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Mathematical modeling of surfactant self-organization in water solution in the presence of carbon nanotubes

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Abstract Based on the experimental results mathematical modeling of surfactant molecules organization in aqueous solutions into nanostructured formations was performed. The effect of the addition of carbon nanotubes on the processes was investigated. Numerical calculations of CTAB micelles dimensionless electrostatic potential were carried out in the framework of two most commonly used approximations: the Poisson-Boltzmann model and the jellium-approximation model for various surfactant concentrations in the presence and without of carbon nanotubes. A calculation procedure was developed that made it possible to determine the region of the most active counterions redistribution. The possibility of the interaction between micelles was noted, as a result of which a common self-consistent electric field appears, leading to spatial ordering in the bulk of solution. It was shown that there is a more rapid decay of the potential for the case of CTAB micelles in the presence of carbon nanotubes, which may indicate a change in the micelles morphology and their transition to a more compact form. It has been suggested that because increasing in the local surfactant concentration is observed near the carbon surface, carbon nanotubes can act as stimulators for the formation and growth of supramolecular structural complexes.

Introduction

Surfactants are widely used in a large variety of technological applications. The versatility of practical use of surfactant dispersions both in pure form and in various mixtures gives a basis for their comprehensive including theoretical study [1-4]. One of the modern applications of surfactants is their use for dispersing and functionalizing carbon nanotubes (CNTs) [5-9]. Carbon nanotubes are employed for many practical purposes, including for creation of advanced polymer, construction and rubber composite materials [10,11] and even in the additives for motor [12-14] and boiler fuel [15,16].

In many cases for a uniform distribution over the bulk carbon nanotubes are previously dispersed in aqueous surfactant solutions under the ultrasound influence. In different solvents through the features of their structure surfactant molecules have the ability to adsorb on surfaces and to spontaneous aggregation into various nanostructures. Due to adsorption and appearance of supramolecular formations, surfactant molecules functionalize carbon nanotubes, preventing them from re-adhering. Theoretical and experimental study of the processes occurring under the interaction of carbon nanotubes and the surrounding supramolecular complexes with the dispersion medium are important and relevant for all areas of technical use of CNTs. Since in the organized solutions the changes in the spatial distribution of charges occurring in any part of its volume inevitably must affect other parts of it, in this paper we attempted to theoretically analyze the processes occurring in a surfactant solution in the



presence of carbon nanotubes. The aim of this work was the mathematical modeling of the character of the surfactant molecules organization in aqueous solutions into nanostructured formations and the effect of the addition of carbon nanotubes on the occurring processes.

Experimental results

Experimental study of the processes occurring in pure anionic surfactant water solutions [17] and at the dispersing of multiwalled carbon nanotubes of the carbon nanomaterial "Taunit" produced by "NanoTechCenter" (Tambov, <http://www.nanotc.ru>), including the determination of the type of dominant mechanisms of interaction of surfactants with a carbon surface, was carried out by us in [9,18]. However, many authors believe that the most successful is dispersing of carbon nanotubes in cationic surfactant solutions [19], such as cetyltrimethylammonium bromide (CTAB) [8], dodecylpyridinium bromide [20,21], etc. This is due to the fact that the carbon nanotubes surface in an aqueous solutions has a negative charge and the positively charged hydrophobic hydrocarbon tails of cationic surfactants can bond more firmly to the surface of the CNT, stabilizing it in solution. Typically, CTAB with the chemical formula $C_{19}H_{42}BrN$ and a molar mass of 364.46 g/mol are used to disperse the CNTs. High critical micelle temperature (Kraft point is near 25-30 °C) and low critical micelle concentration (CMC), not exceeding 1 mM, are characteristic for CTAB dispersions. The rest of the literature data, describing the dispersions of CTAB, are highly contradictory. Thus for example at 30 °C the micelle aggregation number is 70-120, the degree of micelle ionization is 0.1-0.24, and the micellar radius is 2.56-3 nm. And only when determining the critical micelle concentration the values obtained by different authors are fairly uniform and fall within the interval 0.9-1 mM. The relatively low value of the CMC may have a significant effect on the spontaneous self-organization of CTAB molecules into the supramolecular structural complexes of the nanosheets type and the nanoflowers type described by us in [8,22].

