Carbon nanotubes in the surfactants dispersion: formation of the microenvironment

A O Borovskaya[1], B Z Idiatullin[2] and O S Zueva[1]

[1] Kazan State Power Engineering University, 51 Krasnoselskaya str., Kazan 420066, Russia
[2] Kazan Institute of Biochemistry and Biophysics of Kazan Scientific Center of RAS, 2/31 Lobachevsky str., Kazan 420111, Russia

E-mail: tat355@mail.ru

Abstract. The chemical shifts from the protons belonging to surfactants differing only by the nature of counterions (Li, Na, Cs) are considered in their interaction with the surface of carbon nanotubes. It was shown that the dominant mechanisms of interaction of the surfactant molecules with the nanotubes surface in aqueous solutions depend on the nature of counterions. In particular, sodium dodecyl sulfate molecules interact with the nanotubes surface mainly by their head groups instead of tail groups, and thus it can be assumed that the surface of nanotubes can be coated with a layer of flattened micelles. In the other cases, a structureless random adsorption of surfactant molecules with partially ordered arrangement of head and tail groups, incompact for the molecules of lithium dodecyl sulfate or cling swarm round for the molecules of cesium dodecyl sulfate is more likely.

1. Introduction

In systems of nanoparticles there is a significant percentage of their constituent atoms residing at the surface, whereby the properties of nanomaterials are extremely sensitive to the microenvironment. Any change in the microenvironment, such as surface doping, functionalization of the surface by means of organic functional groups or its modification by coating of molecules layers causes a change in electronic and photophysical properties of nanoparticles. This sensitivity to external influences opens up the possibility not only for creating materials with desired properties, but also for the controlled variation of these properties.

In particular, carbon nanotubes because of the nature of their structure are considered as one of the most versatile nanomaterials. Single-walled carbon nanotubes consisting of atoms constituting the graphene plane rolled into a tube are almost perfect one-dimensional systems in which there is a quantum confinement and the high correlation between the charge carriers. Depending on the arrangement of carbon atoms with respect to their axes (viz. chirality) the nanotubes can be direct bandgap semiconductors, or metals with nearly ballistic conduction. Features of the structure of carbon nanotubes allow using them to create the various devices in photonics and optoelectronics. Of particular interest are the unique optical properties of semiconducting nanotubes – their ability to near-infrared emission of semiconducting species under electrical or optical excitation with certain parameters. Other intensively developed applications are creating nanotransistors, field emission displays, fuel cells, solar cells, photodetectors, switches, gas- and chemosensors based on carbon nanotubes [1–5].

Note that the electronic and optical properties of nanotubes, all of which are surface atoms, are extremely sensitive to the atoms of nearest microenvironment. There is a way to change the electronic properties of nanotubes by purposefully forming atoms of the local environment in a certain way. The appearance of methods that allow to obtain a stable suspension of carbon nanotubes in the surfactants dispersion [6] has led to the possibility of controlling the optical characteristics of nanotubes due to the change of dielectric properties of the local environment (by the surface modification) [7].

Another area of using carbon nanotubes stabilized by the surfactant is creating a system that can limit the nonlinear laser radiation with increasing intensity, which is important in developing practical tools for creating protection for eyes and sensors. Designed suspension limits the laser light in a broad spectral range by scattering of incoming radiation by light-induced inhomogeneities of the medium. Possibilities of parameter control of nonlinear optical limiting by varying the composition and properties of the system components are considered in papers [8, 9].

Nevertheless, despite the fact that carbon nanotubes have attracted extensive research interest, their practical usage in many areas is still hampered by the difficulty of their separation into monodisperse in diameter, length and chirality fraction. In papers [10–12], it was shown as surfactants can be used to achieve the desired separation. However, it is necessary to know the mechanisms of surfactant molecules adsorption on carbon nanotubes to further improve this procedure, as well as for the controlled change of properties of the systems containing the nanotubes.

2. Methods and materials

The method of nuclear magnetic resonance (NMR) which has been successfully applied to solve many problems of colloid chemistry was used as the main method of experimental study of the morphology of multicomponent systems [13–15]. The chemical shifts of NMR signals of proton, carrying information about their immediate environment and the dynamic processes occurring within the system were studied. All experiments were carried out on ^{1}H nuclei using an AVANCE III spectrometer (Bruker, Germany) operating at a proton-resonance frequency of 600.03 MHz. The parameters of spectrum registration were as follows: spectrum width, 7211.5 Hz; number of points, 64K; number of scans, 8; relaxation delay, 5 s; and duration of the 90° pulse, 8.3–10.7 s. Under the experimental conditions due to the short lifetime of the surfactant molecules in various states ($\sim 10^{-6}$ s), the observed signal was a weighted sum of contributions from molecules in different states: a) monomer, b) micellar, c) associated with the nanotube surface. The resonance frequency was determined with an error of 0.1 Hz which corresponds to $0.17 \cdot 10^{-3}$ ppm.

