

Block copolymers as dispersants for nanomaterial added to fuel

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Abstract. Development and optimization of technologies using nanocomposite materials is one of important areas in modern industrial engineering. In transport industry and in fuel power engineering the use of nanoparticles can optimize fuel consumption, reduce pollutants, and increase aggregate productivity. A special role belongs to carbon nanomaterials, primarily to multi- and single-walled carbon nanotubes, since, beside the improvement of fuel characteristics, they can be completely utilized during combustion. Application of nanoparticles requires the preparing of stable suspensions suitable for various technological processes. In this work by the help of NMR spectroscopy the dispersing of nanomaterial by block copolymers was considered: by poloxamers (P184 and P407) in aqueous medium and by poloxamine (Diproxamine-157) and its mixture with liquid poloxamer P184 in oil medium. Good dispersibility of nanomaterial and stability of aqueous dispersions obtained with the help of poloxamers have been shown. Also, it has been established that pure liquid reverse-sequential poloxamines can be used to create oil-soluble dispersions of nanomaterial. Possible mechanisms to prevent reagglomeration by the help of poloxamines have been considered. Keywords: nanocomposite fuel, carbon nanotubes, dispersibility, poloxamer, poloxamine.

1 Introduction

One of the areas of modern industrial and environmental engineering is the development and the optimization of technologies based on materials, containing nanoparticles. In general, the design of materials is transformed due to dependence of nanostructures and their environment on the type, size and shape of nanoparticles. Addition of certain type of nanoparticles in the required concentration allows to control the properties of materials. The most reactive and at the same time highly toxic are engineered nanoparticles (ENP) with sizes less than 50 nm (Klaine et al., 2008; Nowack et al., 2007; Turan et al., 2019).

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The most prevalent nanoparticles are carbon nanomaterials, primarily single- and multi-walled carbon nanotubes. The addition of small amounts of carbon nanotubes (CNTs) leads to significant increase in the strength characteristics of structural and functional materials, which makes it possible to create improved construction of polymer and rubber-technical nanocomposite materials. The introduction of CNTs into the structure of viscoelastic materials can significantly expand the range of their mechanical and conductive properties (MacDonald et al., 2008; Voge et al., 2013) and change their structural parameters (Zueva et al., 2020).

The use of nanoparticles to improve the environmental situation in transport industry and in fuel power engineering can play a special role. There are three ways to improve the quality of exhaust fuel gases. The first two are related to improvement of exhaust systems of engines: the development of filters that delay some emissions, and devices (converters) that use the catalytic properties of various substances to more completely burning all the components of the fuel. The third way is to append catalytic additives directly into the fuel. It turns out that the adjunct of functional nanoscale structures to diesel fuel, such as nanoparticles of metals, oxides, carbides, nitrides (Kannan et al., 2011; Shaafi et al., 2015; Najafi, 2018), carbon nanomaterials (Heydari-Maleny et al., 2017; Zhang et al., 2014; Singh et al., 2015; El-Seesy et al., 2017, 2019) also leads to improvement in engine performance and to decrease in emissions of harmful gases. A strong effect is exerted by nanoparticles of aluminum Al and aluminum oxide Al_2O_3 , nanoparticles of Mn, Mg, Fe, Ag, B, CeO_2 , CuO, ZnO, as well as graphene. However, the effect observed in each specific case depends very much on the composition of fuel and raw materials from which it is made, as well as on the design and characteristics of engine, size and concentration of nanoparticles used (Venkatesan et al., 2017).

To improve the environmental characteristics of fuel oil, the main emphasis is not the perfection of designed features of boiler furnaces, but improvement the operating characteristics of fuel at maximizing removal the adverse environmental consequences of its combustion. Accordingly, solutions of the problem should be sought in the improvement of flue gas filtration systems and in the development of effective new generation of fuel additives. It should be noted that the composition of petroleum fuel oil has its own characteristics, such as the presence of large amounts of sulfur compounds and appreciable amounts of vanadium and sodium compounds. Method to reduce emissions includes addition of substances that bind sulfur, vanadium, and sodium to non-volatile compounds in the combustion zone of the fuel, as well as substances that contribute to the most complete combustion of the remaining fuel components.

One of the ways to solve the formulated problem is the use of nanoparticles, and preference should be given to carbon nanoparticles, such as single-walled and multi-walled carbon nanotubes, graphene oxide, graphene nanoplatelet, carbon quantum dot nanoparticles, and other carbon nanomaterials. These particles can optimize fuel consumption, reduce pollutants, and increase equipment performance. Although they are engineered nanoparticles, they can (and should) burn completely before they enter the atmosphere.

