АДСОРБЦИЯ ОКСИЭТИЛИРОВАННЫХ ИЗОНОНИЛФЕНОЛОВ НА УГЛЕРОДНЫХ НАНОТРУБКАХ ИЗ ВОДНЫХ РАСТВОРОВ

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Одним из подходов к решению проблемы получения дисперсий углеродных нанотрубок является использование неионогенных поверхностно-активных веществ в процессах ультразвуковой обработки углеродных наноструктур в водных растворах. Эффективность диспергирующего и стабилизирующего действия неионогенных поверхностно-активных веществ определяется адсорбционным взаимодействием молекул поверхностно-активных веществ с графеновой поверхностью, исследование которого может выявить важные закономерности получения стабильных дисперсий углеродных нанотрубок при ультразвуковой обработке в жидкостях. Целью данной работы было исследование адсорбции серии оксиэтилированных изононилфенолов с варьируемой средней степенью оксиэтилирования на одностенных и многостенных углеродных нанотрубках из водных растворов. Вычисление адсорбции неионогенных поверхностно-активных веществ на углеродных нанотрубках было рассчитано на основании изменения равновесной концентрации оксиэтилированных изононилфенолов в растворе в присутствии углеродного наномодификатора. Равновесная концентрация неионогенных поверхностно-активных веществ определялась методом абсорбционной спектроскопии. Установлено, что форма изотерм адсорбции оксиэтилированных изононилфенолов на углеродных нанотрубках из водных растворов до ультразвуковой обработки соответствует ленгмюровской изотерме адсорбции L2. Показано, что с увеличением средней степени оксиэтилирования значения максимальной адсорбции оксиэтилированных изононилфенолов снижаются. Очевидно, это связано с конформационными изменениями оксиэтиленовой цепи, оказывающими влияние на размер мицелл и структуру адсорбционного слоя. Установлено, что гидрофобное взаимодействие углеводородного радикала поверхностно-активных веществ с графеновой поверхностью является основным механизмом адсорбции оксиэтилированных изононилфенолов на углеродных нанотрубках. Получены и исследованы дисперсии углеродных нанотрубок в мицеллярных растворах неионогенных поверхностно-активных веществ. Показано, что ультразвуковая обработка приводит к изменению механизма адсорбции неионогенных поверхностно-активных веществ на углеродных нанотрубках.

Ключевые слова: поверхностно-активные вещества, углеродные нанотрубки, адсорбция, адсорбционный слой, ультразвуковая обработка

ADSORPTION OF ETHOXYLATED ISONONYLPHENOLS ON CARBON NANOTUBES FROM AQUEOUS SOLUTIONS

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One of the approaches to solving the problem of carbon nanotubes dispersions obtaining is the use of nonionic surfactants in the processes of ultrasonication of carbon nanostructures in aqueous solutions. The effect of nonionic surfactants on dispersing and stabilizing is determined by the adsorption interaction of surfactant molecules with a graphene surface, the study of which can reveal important patterns of stable carbon nanotubes dispersions obtaining during ultrasonic treatment in liquid media. The aim of this work was to study the adsorption of ethoxylated isononylphenols with a variable average degree of ethoxylation on single-walled and multi-walled carbon nanotubes from aqueous solutions. The value of adsorption of nonionic surfactants on carbon nanotubes was calculated on the basis of changes in the equilibrium concentration of ethoxylated isononylphenols in the solution at presence of carbon nanotubes. The equilibrium concentration of nonionic surfactants was determined by absorption spectroscopy. It was found that the shape of adsorption isotherms of the ethoxylated isononylphenols on carbon nanotubes from aqueous solutions before ultrasonic treatment corresponds to the Langmuir adsorption isotherm L2. The values of maximum adsorption of ethoxylated isononylphenols were shown to decrease with an increase in the average degree of ethoxylation. Obviously, this is due to conformational changes in the polar chain, showed in the sizes of ethoxylated isononylphenols micelles, in the structure of the adsorption layer. It has been established that the hydrophobic interaction of the surfactants hydrocarbon radical with a graphene surface is the main mechanism for the adsorption of ethoxylated isononylphenols on carbon nanotubes. The dispersions of carbon nanotubes in micellar solutions of nonionic surfactants were obtained and studied. It was shown that ultrasonic treatment leads to a change in the mechanism of nonionic surfactants adsorption on carbon nanotubes.