For this study we have chosen multiwall carbon nanotubes of carbon nanomaterial "Taunit" dispersed in solutions of three surfactants differing of counterions nature – sodium, lithium and cesium dodecyl sulfates, in deuterated water (Deuteriumoxid 99.9%) at a temperature $T = 30$ °C (Na, Li) and $T = 40$ ℃ (Cs). For the preparation of suspensions, ~ 5 mg carbon nanotube samples were filled with surfactant solutions in deuterated water of the desired concentration to the volume of 1 ml. The need to use deuterated water was dictated by the possibility of removing the strongest contribution of the signal coming from the protons of ordinary water, which makes it possible to study the signals from protons that are a part of the hydrocarbon chains of surfactant. Solutions with nanotubes were subjected to ultrasonication for 15 minutes by an Elma Sonic S 40H device, then centrifuged at an ELMI centrifuge for 10 minutes at 10,000 g. The upper part of the solution above the dense sediment was selected for measurements.

Surfactant content was varied in a range of 1–100 mM. Sodium dodecyl sulfate, SDS, (Sigma, L4509) and lithium dodecyl sulfate, LiDS, (ACROS Organics) with a main substance content of 99% were used as received. Cesium dodecyl sulfate, CsDS, was obtained from SDS by ion exchange in CsCl (from ECROS) solution. A mixed solution of SDS (0.5 M) and CsCl (1.0 M) was prepared at 50 °C. Then the solution was allowed to stand at 50 °C for 2 h and at room temperature for next 12 h. The sediment was separated from the solution using a Buchner funnel and again dissolved in CsCl solution. After three consecutive recrystallizations, the sediment was washed with acetone and dried over sulphuric acid till constant mass was obtained. The product yield was about 85%. The degree of

ion exchange for Na^+ and Cs^+ was determined by flame photometry (air–acetylene mixture) at 2,300°C and it was not lower than 96%.

3. Experiment

In this paper, an experimental study of the processes occurring on the surface of carbon nanotubes when modifying them by the surfactants was carried out. As a result of the measurement, the data array on the individual chemical shifts of the protons resonant lines from investigated surfactant in the concentration range of 1 mM to 100 mM was formed in the absence and in the presence of carbon nanotubes. Analysis of the concentration dependencies of proton chemical shifts of surfactants and response of the chemical shifts to the presence of the carbon nanotubes gave the opportunity to explore the adsorption of surfactant molecules on the surface of nanotubes and their self-assembly into micellar formation appearing in the dispersions of the surfactants, and possibly on the surface of carbon nanotubes.

The structural formula of dodecyl sulfate macroion can be written as $^-SO_4$-CH_2-CH_2-$(CH_2)_9$-CH_3. The observed chemical shifts were caused by the existence of four nonequivalent positions of protons in the molecule of surfactant, namely: a) the protons of α-CH_2 group which are closest to the head group SO_4 of the hydrocarbon chain, b) the protons of β-CH_2 group, c) the protons of the middle molecule methylene units which are almost equivalent, d) the protons of the tail group CH_3 of the molecule.

In the case of SDS (NaDS) dispersions, the maximum deviations of the chemical shifts due to the presence of carbon nanotubes were observed for the protons of α-CH_2 group of alkyl chain which are closest to the head group SO_4. The concentration dependence of difference of the proton chemical shifts for α-CH_2 groups of SDS in the presence and absence of carbon nanotubes is shown in figure 1 (left). Some, but much weaker, changes were observed for the group of β-CH_2. At the same time, no changes in proton chemical shifts for other groups were observed.
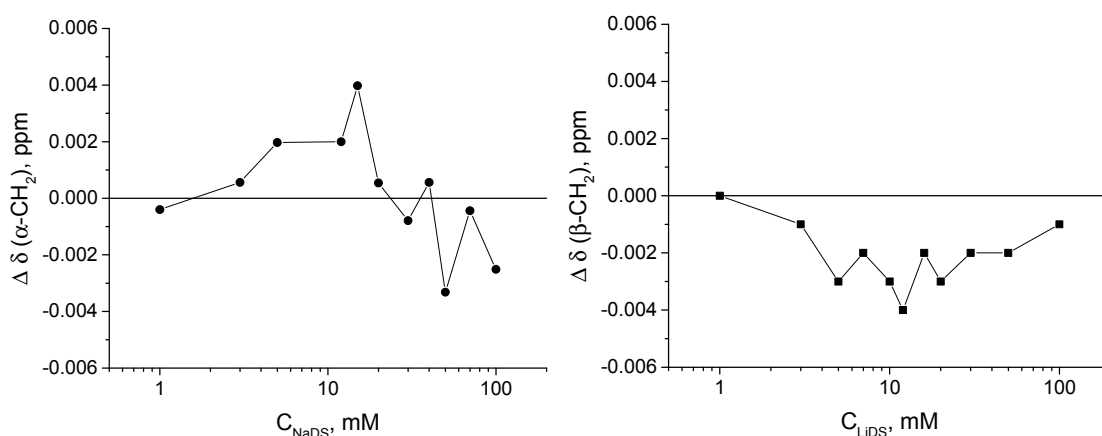