CTAB dispersions and suspensions of carbon nanotubes in CTAB dispersions at 30 °C were investigated in our work [23] by two methods: conductometry and tensiometry. Comparison of the behavior of SDS and CTAB dispersions in the presence of carbon nanotubes and without them, together with available data on the behavior of SDS molecules on carbon surface, led to the conclusion that the carbon nanotubes strongly influence the aggregation properties of CTAB micelles. The obtained by us experimental data do not contradict the fact of the simultaneous existence of micelles with different aggregation numbers and different ionization degrees. The fact that part of CTAB ions are adsorbed on carbon nanotubes surfaces leads to an apparent change in the CMC with 1 mM for pure CTAB dispersion to 1.3-1.4 mM for CNT suspensions in CTAB dispersions.

In addition, data on specific electrical conductivity in the presence of CNTs and without them indicate a possible change in the micelles conformation toward to small micellar formations that have a larger mobility and a larger ionization degree. Earlier we showed that the dominant mechanism of adsorption of some anionic surfactants can be micellar [9,18]. Adsorption of surfactant molecules on carbon surface leads to an increase in their local concentration near the nanotubes. Most likely, rather uniform configurations of surfactant associates having a micellar or hemimicellar structure appear on the surface of CNTs. The contact and interpenetration of remote parts of diffusion shells of micelles leads to interaction of micelles on the surface and in the bulk. As a result, a common self-consistent electric field appears in the solution, leading to spatial ordering throughout the solution. Thus in organized media the orderliness of the conformational properties of micelles arising near the CNT surface due to interaction between micelles is transmitted throughout the bulk. This is facilitated by a short lifetime of a single micelle ($10^{-5} - 10^{-3}$ s) in an equilibrium disperse system.

Theory and calculations

For theoretical description of the phenomena occurring in organized solutions, an approximate statistical method – the self-consistent field method is usually used. The possibility of independent ion motion is allowed in this field. In the framework of the self-consistent field method, the electrostatic potential $\Psi(r)$ created by the micelle nucleus of radius a at the points of the diffuse part of the micelle is associated with the spatial distribution of the charge density around the micelle by the Poisson

equation [24, 25]

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Psi(\vec{r})}{dr} \right) = -\frac{\rho_c(\vec{r})}{\varepsilon_0 \varepsilon} \quad (1)$$

Here r is the radial coordinate with the origin at the center of the particle, $\rho_c(\vec{r})$ is the charge density of the diffuse part of the micelle, ε_0 and ε are the dielectric constant and the relative permittivity of the medium. As boundary conditions, the potential value $\Psi(a)$ on the surface of the micelle is used, as well as the fact that at large distances from the particle ($r = \infty$) the electrostatic potential tends to zero. The solutions of the Poisson equation allow us to determine the potential value $\Psi(r\vec{r})$, electric field strength $E = -d\Psi(r\vec{r})/dr$ and counterion concentration $\rho_c(r\vec{r})$ at any point near the micelle core.

In the relation (1) one can proceed to the dimensionless potential defined as $\Phi = \pm e \Psi(r\vec{r})/(kT)$, where k is the Boltzmann constant, and T is the absolute temperature. The choice of signs on the right-hand side of this relation corresponds to the fact that the dimensionless potential Φ must be essentially positive.

In the framework of the theoretical description of phenomena, we have studied numerical solutions of the Poisson equation that give the dimensionless electrostatic micelle potential $\Phi(r/a)$ as a function of the relative distance from their center r/a for various concentrations of dissolved surfactant (2, 4, 8, 16, 32, 64, 128 mM). Similar dependencies were calculated for the CTAB dispersions for the Poisson-Boltzmann (PB) model and the jellium-approximation (JA) model [24,25] which differ in the spatial micelles distribution in solution. The Poisson-Boltzmann model is based on the assumption that the spatial distribution of all particles, including micelles, is described by the Boltzmann distribution. In the jellium-approximation model, it is believed that micelles are distributed uniformly and surrounded by an ionic atmosphere in which counterions are subject to the Boltzmann distribution. For these models, the Poisson equation has a simpler species, but still requiring a numerical solution. In the course of numerical calculations, the following values of the main parameters of the CTAB micelles were used: the critical micelle concentration by our data [23] at $T = 30^\circ \text{C}$ was taken equal to $C_{\text{KKM}} = 1 \text{ mM}$, the degree of micelle ionization $\alpha = 0.24$, the average aggregation number of ions in micelle $N_{\text{agg}} = 70$, micellar radius $a = 2.56 \text{ nm}$, micelle surface potential $\Psi(a) = 101 \text{ mV}$ [26-28].

