determining collective 35 behavior of amphiphilic molecules in solutions play an important 36 role in the formation of the structure of high-molecular compounds 37 forming living organisms: proteins, nucleic acids, polysaccharides 38 etc. [8,9]. Recently, the interest in micellar solutions of amphiphilic 39 compounds rose due to the opportunity of using micelles as reactors 40 for the synthesis of nanoparticles of metals and their compounds 41 with fundamentally new properties [10], and also the opportunity 42 of using micelles as components of agents for drug transport in 43 bionanomedicine [11].

Dissolution of amphiphilic molecules in water is accompanied by a 44 complex of interesting physico-chemical phenomena [12]. At low 45 concentrations, the solution behaves as a usual strong electrolyte. When 46 some specific concentration (critical concentration of micellization) is 47 reached, the system undergoes a self-organization process – formation 48 of micelles consisting of tens, hundreds or thousands of molecules. With 49 further increase of concentration of amphiphilic molecules, the micelles 50 undergo various transformations of their shape, sizes, and properties. 51

The process of self-organization of the system is not finished when the 52 limit of solubility of surfactants in water is reached. Above the solubility 53 limit the system turns anisotropic and transfers to different liquid 54 crystal phases [1,3]. 55

At present there is no generally recognized theory describing the 56 self-organization process [3]. The models used in practice often allow 57 one to explain a number of properties and effects observed experimen- 58 tally, but they are not universal, and they are unable to cover the whole 59 diversity of the phenomena taking place in the system. It is considered 60 that the surfactant sodium dodecyl sulfate (SDS, C₁₂H₂₅SO₄Na) is the 61 most studied amphiphilic substance [3]. However, even sizes and com- 62 position of aqueous SDS micelles are still not determined explicitly. 63 Different methods determine different sizes of micelles (see Table 1). 64 Static methods of SAXS and SANS show that micelles consist of 60–70 65 molecules [13], while dynamic methods of NMR, DLS determine 66 approximately 2 times less molecules [14]. While micellization of SDS 67 is well explained by the phenomenological theory of hydrophobic inter- 68 action [3], the kinetics of micelle formation has many problems with 69 explanation of experimental results [15]. Even the thermodynamics of 70 formation of micellar systems is not developed completely. 71

It should be noted that a very important point in the investigation of 72 the solutions of amphiphilic compounds is the study of the influence of 73 micellization on the structure of the solvent. This is even more so if the 74 solvent is water, whose properties and structure still remain far from 75 being understood. With perfection of the equipment and methods of in- 76 vestigation, completely new and unexpected properties of water are re- 77 vealed. Numerous theoretical and experimental studies of water 78 properties show that in the scale of ≈ 1 nm there are clusters of low 79

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Table 1
Measured values of critical concentration of submicellization (CCSM) and critical micelle concentration (CMC) of sodium SDS in water.

Method of determination	CCSM, M	CMC, M
Fluorescence		$7.4 \cdot 10^{-3}$ [48], $8.0 \cdot 10^{-3}$ [49]
Surface tension, conductance		$8.0 \cdot 10^{-3}$ [32], $7.2 \cdot 10^{-3}$ [50]
Conductance		$8 \cdot 10^{-3}$ [48], $5.5 \cdot 10^{-3}$ [48], $6.7 \cdot 10^{-4}$ [51]
Benzoylacetone (BZA)-abs. (BZA)-abs.		$7.8 \cdot 10^{-3}$ [48]
Resonance Rayleigh scattering	$1.4 \cdot 10^{-4}$ [32]	$2.8 \cdot 10^{-3}$ [48]
Isothermal compressibility	$3.0 \cdot 10^{-4}$ [47]	$8.0 \cdot 10^{-3}$ [32]
Viscosity	$3.5 \cdot 10^{-4}$ [47]	
Shift of water band (5181 cm^{-1})	$3.2 \cdot 10^{-4}$ [47]	
Activity coefficient	$7.3 \cdot 10^{-4}$ [52]	
Raman spectroscopy	$6.0 \cdot 10^{-4}$, present work	$6.0 \cdot 10^{-3}$, present work

density liquid (LDL) and high density liquid (HDL), and phase LL-transition (liquid–liquid transition) between them can take place in the supercooled region [16–20]. Hypothesis of existence of the second critical point in water is under general discussion in literature now. Calculations show that the hypothetical “second” critical point of LL-transition in water is located in the region of the pressure–temperature phase diagram known as “no man’s land” at temperature below the homogeneous nucleation temperature $T < T_H = 235 \text{ K}$ [16–20]. In many publications, theoretical and experimental evidence of possible existence of LL-transition in water and in aqueous solutions in supercooled state is presented [16–18,21]. Since experimental study of liquids in supercritical states is almost an impossible task, it is very hard to get convincing evidence of existence of phase LL transition in water. Nevertheless, many researchers try to obtain experimental verification of coexistence of LDL and HDL clusters in supercooled water and water solutions. For example, the authors of [22] discovered the change of ratio of LDL and HDL clusters in water in the temperature range from 183 K up to 273 K by temperature dependences of half width and of integral intensities of the components of valence and bending bands of FTIR spectra of water. Experimentally, Mishima [23] found polyamorphic phase separation in water/LiCl solutions: an LL-transition of water itself induces phase separation between LDL with less solute and HDL with more solute. This finding is also supported by recent numerical simulations [24].