Figure 1.The difference of the proton chemical shifts for α-CH_2 group of SDS (left) and of the proton chemical shifts for β-CH_2 group of LiDS (right) between systems with and without carbon nanotubes in the solution at the same concentration of surfactants.

In the case of LiDS dispersions, the maximum deviations of the chemical shifts due to the presence of carbon nanotubes were observed for the protons of β-CH_2 group rather than for the protons of α-CH_2 group. The concentration dependence of the maximum response of proton chemical shifts for the proton β-CH_2 groups in the presence of carbon nanotubes is shown in figure 1 (right).

The proton resonance lines shifts corresponding to all four non-equivalent proton positions are clearly seen in cesium dodecyl sulfate (see figure 2). It should be noted that the maximum response of

the proton chemical shifts due to the presence of the carbon nanotubes in this case is much larger, and hence, the interaction of molecules with the surface of nanotubes CsDS is much stronger.
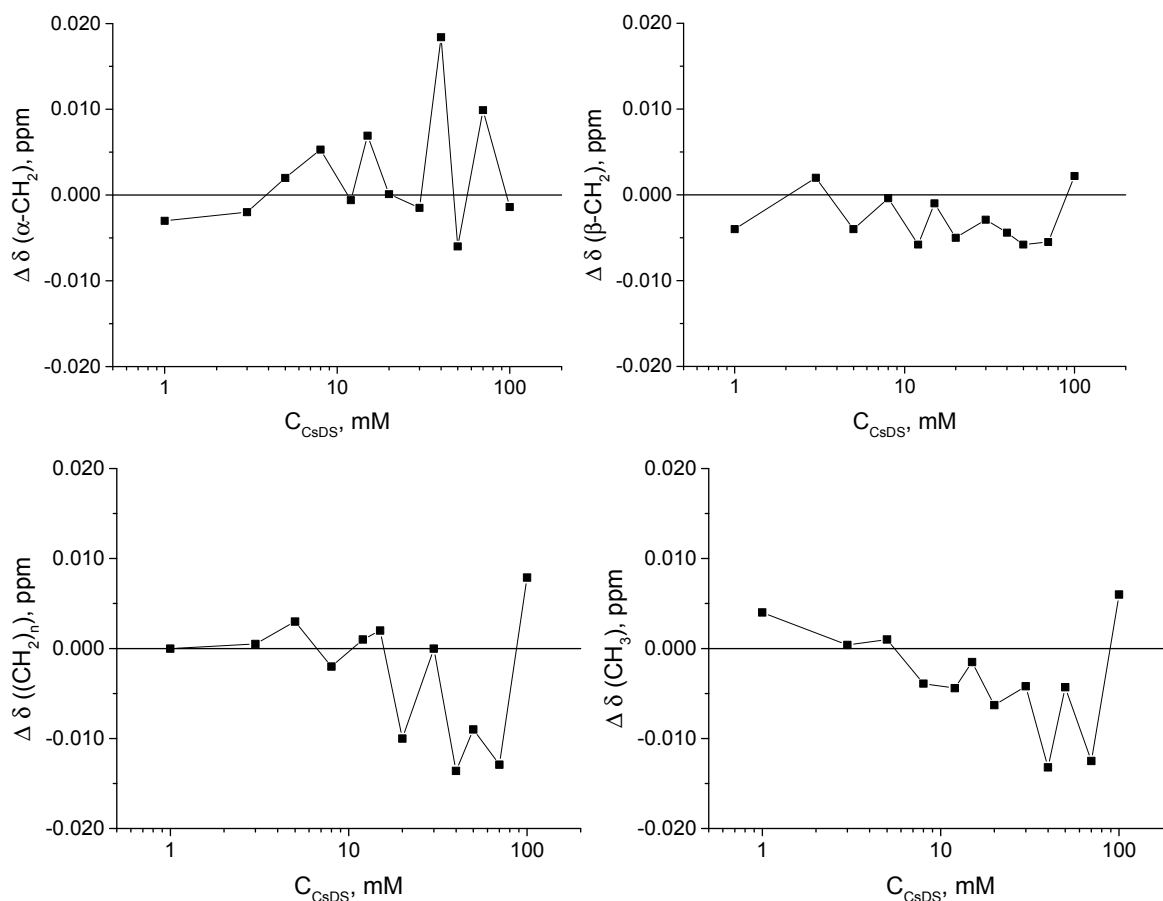