The use of nanoparticles, especially carbon nanotubes, is hindered by the fact that they tend to associate due to van der Waals interactions. Therefore, for using nanomaterials in various technological processes the creation of stable suspensions with effectively dispersed nanoparticles requires. In this work, we studied the dispersibility of nanomaterials by block copolymers: by poloxamers (P184 and P407) in aqueous medium and by poloxamines (diproxamine) in oil medium. The possibility of joint use of a mixture of two different liquid surfactants (diproxamine with poloxamer P184) has also been studied. The dispergation of CNTs with the use of block copolymers has already been considered in literature (Huang et al., 2012; Frise et al., 2012; Fernandes et al., 2018; Kato

et al., 2014; Zueva et al., 2022a), but the results were partly contradictory and depended on the type of dispersed material. Efficient disintegration of CNTs in oil media and finding the right compositions of dispersion media miscible with oil media will make it possible to use them as motor fuel additive.

2 Materials

Carbon nanomaterial Taunit (NanoTechCenter, <http://www.nanotc.ru>) consisting of multi-walled carbon nanotubes (CNTs) were used. In studied solutions, preparing on the base of purified water (MilliQ) and deuterated water (Aldrich, 99.9%), concentration of CNTs was equal to 3 mg/ml. Nonionogenic surfactants formed by block copolymers were used to disperse CNTs.

Poloxamers are nonionogenic triblock copolymers composed of a central hydrophobic polyoxypropylene (PPO) chain with n monomer units, connected at both terminals to two hydrophilic polyoxyethylene (PEO) chains from m monomer units (Zueva et al, 2022b). The chemical and structural formulas of poloxamers are shown in Figures 1a–1c. Poloxamers can be used as a component in dewatering and desalting compositions in oil fields and refineries.

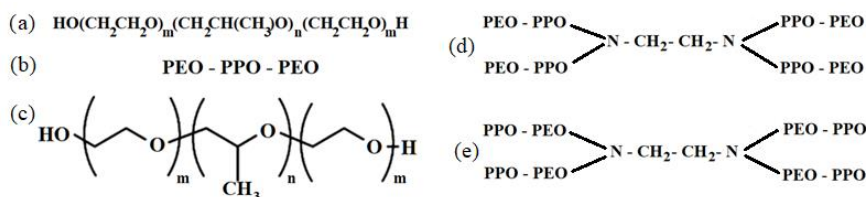


Fig. 1. The chemical formula of poloxamers (a), a symbolic notation of this formula (b), the structural formula of poloxamers (c), a symbolic notation of a sequential (d) and a reverse-sequential (e) structures of poloxamines. The structures of hydrophobic polyoxypropylene and hydrophilic polyoxyethylene blocks are designated by the symbols PPO and PEO.

One of the applied block copolymers was liquid poloxamer P184 with molecular weight 2900, the number of units of hydrophobic and hydrophilic blocks $n = 30$, $m = 13$, respectively. Also flake poloxamer P407, which has more hydrophilic properties was used. Its molecular weight is 12600, the number of units of the hydrophobic and hydrophilic blocks is approximately equal to $n = 65$, $m = 100$, respectively.

Poloxamines are composed of four polyoxypropylene/polyoxyethylene chains linked together by a central ethylenediamine bridge (Figs. 1d–1e) (Alvarez-Lorenzo et al., 2010; Almeida et al., 2018). Poloxamines can be synthesized with a direct sequence of units (Fig. 1d), in which the outer ends of the chains are polyoxyethylene and are hydrophilic. However, another variant is also possible. In Fig. 1e poloxamine molecule with a reverse sequence of units is shown, in which the outer ends of the chains consist of polyoxypropylene and are hydrophobic. Reverse-sequential poloxamines mix well with oils, petroleum, alcohols, aromatic hydrocarbons, but are poorly soluble in water and most often used as nonionogenic surfactants for solving problems in petroleum industry.

Diproxamine-157 (DPA-157) produced by Kazanorgsintez (www.kazanorgsintez.ru) was chosen as reverse-sequential poloxamine. Diproxamine is one of the universal domestic demulsifiers and inhibitors of paraffin deposition. It is liquid nonionogenic surfactant with a density of 1020-1050 kg/m³. Average molecular weight of diproxamine polymer molecules is 4500-5000. The total number of hydrophobic units in all four blocks is 27-28, and the number of all hydrophilic units is 59-61. The commercial form contains 65% of the base in a solvent - methanol. Composite samples were prepared using pure

diproxamine.

