Carbon Nanotubes Microenvironment in Ionic Surfactant Water Solutions

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Abstract. The processes of aggregation of anionic (SDS) and cationic (CTAB) molecules into supramolecular formations and the effect of carbon nanotubes on the processes were investigated by conductometry and tensiometry methods. Concentration dependences of the specific electrical conductivity and surface tension of aqueous SDS and CTAB dispersions and suspensions of carbon nanotubes of the carbon nanomaterial Taunit in these dispersions were obtained. A conclusion on the change in the conformation of CTAB micelles in the presence of carbon nanotubes was drawn. A significant increase in the packing density of CTAB molecules and their ordering in the monomolecular layer at the water-air interface in the presence of carbon nanotubes was shown. In particular, this makes it possible to control the properties of the surfactant surface layer by means of carbon nanotubes.

Introduction

The peculiarities of the structure and the properties of carbon nanotubes allow to use them in engineering of various devices, including for soft electronics (flexible and stretchable electronics) [1,2], as well as for photonics and optoelectronics [3,4].

The technical devices using carbon nanomaterials in aqueous surfactants dispersions are improved [5]. Dispersions of nanoparticles are used also for modifying the properties of various technological media. It should be noted that in the presence of nanostructures, the properties of liquid heterogeneous media change only due to the tendency of molecules to self-organization and the formation of supramolecular structures [6]. In particular, in the case of liquid hydrocarbon fuel [7-11], the addition of nanoparticles at a certain concentration can lead to a change in the rheological properties of the fuel. The effect of reducing viscosity can help decrease the energy intensity of production processes and promote energy saving. Carbon nanotubes can be used as nanoparticles to modify fuel media. They are the most universal additional material which is completely combustible jointly with fuel. The range of possible applications of CNTs is increasingly expanding, production is growing, and the price is decreasing.

The use of dispersions raises the question about the most effective methods for the uniform distribution of carbon nanotubes in the bulk and about the occurring processes [12-14]. Surfactants molecules in various solvents because of the structure features have the ability to adsorb on surfaces and to spontaneously aggregate into various nanostructures. The result of interaction with the carbon surface can be both the structureless adsorption of surfactant molecules and the formation of CNT / surfactant / water complexes, which have the form of micelles, mono- and bilayers, vesicles, etc. Due to adsorption, surfactants molecules functionalize carbon nanotubes by coating their surface and preventing them from re-adhering. Characterization of the adsorption mechanisms of surfactant molecules on carbon nanotubes, theoretical and experimental study of the processes occurring in the interaction of carbon nanotubes and their complexes with the dispersion medium are important and relevant for all areas of technical use of CNTs.

The processes occurring in anionic surfactants solutions in the absence [15] and at the dispergation of multi-walled carbon nanotubes of the carbon nanomaterial Taunit were investigated by us in [16,17] including the determination of the type of dominant mechanisms of interaction of

surfactants with carbon surface. The dynamic processes occurring near CNT surface at the adsorption of surfactants molecules and their self-aggregation into different structures were studied by NMR and infrared spectroscopy methods. It was shown that in the case of sodium and lithium dodecyl sulfates micellar self-organization of surfactant on the nanotube surface is the dominant one, but the form of micellar structure depends on the counterions. These conclusions are similar to the results of [18] in which it was shown that the sapphire surface is covered with a loose layer of flattened micelles at the adsorption of SDS molecules.

However, many authors believe that the most successful is the dispergation of carbon nanotubes in cationic surfactants solutions [19], such as cetyltrimethylammonium bromide (CTAB) [13], dodecylpyridinium bromide [20, 21], etc. This is due to the fact that the surface of carbon nanotubes has a negative charge in aqueous solutions. It is believed that positively charged hydrophobic hydrocarbon radicals of cationic surfactants are more strongly (as compared to anionic) binding to the surface of CNTs.

The purpose of this paper was a comparative study of the spatial organization processes of anionic and cationic surfactants molecules in supramolecular structures and the effect of carbon nanotubes on the processes occurring.

Methods and Materials

In this paper an experimental study of the morphology of heterogeneous systems water / surfactant / CNT were carried out for the two most common types of surfactants: anionic (sodium dodecyl sulfate, SDS, Sigma, $C_{12}H_{25}SO_4Na$) and cationic (cetyltrimethylammonium bromide, CTAB, Merck, $C_{19}H_{42}BrN$) with a molar mass of 288.38 g/mol and 364.45 g/mol, respectively. The choice of surfactant data was determined by their prevalence in technological applications and the authors' experience with them [13,22-24].