Key words: surfactants, carbon nanotubes, adsorption, adsorption layer, ultrasonication

INTRODUCTION

Carbon nanotubes (CNT) are the subject of a variety of fundamental and applied research due to their mechanical, electrical, and thermally conductive properties. The prospect of using CNTs when creating new functional composite materials or modifying existing ones is relevant for materials science and polymer chemistry [1, 2].

At the same time, the aggregated state of CNTs doesn’t allow obtaining stable dispersions of nanotubes in aqueous and organic media, including polymeric ones, and prevents their uniform distribution in the volume of the composite material [3, 4].

One of the approaches to solving the problem of nanotubes aggregation is non-covalent modification of the CNTs surface by adsorption of anionic, cationic and nonionic surfactants [5-7]. Dispersion of carbon nanotubes in aqueous solutions of the surfactants, as a rule, is carried out using ultrasonic (US) treatment. US treatment promotes the exfoliation of nanotubes from each other, while surfactant molecules penetrate into the spaces between the tubes and prevent their re-aggregation [5, 8, 9]. In a number of studies, the optimal surfactant / CNT ratios were revealed at which stable concentrated dispersions of nanotubes with a small particle size can be obtained [10]. At the same time, it was shown that the quality of dispersions dependence on the surfactant / CNT ratio is implicit [11]. Most studies in this area are related to the dispersion of CNTs at surfactant concentrations in solution higher than the critical micelle concentration (CMC) [12]. However, it was shown that the formation of micelles isn’t an important condition for the dispersion of nanotubes, and the surfactant concentration in solution below the CMC is also effective [13]. These contradictions are obviously based on differences in the adsorption interaction of surfactant molecules with the CNTs surface. Despite the fact that considerable attention has been paid to the interaction of surfactants with the surface of nanotubes, the question of the morphology of the adsorption layer of surfactant molecules on the CNTs surface remains open.

Previously, we studied the effect of nonionic surfactant additives – ethoxylated isononylphenols (EONP) on the process of ultrasonic dispersion of fullerences C_{60} and CNTs and obtained results [14, 15], which give evidence to the significant effect of the...
number of ethoxylated groups of the surfactant molecule on the complex of dispersion properties. There is insufficient information in the literature on the effect of the ethoxylation degree of nonionic surfactants on the nature of adsorption on CNTs. The effect of ultrasonic treatment on the adsorption layer morphology hasn’t been studied. A correlation analysis of the data on the adsorption interaction of nonionic surfactants with nanotubes and the colloid-chemical properties of disperse systems obtained by ultrasonic treatment can be useful to identify important aspects of the preparation of CNT dispersions in aqueous and organic media.

The aim of this work was to study the adsorption of a series of EONP on CNTs depending on the ethoxylation degree of nonionic surfactants, the morphology of nanotubes, pH and ultrasonication.

EXPERIMENTAL PART

The objects of the study were nonionic surfactants – EONP produced by PJSC “Nizhnekamskneftekhim” with an average degree of ethoxylation n = 8, 10, 12. It was found by gel permeation chromatography that they are characterized by low polydispersity: 1.05-1.10 [16].

Single-walled and multi-walled carbon nanotubes were used in the work without preliminary purification of the starting material. Single-walled CNTs (SWCNT) of the “Tuball” brand (CNT content 75% wt., diameter d = 1.8 nm, length l > 5 μm, specific surface \( S_{SP} = 422 \text{ m}^2/\text{g} \)) and “Tuball R&D” brand (CNT 80% wt., d = 1.8 nm, l > 5 μm, O ≈ 5% wt., \( S_{SP} = 600 \text{ m}^2/\text{g} \)) manufactured by OCSIAl company (Novosibirsk) were synthesized by the plasma-chemical method according to the technology of academician M. Predtechensky. Multi-walled CNTs (MWCNT) of the “Taunit” brand (CNT > 99 wt., d = 20–40 nm, l > 2 μm, O < 6% wt., \( S_{SP} > 120 \text{ m}^2/\text{g} \)) manufactured by LLC “NanoTechCenter” (Tambov) obtained by chemical vapor deposition (CVD) method in the process of catalytic pyrolysis of hydrocarbons.