Figure 2. The difference of the proton chemical shifts corresponding to all non-equivalent proton positions for CsDS between systems with and without nanotubes in the solution at the same concentration of the surfactant

4. Results and discussion

The fact that in the case of sodium dodecyl sulfate the maximum deviations of chemical shifts were observed for protons of α-CH$_2$ group of alkyl chain which are closest to the head group SO$_4$ suggests that the adsorption of SDS occurs not as it was originally proposed in [6] and is still considered valid by many authors, for example, [16]. Previously, it was thought for reasons of chemical affinity that the hydrophobic molecules of SDS interact by their hydrocarbon tails with the hydrophobic surface of carbon nanotubes, shielding them from contact with water, and the hydrophilic head groups are turned to the aqueous surfactant phase, facilitating solubilization of the nanotubes. Some authors suggest that structureless random adsorption with no preferential arrangement of the head and tail groups is responsible for the stabilization of the dispersions [17, 18].

On the one hand, since the nanotubes are dispersed well enough with SDS [19], we may conclude that the head groups of the surfactant molecules are really rotated to the aqueous medium. On the other hand, our data suggest that the surfactant molecules interact with the surface of nanotubes by means of their head groups. Tail groups are not involved into the interaction. This means that the dominant adsorption mechanism is another one. It can be assumed that at concentrations above the critical

micelle concentration, the surface of nanotubes is coated with a layer of flattened micelles, like during adsorption of molecules SDS on the aluminum oxide surface [20]. The images of similar formations on the nanotube surface which is functionalized by another amphiphilic compound are presented in [21]. Incidentally, the dense arrangement of flattened micelles is to some extent similar to a bilayer. In addition, we can assume the presence of adsorption on carbon nanotubes not only of surfactant macroions, but also of a certain amount of sodium counterions with possible recovery of integrity of some dissociated macromolecules. A significant relative change in the conductivity of SDS dispersions observed by us (unpublished data) at low concentrations of surfactants in the presence of nanotubes can only be explained by a significant decrease in the number of carriers of both signs in the solution. It should be noted that the adsorption of positive sodium counterions is not surprising because the surface of nanotubes in the aqueous solutions charged negatively in accordance with existing literature data. Sodium counterion adsorbed due to Coulomb interaction attracts surfactant macroion recovering for some time (since all the processes possess dynamic nature) integrity of the molecule. That is why the micelles may have a flattened shape being essentially transitional option from gemimicelles to micelles.

In the case of lithium dodecyl sulfate the following picture can be proposed. Largely hydrated lithium counterions can not be adsorbed on the surface of nanotubes. However, the presence of lithium counterions near the surface causes the head groups to come off from the surface to interact with them. That is why the maximum response of chemical shift was observed not for α-CH$_2$ groups but for β-CH$_2$ groups. For the rest of surfactant ions, the most probable is the structureless random adsorption with partially ordered arrangement of head and tail groups, incompact for the molecules of lithium dodecyl sulfate because the head and tail parts are not strongly associated with the nanotubes.

A slightly different picture was observed for cesium dodecyl sulfate. The addition of cesium ions to SDS can isolate the carbon nanotubes from direct contact with water molecules more effectively, as noticed in [7]. According to our data, the dominant mechanism of adsorption of CsDS is characterized by a strong interaction of all parts of the molecule with the nanotubes surface. This means that some counterions can be adsorbed on the surface of nanotubes, thus connecting with the surfactant ion sufficiently to form a stable and electrically neutral molecule. Then, the surfactant molecules are located almost parallel to the plane of the carbon sheet due to weaker interactions. As a result, the surfactant ions densely lie on the surface characterizing the cling swarm round structureless adsorption. Therefore, the use of DSC leads to surface modification of carbon nanotubes at much lower concentrations.

5. Conclusion

The study of chemical shifts from the protons belonging to the three surfactants differing only by the nature of counterions in their interaction with the surface of carbon nanotubes was carried out. It was shown that the dominant mechanisms of interaction of the surfactant molecules with the nanotubes surface depend on the nature of counterions. In particular, sodium dodecyl sulfate molecules interact with the nanotubes surface mainly by their head groups instead of tail groups, and thus it can be assumed that the surface of nanotubes can be coated with a layer of flattened micelles. In the other cases, the most likely is a structureless random adsorption of surfactant molecules with partially ordered arrangement of head and tail groups, incompact for the molecules of lithium dodecyl sulfate or cling swarm round for the molecules of cesium dodecyl sulfate. It was suggested that a modification of nanotube surfaces is related to the processes of a dynamic nature: adsorption of some of the counterions and restoring the integrity of a certain number of dissociated surfactant molecules.

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