Dispersed in solutions of these surfactants multiwall carbon nanotubes from the carbon nanomaterial Taunit (NanoTechCenter, Tambov, Russia, http://www.nanotc.ru) were taken as the objects of study. For preparation of solutions the distilled water purified using a Milli Q system was employed. To obtain the samples, 2 ml of aqueous solutions of the required surfactant at the needed concentration were prepared first under the heating to 40 °C. Then, in 1 ml of every surfactant solution 5 mg of CNTs was dispersed with the following 10 minutes ultrasonication using Elma Sonic S 40H device, then centrifuged at ELMI centrifuge for 10 minutes at 10,000 g. The upper part of the solution above the dense sediment (supernatant) was selected for measurements.

Conductometry and tensiometry methods were used to study multicomponent systems. Concentration dependences of the specific electrical conductivity were determined using an InoLab COND 7310 conductometer. To study the surface tension, a tensiometer KRUSS K6 was used. The surface tension was determined by the anchor-ring method Due-Nui. For each concentration three values were measured and their arithmetic mean was searched.

All measurements were carried out at the temperature 30 ^{o}C.

Experiment

Conductometry measurements (Fig. 1), reflecting the processes of diffusive transport of matter, made it possible to obtain concentration dependences of the specific electrical conductivity of water dispersions and suspensions of the carbon nanomaterial Taunit of SDS (left) and CTAB (right).

In the course of tensiometric studies performed at various surfactant concentrations, the surface tension values of aqueous dispersions of SDS (left) and CTAB (right) and suspensions of carbon nanotubes of the carbon nanomaterial Taunit in dispersions of these surfactants were determined. The results are shown in Fig. 2.
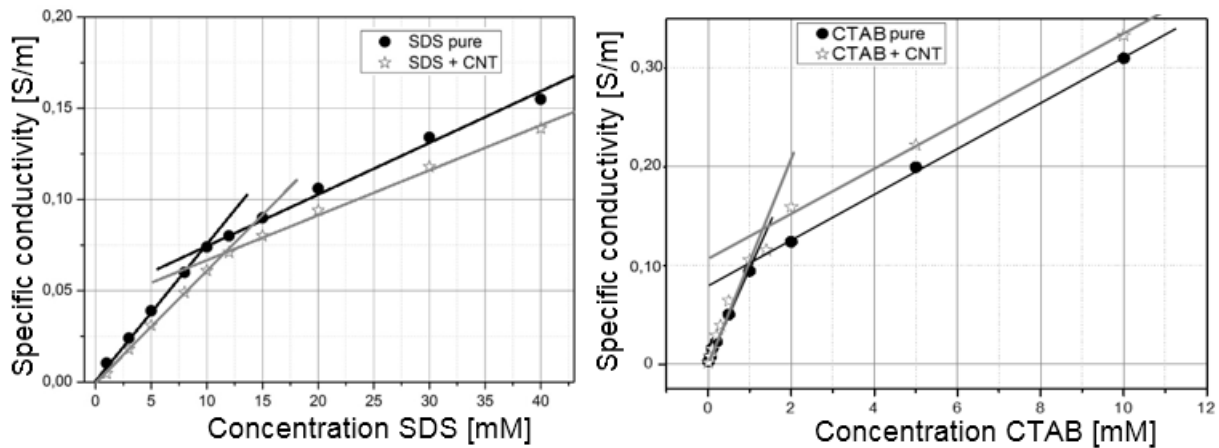
Fig. 1. Concentration dependences of the specific electrical conductivity of aqueous dispersions of SDS (left) and CTAB (right) and suspensions of the carbon nanomaterial Taunit.
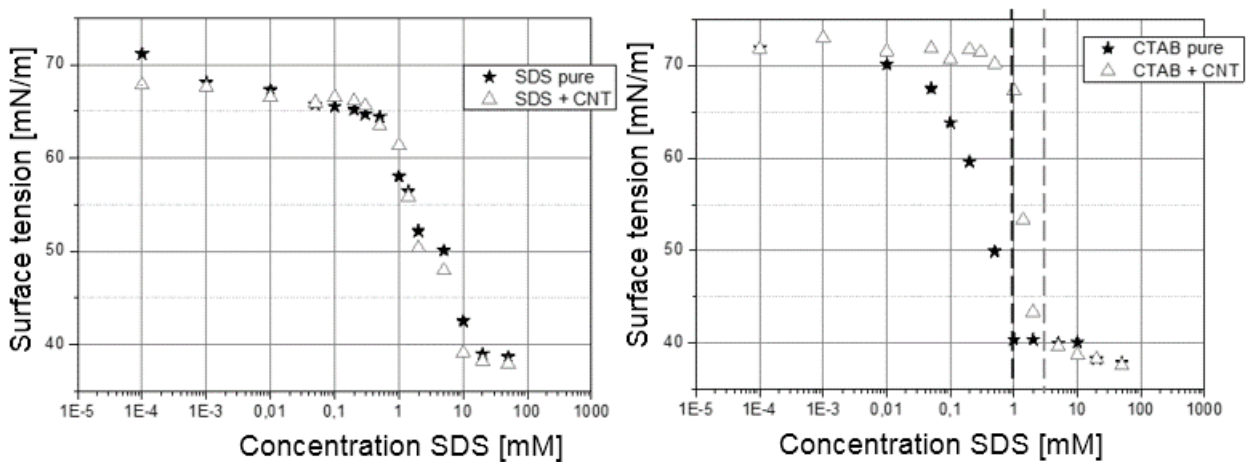