Aqueous solutions of nonionic surfactants with a pH value of 2, 4, 6, 8, 10, and 12 were prepared using HCl (0.01N, pH 2) and NaOH (0.01N, pH 12). Decreasing the pH of solutions below 2, or increasing more than 12, leads to salting-out of nonionic surfactants. Surfactant solutions with a 20 ml volume in the presence of nanotubes (0.1% wt.) were mixed on a LOIP LS-110 device at 200 rpm for an hour, then they were kept for 24 h to achieve adsorption equilibrium. A further increase in the duration of mixing or storage doesn’t lead to a change in adsorption values. Adsorption isotherms were calculated on the basis of equilibrium concentrations of nonionic surfactants in aqueous solutions in the absence and presence of nanotubes, which were determined by absorption spectroscopy on a Perkin Elmer “Lambda 35” spectrophotometer using a calibration curve at a wavelength \( \lambda = 275 \text{ nm} \) [17].

Dispersions of CNTs in water and in aqueous surfactant solutions were obtained by ultrasonication in a YX2100 ultrasonic bath for 20 min at a frequency of 42 kHz and a power of 50 W. The initial content of CNTs was 0.1% wt.

The study of the adsorption interaction of EONP with CNT after ultrasonication was carried out by measuring the surface tension of surfactant solutions in the presence of nanotubes on a K6 KRUSS tensiometer according to the Du Nui ring method in a temperature-controlled cell at a temperature of 25 °C and pH = 6.0 [18].

RESULTS AND DISCUSSION

In Fig. 1 shows the adsorption isotherms of EONP on CNTs. It can be seen from the figure that the curve of the adsorption isotherm corresponds to the adsorption isotherm L2 according to the Gils classification. The maximum adsorption \( A_{max} \) on SWCNTs is higher than on MWCNTs, which can be explained by the larger specific surface area of SWCNTs. With an increase in the ethoxylation degree, the values of \( A_{max} \) decrease. Obviously, this is due to the conformational changes in the oxyethylene chain that we studied earlier [19]. They affect the adsorption capacity at various interfaces and on the size of micelles.
result of oxidation by acids during the purification of the starting carbon material from catalyst impurities. Analysis of the fig. 1 showed that despite the fact that the SWCNT “Tuball R&D” are characterized by a higher specific surface area than the SWCNT “Tuball”, it has a lower value of the maximum nonionic surfactant adsorption. Adsorption of EONP n = 12 on the oxygen-containing surface of “Tuball R&D” is completely absent, but it is observed for the MWCNT “Taunit” (d = 20-40 nm). This indicates the dependence of nonionic surfactants adsorption on the ethoxylation degree, the presence of polar groups on the graphene surface, and the diameter of the nanotubes. The absence of adsorption on SWCNT “Tuball R&D” can be explained by the fact that it is energetically more favorable for EONP n = 12 molecules to be in the solution volume in the form of free molecules or as a part of micelles.

One of the methods for assessing the effect of polar groups on a graphene surface on the adsorption of nonionic surfactants is the study of changes in adsorption depending on the pH of the medium [20].

In Fig. 2 shows the dependence of EONP adsorption with the ethoxylation degree n = 8 and n = 12 on the pH of the solutions (C_{surf} = 4·10^{-4} mol/L). An analysis of the figure shows that the nature of the dependence of adsorption on the surfactants degree of ethoxylation and the morphology of carbon nanotubes is preserved. The adsorption of EONP on SWCNT «Tuball» remains constant for n = 8 in the pH range 4-12, and for n = 12 pH range 2-12, which indicates that the main mechanism of adsorption of nonionic surfactants on the surface of non-oxidized nanotubes is hydrophobic interaction of the EONP hydrocarbon radical with the graphene surface of nanotubes. The EONP structure contains a benzene ring, which, according to some data, has an affinity for the surface of nanotubes [21]. At the same time, SWCNT “Tuball R&D” and MWCNT “Taunit” showed a slight decrease in the adsorption of nonionic surfactants with increasing pH. Obviously, in addition to the hydrophobic interaction, the formation of hydrogen bonds between the oxyethylene groups of nonionic surfactants and the polar groups of CNTs affects adsorption. At pH = 2-4, one can note the adsorption of EONP n = 12 on the surface of the SWCNT “Tuball R&D”. A sharp increase in the adsorption of EONP at low pH is obviously due to a decrease in the solubility of nonionic surfactants in water, and an increase, as a result, of surface activity.