Sample preparation. To prepare the samples, liquid poloxamer P184 or flake poloxamer P407 were dissolved to the required concentrations at room temperature in purified water (MilliQ) containing 10% deuterated water (Aldrich, 99.9%) required for NMR experiments. To carry out studies with carbon nanotubes, the CNTs amount corresponding to concentration of 3 mg/ml was poured with half of the prepared solution. The other half was kept for comparison. Then the samples with CNTs were placed in a Bandelin SONOREX TK52 ultrasonic disperser (Germany, 100 W, 35 kHz) for 20 min at $T = 40^\circ\text{C}$. To separate the solid sediment, the samples with CNTs were centrifuged for 10 min at 10000 g in a CM 50V Elmi centrifuge (Latvia). The supernatant was taken for research.

Poloxamine (Diproxamine-157) was used for dispersing CNTs in a similar way at $T = 50^\circ\text{C}$. It was noticed that reduction in temperature to 40°C led to strong decrease in the amount of dispersed CNTs. To disperse the samples in a mixture of diproxamine (80 wt %) with poloxamer P184, the combined liquids were pretreated in an ultrasonic disperser at $T = 40^\circ\text{C}$ for 20 minutes. The resulting mixture was used in the same sequence as pure diproxamine.

3 Method

Nuclear magnetic resonance (NMR) spectroscopy has proven to be very useful for studying the processes occurring in block copolymers solutions (Frise et al., 2012; Fernandes et al., 2018; Kato et al., 2014). Proton NMR spectra were recorded at $+30^\circ\text{C}$ on an AVANCE III 600 MHz NMR spectrometer (Bruker) operating at a proton resonance frequency of 600.13 MHz and equipped with a high-resolution inverted probe (TXI, 5 mm). Details of the measurement process were given in (Zueva et al, 2022a).

Pulsed Field Gradient NMR. The self-diffusion coefficients were measured by spin echo method (Zueva et al., 2022a).

4 Experimental Section

Nanomaterials dispergation using poloxamers in aqueous media. We have considered already the issues of dispersing carbon nanotubes using various substances (Zueva et al., 2020; Makarova et al., 2020). Nevertheless, CNTs dispersed by us did not form sufficiently stable emulsions. The variant of poloxamers attracted us by the peculiarities of their molecular structure. Performed for poloxamer P407 calculations showed that the hydrophobic part of one molecule envelops the surface region of a single-walled nanotube up to 40 nm^2 (Fernandes et al., 2018). The presence of hydrophilic chains that create a “crown” around nanotubes also helps to repel CNTs and prevent reagglomeration.

Certain information on the behavior of block copolymer molecules in aqueous solutions and dispersions can be obtained by studying the ^1H NMR spectra. The spectra regions responsible for poloxamers NMR signals in the absence of CNTs (plot 1) and in their presence (plot 2) for liquid poloxamer P184 solution (concentration 20 wt.% = 69 mM) and higher molecular weight flake poloxamer P407 solution (concentration 0.5 wt.% = 0.4 mM) were presented in Figure 2. The observed lines correspond to the proton signals of CH_3 ($\delta = 1.16\text{ ppm}$), CH ($\delta = 3.52\text{ ppm}$) and CH_2 ($\delta = 3.65\text{ ppm}$) groups of the PPO blocks and CH_2 groups ($\delta = 3.67\text{ ppm}$) of the PEO blocks.

Comparison of the spectra for pure solutions P184 and P407 (1) and dispersions of CNTs (2) indicates the existence of small differences between these spectra, which may be evidence of the formation of complexes between functional groups of hydrophobic blocks of studied poloxamers and carbon surface. In addition, the spectra show a weak broadening

of resonance lines in the presence of nanotubes, which can also be explained by interaction of poloxamers with CNTs. The presence of interactions is confirmed by stability of CNT suspensions.