An active discussion about existence of water inhomogeneity on the nanometer-length scale at ambient conditions was opened in literature [25–29]. Wikfeldt et al. [25–27] have performed theoretical calculation and experimental demonstration of existence of density fluctuations in water at ambient conditions at 1 nm scale by the method of small-angle X-ray scattering (SAXS). Basing on SAXS data and X-ray Raman spectroscopy (using synchrotron radiation), the authors proposed that the density fluctuations were caused by difference between tetrahedral-bonded water molecules and molecules with broken hydrogen bonds, i.e., between low and high density water clusters. The authors of [28,29] claim that spectroscopic (Raman, IR, XAS, XES, etc.) data from water cannot be used to imply two-state behavior. Such debates are evidence of the fact that this problem is far from its solution.

In [30,31], the hypothesis that formation of micelles in aqueous solutions is accompanied by sharp fluctuations of concentrations of LDL and HDL clusters is set up. When amphiphiles are dissolved in water, hydrophobic hydration of hydrocarbon groups results in forming of a thin layer of water molecules around them, with a special near structure. In [30], this aggregate of water molecules, formed as the result of dissolving of an amphiphile, was called a nanocluster, or a small system. Nanoclusters are built into a continuous network of hydrogen bonds of water. They are stabilized by the hydrocarbon part of the molecule of amphiphile, and they have greater lifetime compared to other water clusters. At increasing concentration of amphiphiles, a transfer from hydrophobic hydration to hydrophobic interactions of hydrocarbon groups takes place. The concentration corresponding to this

transition is called either critical concentration of submicellization (CCSM) [31] or critical premicelle concentration (CPC) [32].

The concentration, at which the ability of water network of hydrogen bonds to include amphiphilic molecules is exhausted, and they form micelles, is critical for the structure of the solution, and it is called critical micellization concentration (CMC). For water solutions of SDS, the value of CMC equals $(8.0 \pm 0.2) \cdot 10^{-3} \text{ M}$ [32]. At CMC, abrupt change of surface and volume properties of aqueous solutions (surface tension, electrical conductivity, light scattering etc.) occurs [2,4,33]. Micellization is accompanied both by sudden change of enthalpy (it characterizes first-order phase transitions) and by sudden change of isobaric heat capacity showing manifestation of second-order phase transition [2,4]. Thus, behavior of thermodynamic characteristics of aqueous solutions of amphiphiles at micellization can indicate possible significant structure changes in thin water layers around hydrocarbon groups of amphiphiles in concentration region of their aggregation, when their practically important properties become apparent – detergent effect, wetting, foam formation etc.

At present time, investigations of aqueous solutions of amphiphilic molecules are still topical, and they are conducted at the highest possible experimental level, including methods of vibrational spectroscopy [1,34–37]. However, nearly in all studies, Raman and IR spectroscopy are used to study the behavior of carbon tails of amphiphilic molecules in water, micelles, and in micelle associates by the behavior of vibrational bands of CH-groups. So, the authors of [34] studied the dependence of the intensity variations of both the symmetrical and antisymmetrical vibration modes of CH_2 groups situated in the region $2800\text{--}3000 \text{ cm}^{-1}$ and of skeletal vibrations (C–C binding) in the region $1050\text{--}1150 \text{ cm}^{-1}$ on concentrations of amphiphiles. Actively studied were the changes of conformational order of the SDS alkyl-chain at the air–solution interface and in the bulk with increasing SDS concentrations and temperature of solutions by IR bands of CH and CH_2 [36–38], and by the behavior of $\text{CH}_2\text{--CH}_2$ and $\text{CH}_2\text{--O}$ IR bands [39]. The authors of [1] determine the state of alkyl chains of SDS in water by the ratio of intensities of the bands of asymmetric valence vibrations of methylene (2925 cm^{-1}) and methyl (2960 cm^{-1}). In [40], it has been demonstrated that the separation between the two peaks of the most intense band in the SDS spectrum – the SO_2 asymmetric vibrational feature (1219 and 1249 cm^{-1}) – is an indicative of the conformational structure of amphiphilic molecules.

In this paper, the results of studies with laser Raman spectroscopy of structural peculiarities of SDS solutions during micellization are presented. The changes of the band of valence vibrations of OH– groups in the concentration range from $1 \cdot 10^{-4} \text{ M}$ to $3.5 \cdot 10^{-2} \text{ M}$ have been studied. Significant changes of quantitative characteristics of water valence band at the moment of micellization have been observed. This was confirmed by the results of using the multivariate curve resolution method. The observed structural changes in water are interpreted as significant fluctuations of the size of populations of LDL and HDL clusters. A method of CCSM and CMC value estimation using concentration dependences of Raman spectra has been proposed.

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