Fig. 2. Concentration dependences of the surface tension of aqueous dispersions of SDS (left) and CTAB (right) and suspensions of the carbon nanomaterial Taunit.

Results and Discussion

An investigation of the concentration dependences of the specific electrical conductivity of dispersions (Fig. 1) provides information about the kinetic phenomena that occur in solutions including the processes of ion association into micelles. The specific electrical conductivity of the solution of electrolyte $\kappa(C)$ is determined by the number of positive and negative ions, as well as the mobility of ions in the medium under the action of an electric field [14]. In the premicellar range, the graph of $\kappa(C)$ corresponds to a straight line passing through the point $C = 0$.

When a certain threshold concentration called the critical micelle concentration (CMC) is reached, spheroid associates of surfactant ions (micelles) form. The core of micelle consists of a certain number N_{agg} (usually several tens) of surfactant hydrocarbon radicals, and the shell is formed by polar parts of surfactant molecules oriented from the core to aqueous phase. In micelle of ionic surfactant the shell is a layer of potential-determining ions and carries an electric charge eN_{agg}, partially compensated to the value $q_M = e\alpha N_{agg}$ due to attraction of counterions and appearance of a double ionic layer. The coefficient α is called the degree of micelle ionization.

At concentrations exceeding the CMC the specific electrical conductivity of surfactant dispersions is determined by the presence of another type of mobile charged particles, micelles. A change in the solution morphology leads to a change in a slope of the graph of the specific electrical conductivity which no longer passes through the point $C = 0$. Therefore, the critical micelle concentration can be found as the point corresponding to the fracture of a straight line (Fig. 1).

As was to be expected, without CNTs the detected values of CMC were corresponded to standard values which are near 8.5 mM for SDS and 1 mM for CTAB. However, the introduction of carbon nanotubes revealed unexpected features. In the case of SDS the specific electrical conductivity of solutions decreased insignificantly throughout the entire concentration range studied (Fig. 1, left), with this percentage being the most perceptible with a small surfactant content. We attribute the decrease in the specific electrical conductivity of SDS dispersions by two factors: 1) due to adsorption of a small amount of positive counter ions Na^+, neutralizing the excess negative charge of CNT, 2) due to adsorption of SDS ions occurring after neutralization of the CNT surface. In the region of small surfactant concentrations, the CNT surface is obviously more preferable for adsorption of SDS than existence in ionic form in an aqueous medium. With an increase in SDS concentration the difference in the specific electrical conductivity is leveled, since at a certain concentration the vacancies on the CNT surface become occupied, functionalization of the nanotube is completed and SDS ions above the CMC assemble into micelles in solution. However, part of the surfactant ions associated with CNTs remains removed from the charge transfer processes and does not contribute to the specific electrical conductivity. The values of the CMC because of adsorption of a part of surfactant ions and due to decrease in their real concentration in the bulk of solution are shifted closer to the value of 12 mM.

