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The effect of additives of single-wall and multi-wall carbon nanotubes on the rheological characteristics of inverse emulsions

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In this study, the rheology of inverse emulsions based on mineral oil modified with single-walled carbon nanotubes (SWCNTs) was studied and compared with the results of the influence of multi-walled carbon nanotubes (MWCNTs) additives. The mass concentration of SWCNTs in emulsions varied from 0.01 to 0.1 wt%. Dependences of rheological characteristics on SWCNT concentration were obtained. Based on the results of the study, it was shown that nanotube additives can significantly change the rheological characteristics of emulsions. The use of SWCNTs to improve the rheology of drilling emulsions is several times more efficient than MWCNTs and hundreds of times more effective than additives of spherical nanoparticles.

Keywords: inverse emulsion, single-walled and multi-walled carbon nanotubes, viscosity, rheology, drilling fluid.

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Owing to their unique properties, carbon nanotubes (CNTs) are currently used widely to modify various materials [1,2]. Nanotubes are used to enhance the thermal conductivity of heat-conducting pastes and coolants in cooling systems for electronics and solar power engineering applications and to raise the electric conductivity of coatings and composite materials. They have been proven efficient in adjusting the structure and enhancing the adhesion of varnishes and paints, raising the strength of rubber resins and plastics, enhancing the performance of current sources, etc [3,4]. It is well known that added CNTs alter the viscosity and rheology of fluids [5]. It appears promising in this context to use them to adjust the properties of drilling fluids. This is a hot research topic at present [6]. It has been demonstrated that CNTs have the capacity to enhance considerably the parameters of drilling fluids. CNTs may act here as alternatives to spherical nanoparticles, which are currently used widely to improve the characteristics of drilling fluids [7]. However, most studies published to date were concerned with the application of multi-walled CNTs (MWCNTs) for these purposes. In addition, the majority of studies were limited to water-based drilling fluids. At the same time, hydrocarbon-based solutions, which are inverse emulsions, are the ones that are used in most cases in practice. No systematic data regarding the influence of single-walled CNTs (SWCNTs) on the rheological properties of inverse emulsions are currently available.

In the present study, the shear rheology of hydrocarbon-based drilling emulsions with added SWCNTs and MWCNTs is examined systematically. The base hydrocarbon-based solution was an inverse emulsion (oil in water). The following hydrocarbon base/aqueous salt solution ratio, which is the most common one for drilling fluids, was studied: 65/35 vol.%. The procedure for preparation of inverse emulsions with added CNTs was optimized. A high-concentrated aqueous solution of calcium chloride (19 wt.%) was made first. This salt solution was then used to produce a suspension of carbon nanotubes, which was used later to prepare a drilling fluid. The aqueous CNT suspension was prepared with the application of ultrasonic treatment. A CNT powder was added to the salt solution and stirred with a high-speed stirrer, and the obtained suspension was then processed with a „Volna" ultrasonic disperser. The ultrasonic processing time was 60 min. The salt solution with CNTs was then mixed with the hydrocarbon base in the needed volume ratio. A „REBASE" PC-230 (LLC „NPO „REASIB", Tomsk, Russia) mineral oil with a viscosity of 3.3 mPa $\cdot$ s and a density of 815 kg/m^3 served as the hydrocarbon base of solutions. The oil and the salt solution with CNTs were mixed in droplets under constant stirring with a Hamilton Beach three-spindle mixer at 20 000 rpm. The procedure of preparation of the hydrocarbon-based drilling emulsion with nanoparticles was detailed in [8].

SWCNTs and MWCNTs were used to modify the emulsion properties. Single-walled nanotubes were added in the form of a TUBALL$^{\text{TM}}$ (LLC „OKSiAl.ru", Novosibirsk, Russia) powder. It is a loose powder that is black in color. The mean SWCNT diameter was 1.6 ± 0.4 nm, and the BET (Brunauer–Emmett–Teller) specific surface area was 510 m^2/g. According to the atomic force microscopy data, the length of SWCNTs exceeded 4 μm, and their mean and bulk density was 1.8 and 0.1 g/cm^3, respectively. Multi-walled Taunit-MD (LLC „NanoTekhTsentr", Tambov, Russia) nanotubes were also used. The inner diameter of these MWCNTs was 5–15 nm, and the outer diameter was 8–30 nm. Their specific surface area exceeded 270 m^2/g, and their length was greater than 5 μm. The total number