The addition of carbon nanotubes leads to redistribution of surfactant ions. In solution the number of surfactant ions decreases, since the carbon surface is rather attractive for the adsorption of these ions. However, even those ions that are adsorbed on the surface of CNTs can be organized into micelles or hemimicelles [9,18]. In the presence of carbon nanotubes, the CTAB dispersions have changes associated with alteration in the critical micelle concentration to 1.3 mM due to the adsorption of a certain number of surfactant ions on their surface. Therefore, in the first approximation, a theoretical analysis of the effect of carbon nanotubes can be carried out taking into account the change in this parameter.

We calculated the dimensionless electrostatic potential $\Phi_{\text{CNT}}(r/a)$ of CTAB micelles as a function of the relative distance from their center in the presence of CNTs at various concentrations of the dissolved surfactant (2, 4, 8, 16, 32, 64, 128 mM). Comparison of the corresponding values in the presence of CNTs and without them made it possible to calculate the difference curves

$$\Delta\Phi(r/a) = \Phi(r/a) - \Phi_{\text{CNT}}(r/a), \quad (2)$$

characterizing the potentials of micelles in CTAB dispersions in the absence and presence of carbon nanotubes. Calculations of the change in the dimensionless potential $\Delta\Phi(r/a)$ as a function of the relative distance from the center of the micelles were performed within the framework of the Poisson-Boltzmann model and the jellium-approximation model. The results are shown in Figure 1.

Results and discussion

Within the framework of the considered models taking into account the experimentally obtained parameters of CTAB micelles, we obtained numerical solutions of the Poisson equation that allow us to determine the electric field potential at any point of the diffuse layer of CTAB micelles. Accounting the change in the CMC in the presence of carbon nanotubes made it possible to calculate similar data for CNTs suspensions in surfactant dispersions in the first approximation. Comparison of the corresponding values of the potentials in the presence of CNTs and without them made it possible to find the difference curves $\Delta\Phi(r/a)$ (Fig. 1).

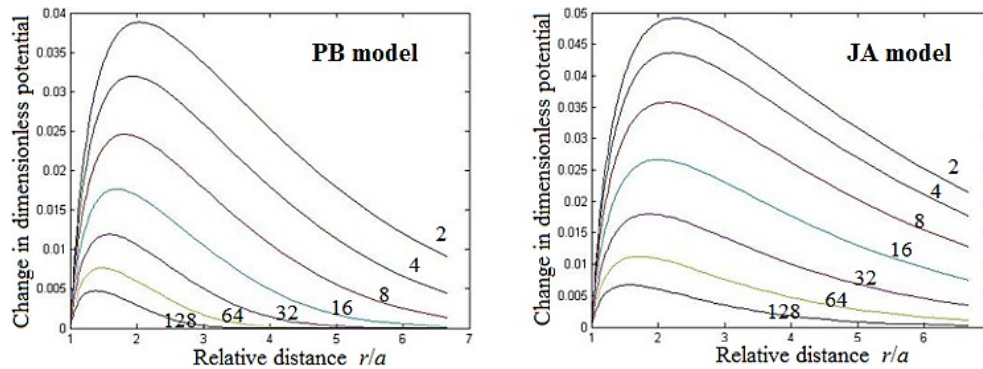


Figure 1. Calculations of the change in the dimensionless potential $\Delta\Phi(r/a)$ of micelles as a function of the relative distance from their center, performed in the framework of the Poisson-Boltzmann model (PB model, left) and the jellium-approximation model (JA model, right) for different concentrations of CTAB (2, 4, 8, 16, 32, 64, 128 mM)

The obtained curves have a clearly pronounced maximum. The presence of maximum indicates the existence of a region of the most active redistribution of counterions. Calculations show that at small distances from the micelle core (of the order of several internuclear distances) there is almost no change in the potential distribution, i.e. the microenvironment of the micelle core is almost constant. The next part of the micelle diffuse layer corresponds to the region of the most active redistribution of counterions. The maximum value of the change in the dimensionless potential $\Delta\Phi(r/a)$ and the value of the relative distance r_{\max}/a corresponding to the maximum change depend on the concentration C of the dissolved surfactant and differ slightly depending on the used model. The values of these quantities (C , $\Delta\Phi(r/a)$, r_{\max}/a) are given in Table 1. Also in Table 1 are presented the results of calculations of the Debye wavelength [29] for particles with the parameters of CTAB micelles for both models. The Debye wavelength λ is introduced to estimate the thickness of the ionic atmosphere created around a weakly charged spherical particle, i.e. to estimate the distance $a+\lambda$ (from the center), which is affected by the electrostatic field of the particle. In addition, Table 1 gives the values of half the relative distance between the centers of the micelles $D/2a$ ($D/2$ is the radius of the sphere per micelle), determined by the volume per micelle

$$\frac{D}{2a} = \frac{1}{2a} \sqrt[3]{\frac{N_{\text{agg}}}{N_A(C - C_{\text{CMC}})}} \quad (3)$$