In the case of CTAB no apparent changes in the specific electrical conductivity were observed in the region of premicellar concentrations. This can be explained 1) by the absence of adsorption of negative counterions Br^- on the negatively charged CNT surface, 2) by low mobility and small premicellar concentration of CTAB ions whose adsorption on the CNT surface does not lead to appreciable changes in the specific electrical conductivity.

In the micellar region, the specific electrical conductivity of CNTs suspensions begins to exceed the specific electrical conductivity of pure surfactant dispersions. Apparently the reason for this phenomenon is the non-uniformity of the CTAB micelle structure. There is the simultaneous existence of micelles with the different aggregation numbers and different conformations. In the presence of CNTs there is a displacement of their conformations toward smaller micellar formations that have a higher mobility and a greater degree of ionization α. Accordingly, such micelles have a larger sum charge and a more number counterions which are not associated with the cores and which contribute to the conductivity.

Indeed, it is necessary to note the inconsistency of the experimental data obtained by various authors for the CTAB. Thus for example at 30 °C the aggregation numbers of CTAB molecules N_{agg} varies from 70 to 120, the degree of micelle ionization α varies from 0.1 to 0.24, and the radius of the micelle varies from 2.56 to 3 nm. And only the values of the CMC obtained by different authors are fairly uniform and fall within the range of 0.9-1 mM [25, 26]. In fact, the presence of CNTs leads to ordering of the dispersion and to a more uniform distribution of micelles over the aggregation numbers. This behavior of surfactants in CNTs suspensions can be associated with the appearance of the most optimal configurations of surfactants associates on the carbon surface which have a micellar or hemimicellar structure. In organized media the orderliness of conformational properties of micelles arising near CNT surface due to their interaction is transmitted throughout the bulk of solution. This is facilitated by the short lifetime of a single micelle (10^{-5}–10^{-3} s) in an equilibrium dispersed system. The fact that some of CTAB ions is adsorbed on carbon nanotubes surfaces leads to an apparent change in the CMC from 1 mM for pure CTAB dispersion to 1.3–1.4 mM for CNTs suspensions in CTAB dispersions.

The surface tension in the dispersions of SDS and CTAB in the CNTs presence (Fig. 2) also behaves differently. It should be noted that carbon nanotubes with small surfactants concentrations float to the interfacial surface and manifest themselves almost as a surface-inactive substance.

In the case of SDS (Fig. 2, left) there are almost no significant differences in the behavior of systems with nanotubes and without them. This suggests that the interfacial surface and the CNT surface are equally preferable for SDS ions.

In the case of CTAB (Fig. 2, right) the concentration changes in surface tension indicate that the surface of carbon nanotubes is much more preferable for adsorption of surfactant ions. Before CMC all added surfactant ions go to the functionalization of CNTs. CTAB ions do not reach until the water-air interface. And only after achieving the CMC, when a part of nanotubes starts to go deep into the solution, the surface tension of water begins to change due to appearance of ions at the interface. We note that in this experiment a much higher concentration of CTAB was required to full functionalize the CNTs on the surface and in the volume of solution. In the conductivity studies changes are recorded that occur only in the bulk of solution. The critical micelle concentration was changed from 1 mM for dispersions up to 3 mM for suspensions in the surface tension case.

It should also be noted that there is a significant difference in the tangent of slope angle of the surface tension for dispersions and suspensions related to the capacitance of the saturated monomolecular layer and to the size of the area occupied by one molecule. The experimental data obtained indicate a considerable increase in the packing density and orderliness of the molecules of the monomolecular layer on the water-air interface in the presence of carbon nanotubes.

Summary

Thus a comparison of the behavior of SDS and CTAB dispersions in the presence of carbon nanotubes and without them, together with the available data on the behavior of SDS molecules on carbon surface, made it possible to infer the strong effect of carbon nanotubes on the aggregation properties of CTAB. This influence is manifested in a change in their structure in the presence of CNTs toward smaller micellar formations that have a higher mobility and a greater degree of ionization. The reason for this behavior can be the appearance of the most optimal configurations of surfactant associates on the carbon surface having a micellar or hemimicellar structure. In addition, a certain role is played by the presence of an organized dispersion medium, through which the ordering arisen near the CNT surface transmitted over the entire sample volume. Investigation of the monomolecular layer created in the CTAB dispersions at the water-air interface indicates a significant increase in the packing density of molecules of the monomolecular layer and their ordering in the presence of carbon nanotubes. This makes it possible to control the properties of the monomolecular layer with the help of CNTs.

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