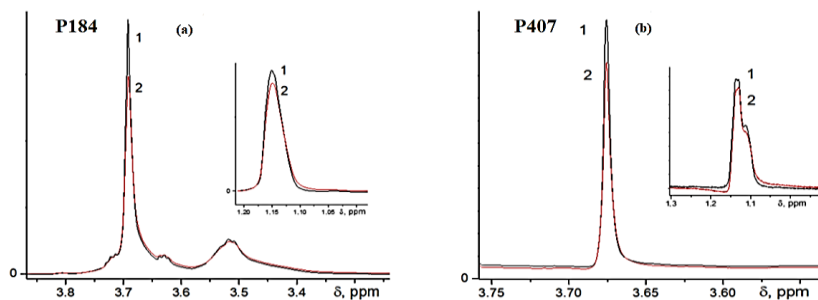


Fig. 2. Regions of spectra responsible for poloxamers NMR signals in the absence of CNTs (plot 1) and in their presence (plot 2) in aqueous solutions: (a) 20 wt% (69 mM) P184; (b) 0.5 wt% (0.4 mM) P407. CNTs concentration was equal to 3 mg/ml.

Nanomaterials dispersion using poloxamines for oil media. As poloxamine, we chose Diproxamine-157, which is reverse-sequential poloxamine used to solve the problems of the oil and oil refining industry. Diproxamine attracted our attention by the fact that it is actively employed as nonionic surfactant, which is a demulsifier and inhibitor of paraffin deposition. It mixes well with oils, petroleum, alcohols, aromatic hydrocarbons, but poorly soluble in water. With the help of diproxamine, we have already dispersed CNTs, achieving a change in the viscosity of the composite boiler fuel (Zvereva et al., 2016a, 2016b, 2017). At that time, the decisive factor for choosing diproxamine as a dispersant was the fact that it was already used to improve the properties of petroleum products. Finding the optimal compositions of dispersion media miscible with oil media would make it possible to use CNTs as motor fuel additive.

In this work, we have studied the properties of CNT dispersions obtained on the basis of (a) pure diproxamine, (b) a mixture consisting of diproxamine (80 wt.%) with liquid poloxamer P184 (20 wt.%). The NMR spectra of the samples of liquids and CNTs suspensions in these liquids are shown in Fig. 3. According to our data, the NMR spectra of pure diproxamine and diproxamine with CNTs (Fig. 3a) differ very slightly. The spectra of diproxamine mixed with poloxamer with and without CNTs (Fig. 3, b) are practically indistinguishable, which indicates the absence of explicit interaction of CNTs with any blocks of these block copolymers. In addition, both signals from poloxamer are blocked by diproxamine. A distinctive feature of the spectra shown in Fig. 3 is the absence of lines from water protons in the spectra of pure block copolymers. It appears only in spectra with nanotubes due to the presence of a small amount of water adsorbed on their surface.

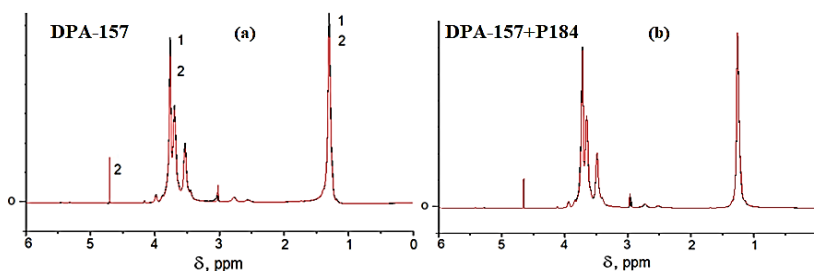


Fig. 3. NMR spectra: (a) pure diproxamine (1) and diproxamine with CNTs (2) at a concentration of 3 mg/ml; (b) diproxamine (80 wt%) + P184 (20 wt%) with and without CNTs (3 mg/ml). In (b) both spectra are identical.

5 Results and discussion

To study the translational diffusion of poloxamers, the signal from the protons of CH₂ groups of polyoxyethylene chains is usually used. Obtained diffusion decays of NMR signal of solutions of both poloxamers were nonlinear (Fig. 4). This fact indicates the existence of different structural states of molecules that varied by self-diffusion coefficients. One of the states at any concentration is a free state of single molecules (unimers). Since micellar concentrations have been studied, another state is a state of molecules located in micelles. In the presence of carbon nanotubes, it appears a state of poloxamer molecules adsorbed on CNTs. From the point of view of diffusion mobility, there is no fundamental difference between poloxamer molecules bound to micelle or to nanotube. The main type of motion both in micelle molecules and in molecules adsorbed on CNT, is the motion of polyoxyethylene chains (PEO blocks) in the bulk of solution (Kato et al., 2014). Moreover, it is believed that a carbon nanotube with adsorbed PPO blocks of poloxamers can also be considered as a cylindrical micelle. Therefore, to describe diffusion decays, one can restrict oneself to consider of two states: fast free and slow bound.