To explain the dispersing and stabilizing effect of nonionic surfactants, it was necessary to study the nature of the adsorption interaction between EONP and CNT in the dispersion obtained by ultrasonication. The indicated parameters of ultrasonic treatment lead to the production of dispersions of the MWCNT “Taunit”, but are insufficient to obtain the dispersions of the SWCNTs “Tuball” and “Tuball R&D”. Therefore, we studied the effect of ultrasonication on the nature of the adsorption of nonionic surfactants on MWCNTs by the tensiometry method. In fig. 3 shows the adsorption isotherm of EONP on CNTs (0.1% wt.) after ultrasonication. According to the Gils classification, the adsorption isotherm refers to the H4 form.

There are no data in the literature on the study of the effect of ultrasonication on the parameters of the adsorption layer of surfactant molecules on CNT. Nevertheless, it is known that ultrasonic treatment intensifies the processes of adsorption of high molecular weight compounds on a solid surface: it contributes to a change in the thickness and structure of the adsorption layers (conformation and orientation of adsorbed molecules) of the polymer on the interphase surface, giving new properties to the surface of the dispersed phase and the colloidal system [22]. The nature and quantitative parameters of adsorption are obviously influenced by an increase in the contacting surface as a result of the dispersion of CNTs in a liquid medium. It is possible that ultrasonic treatment changes the nature of the surface of CNTs so that new centers of planting of nonionic surfactants appear on it, different from untreated CNTs.

During adsorption, the number of EONP molecules on the graphene surface is much larger than in volume. Most likely, nonionic surfactants, depending
on the average degree of ethoxylation, can form various sizes associates (hemi-micelles) of adsorbed EONP molecules on the surface of carbon nanostructures [23]. Using dynamic light scattering, we previously found that the average hydrodynamic size of EONP micelles in aqueous solutions decreases with increasing ethoxylation degree \( n \) (diameter of EONP micelles – \( d_{n=8} = 22.8 \) nm, \( d_{n=10} = 10.6 \) nm, \( d_{n=12} = 7.6 \) nm) [16]. Most likely, this is due to contraction of the oxyethylene chain at certain values of \( n \), leading to an increase in the number of aggregation of EONP associates [19]. Nonionic surfactants forming large micelles in the bulk of the solution can also form larger hemimicelles on the surface of carbon particles, while providing a greater screening effect (Fig. 4). This assumption is consistent with the results of [16] in which the content and electrophoretic scattering of particles of CNT dispersions obtained during ultrasonication are analyzed.

The results of the study can be useful in assessing the dispersing and stabilizing effect of nonionic surfactants when obtaining dispersions of single-walled and multi-walled carbon nanotubes by ultrasonication in aqueous and organic media.

CONCLUSIONS

1. It has been shown that the nature of the adsorption interaction of nonionic surfactants – CNT is significantly affected by the EONP degree of ethoxylation, surface characteristics and diameter of nanotubes.

2. It was shown that with an increase in the average degree of ethoxylation, the values of the maximum adsorption of ethoxylated isononylphenols decrease.

3. It is shown that the adsorption isotherm of nonionic surfactants on CNTs corresponds to the Langmuir adsorption isotherm L2 form according to the Gils classification, and after ultrasonication it has a stepwise character of H4 type.

4. It has been established that the main mechanism of adsorption of ethoxylated isononylphenols on CNTs is the hydrophobic interaction of the hydrocarbon radical with the graphene surface of nanotubes.

The study was financially supported by the Russian Foundation for Basic Research (project no. 17-03-00600 a).

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