In the course of calculations, it was found that the comparison of the Debye length with the distance which is affected by electrostatic field of micelle is not very correct, since the potential at these points is not small. This is also indicated by the fact that the region of the most active redistribution of counterions r_{\max}/a is located close enough to the relative Debye length $(a+\lambda)/a$, and even goes beyond this length for Poisson-Boltzmann model at concentration more than 16 mM. Moreover, practically for

all considered concentrations the potential of the micelles does not vanish even at the boundaries between neighbouring micelles (at distances $D/2$). This means the presence of interaction between the micelles caused by the interpenetration of the remote parts of micelle diffuse layers, as a result of which a general self-consistent electric field appears in the bulk, leading to spatial ordering in the entire solution and to appearance of supramolecular structural complexes [8,22].

Table 1. The concentration C of CTAB in solution, the maximum values of the change in the dimensionless potential $\Delta\Phi(r/a)$, the corresponding relative distances r_{\max}/a , and the relative Debye lengths $(a+\lambda)/a$ calculated for both models.

C (mM)	$R/2a$	Poisson-Boltzmann model			Jellium-approximation model		
		$\Delta\Phi(r/a)$	r_{\max}/a	$(a+\lambda_{PB})/a$	$\Delta\Phi(r/a)$	r_{\max}/a	$(a+\lambda_{JA})/a$
2	9.54	0.039	2.04	3.16	0.049	2.27	4.63
4	6.62	0.032	1.92	2.41	0.043	2.22	4.29
8	4.99	0.025	1.82	1.96	0.036	2.13	3.44
16	3.87	0.018	1.69	1.67	0.027	2.00	3.29
32	3.04	0.012	1.59	1.47	0.018	1.89	2.77
64	2.40	0.008	1.48	1.33	0.012	1.72	2.31
128	1.90	0.005	1.39	1.23	0.005	1.61	1.95

In the presence of CNTs a faster potential drop of CTAB micelles can speak about micelles of a more compact form having a smaller diffuse layer. This assumption allows to explain the observed by us increase in the specific electrical conductivity of CTAB dispersions in the presence of carbon nanotubes. In addition, the adsorption of surfactant molecules on the carbon surface leads to an increase in their local concentration near the nanotubes. This fact can enhance the interaction between micelles and contribute the appearance of centers of spatial ordering of surfactant molecules in aqueous solutions. Thus, carbon nanotubes can act as stimulators of the formation and growth of supramolecular structural complexes. It has been suggested that because increasing in the local surfactant concentration near the carbon surface is observed, carbon nanotubes can act as stimulators for the formation and growth of supramolecular structural complexes.

Conclusions

Based on the experimental results mathematical modeling of surfactant molecules organization in aqueous solutions into nanostructured formations was performed by us. The effect of the addition of carbon nanotubes on the processes was investigated. It was assumed that, in the first approximation, a theoretical analysis of the effect of carbon nanotubes can be performed taking into account the change in the value of the critical micelle concentration. Numerical calculations of CTAB micelles dimensionless electrostatic potential were carried out in the framework of two most commonly used approximations: the Poisson-Boltzmann model and the jellium-approximation model for various surfactant concentrations in the presence and without of carbon nanotubes. A calculation procedure was developed that made it possible to determine the region of the most active counterions redistribution. The possibility of the interaction between micelles was noted, as a result of which a common self-consistent electric field appears, leading to spatial ordering in the bulk of solution. It was shown that there is a more rapid decay of the potential for the case of CTAB micelles in the presence of carbon nanotubes, which may indicate a change in the micelles morphology and their transition to a more compact form. It has been suggested that because increasing in the local surfactant concentration is observed near the carbon surface, carbon nanotubes can act as stimulators for the formation and growth of supramolecular structural complexes.

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