To obtain more detailed information about dispersion of carbon nanotubes in solutions of block copolymers, we studied the diffusion decays of NMR signals of CH₂ protons of polyoxyethylene chains in solutions of poloxamers P184 and P407 (Fig. 4a), and in diproxamine (DPA-157) (Fig. 4b). The self-diffusion coefficients and the fractional intensity contributions calculated within the framework of the described model are shown in Table 1

Table 1. Fractional intensity contributions (FIC) and self-diffusion coefficients (D) of block copolymer molecules with CNTs and without them.

	P184		P407		DPA-157		DPA-157 + P184	
	FIC	D, 10 ⁻¹¹ m ² /s	FIC	D, 10 ⁻¹¹ m ² /s	FIC	D, 10 ⁻¹¹ m ² /s	FIC	D, 10 ⁻¹¹ m ² /s
Fast decay	0.90	6.42	0.86	6.14	–	–	–	–
Fast decay with CNTs	0.95	5.77	0.94	5.76	–	–	–	–
Slow decay	0.10	2.93	0.14	2.16	1.0	0.105	1.0	0.176
Slow decay with CNTs	0.05	1.58	0.06	1.60	1.0	0.105	1.0	0.176

The investigation of processes of polymer molecules diffusion leads to the following conclusions. In poloxamer solutions without nanotubes at temperature + 30 °C, a large fraction of molecules is in a free state. The diffusion coefficients for freely moving poloxamers P184 and P407 are almost the same. Nevertheless, for P184, which has 13 units in polyoxyethylene side chains, the diffusion mobility is slightly higher than that of P407, which contains 100 units in each side chain. When they diffuse in the composition of micelles, the difference becomes more noticeable and already more than 20 %. Obviously, the segmental motion of polymer chains makes a certain contribution to the self-diffusion coefficient of polymer molecules as a whole.

Upon CNTs adding the adsorption of poloxamer molecules onto carbon surfaces is preferable than their existence in micelles. A consequence of this adsorption process is a change in the apparent concentration of solution and, accordingly, in number of micelles. The diffusion mobility of adsorbed surfactant molecules is probably still less than that of molecules organized into micelles. Therefore, the self-diffusion coefficient averaged over both slow states decreases to almost the same value (1.58-1.60) 10⁻¹¹ m²/s. Self-diffusion coefficients corresponding to fast processes also decrease. This result can be associated with the permanent exchange between states. Fast single molecules leave the solution

passing to nanotubes, while slow molecules, on the contrary, replenish the solution. Consequently, the presence of molecules adsorbed on nanotubes leads to a decrease in the total diffusion mobility to the same value $5.77 \cdot 10^{-11} \text{ m}^2/\text{s}$.

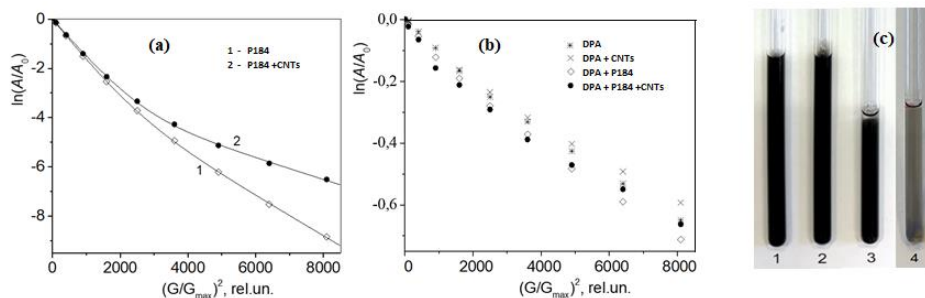


Fig. 4. Diffusion decay of NMR signals with and without CNTs in the bulk of: (a) 20 wt% (69 mM) P184 in water; (b) diproxamine and mixtures of diproxamine (80 wt%) with P184 (20 wt%). Photos (c) of tested samples with CNTs after preparation: 1. P184 in 20 days; 2. P407 in 20 days; 3. DPA-157 in 10 days; 4. DPA-157 (80 wt%) + P184 (20 wt%) in 1 day.

Thus, the differences in the NMR spectra and diffusion mobility of poloxamers in solutions and suspensions of CNTs allow us to conclude existing of interactions of poloxamer molecules with the surface of carbon nanotubes. This interaction prevents reagglomeration of CNTs. The main confirmation of this conclusion is the state of the samples with dispersed CNTs in 20 days after their preparation (Fig.4c, samples 1, 2).

Dispergation with poloxamines has significant differences. Diproxamine contains neither water nor micelles. Only one type of polymer movement is observed, which we attributed to slow movements. The diffusion coefficient of this poloxamine is 20 times less than that of studied poloxamers (Table 1). By its properties, diproxamine is more like a gel. In the presence of CNTs, no explicit interaction between diproxamine and nanotube surface is observed. Even if hydrophobic PPO blocks are nevertheless adsorbed on nanotube surface by one of their four chains, this interaction cannot be strong. It can easily be broken due to thermal vibrations of three more chains which consist of the molecule. Nevertheless, CNTs are dispersed fairly well in diproxamine. Nanotubes surrounded by diproxamine are held in solution by another mechanism, most likely associated with entanglement of chains of poloxamine.

Having averaged data on diproxamine ($MW = 4750$, density 1035 kg/m^3), we calculated the mass of one their molecule $m_D = 7.89 \cdot 10^{-24} \text{ kg}$ and then the volume per one molecule, $v_D = m_D / \rho = 7.62 \cdot 10^{-27} \text{ m}^3$. Thus, the centers of diproxamine molecules are located at average distance of 2 nm. The real size of its molecule can be estimated by comparing it with the size of P184 micelles. Due to the chemical structure and molecular weight, these lengths should not differ greatly from each other and should be approximately equal to 10–12 nm (Bodratti et al, 2018).

According to our calculations, each of four diproxamine chains extends approximately by 5-6 nm, penetrating into the zone of action of another 1-2 molecules. In fact, chains of poloxamine molecules with a rather complex spatial configuration can form claw-like structures leading to appearance of molecules clutch. Therefore, the sedimentation of CNTs, which is characteristic for all CNTs suspensions, takes a long time. Experience shows that a slight layer at the top appeared on the next day (Fig. 4c, sample 3). However, even after 10 days, the suspension looked almost uniform.

Our next step was to study the possibilities of combined use of poloxamers with poloxamines to create water-free oil-soluble media for dispersing CNTs. For this, we took a liquid mixture of diproxamine (80 wt.%) with P184 (20 wt.%). Dispersion of CNTs in this

liquid could theoretically lead to good results if poloxamer was adsorbed on the surface of nanotubes, while in diproxamine they would be in the form of poloxamer/CNT complexes. Since the results obtained even visually indicated poor dispersing (Fig. 4c, sample 4 a day after dispersing), it can be concluded that poloxamer/poloxamine complexes are formed that do not interact with the CNT surface and do not contribute to dispersibility. These conclusions are confirmed by comparing the NMR spectra (Fig. 3b) and the diffusion decay of the NMR signals (Fig. 4b). The calculated self-diffusion coefficients are shown in Table 1.

6 Conclusions

In this work, the possibilities of dispersing carbon nanomaterial Taunit using block copolymers were considered: poloxamers (P184 and P407) in an aqueous medium and poloxamine (Diproxamine-157) and its mixture with liquid P184 in oil medium. The study of aqueous poloxamer solutions by NMR showed the existence of interaction of molecules with the surface of multi-walled carbon nanotubes Taunit. This interaction leads to enveloping carbon nanotubes surfaces by poloxamer molecules and their separation. The result is good dispersibility of CNTs using poloxamers in aqueous medium. The stability of obtained dispersions should also be noted.

Diproxamine-157 was used for dispersion in oil medium. The results obtained using NMR showed that, in the presence of CNTs, heavy interaction between diproxamine and the surface of nanotubes was not observed. The structure of poloxamines is such that the emerging adsorption processes involving one of the PPO blocks are easily disrupted due to thermal vibrations of three more chains available in the molecule. Nevertheless, CNTs are fairly well dispersed in diproxamine due to another mechanism associated with mutual penetration and entanglement of chains of poloxamine molecules. In fact, chains of poloxamine molecules with a rather complex spatial configuration can form claw-like structures leading to molecules clutch. Therefore, the sedimentation of CNTs, which is characteristic of all suspensions, takes a long time. Also it can be concluded that in liquid mixture (diproxamine/P184) poloxamer/poloxamine complexes are formed that do not interact with the CNT surface and do not contribute to dispersibility. Thus, our results indicate that pure liquid reverse-sequential poloxamines can be used to create oil-soluble dispersions of nanomaterial, and their use is optimal in the first few days after preparation.

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