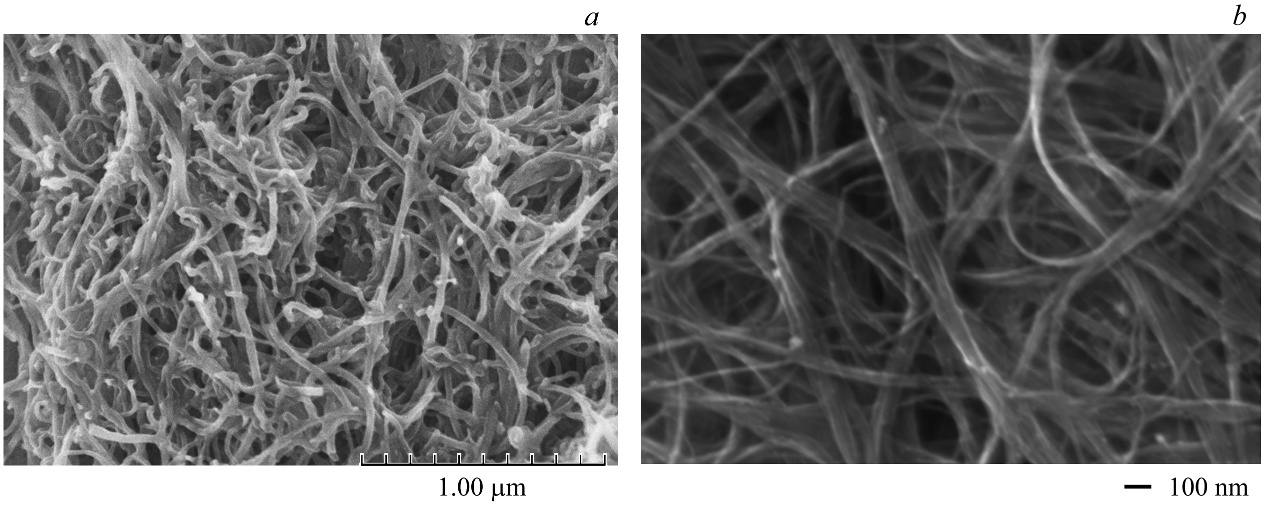

Figure 1. Electron microscopy at a magnification of 50 000. *a* — MWCNTs; *b* — SWCNTs.

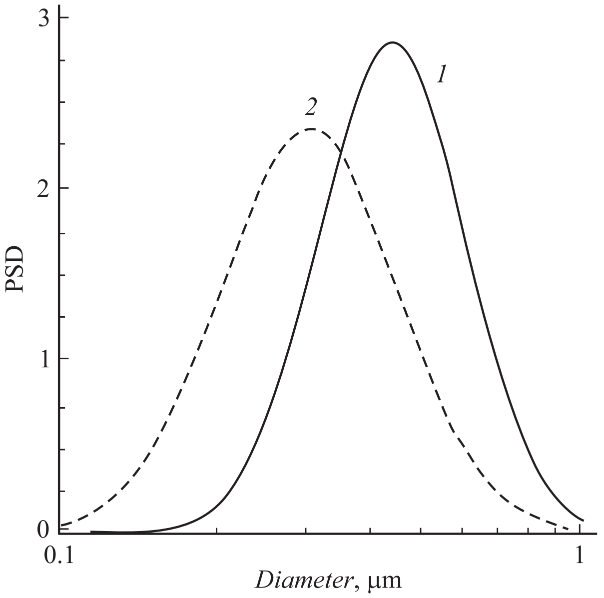

Figure 2. Size distributions of SWCNTs (*1*) and MWCNTs (*2*) in the fluid.

of carbon layers was 30–40. A JSM-7001F (JEOL, Japan) scanning microscope and an S-5500 (Hitachi, Japan) ultra-high resolution scanning electron microscope were used to perform microscopical studies. The standard procedure of preliminary evaporation of the base fluid was performed in electron microscopy. The results of these microscopical studies of nanotubes are presented in Fig. 1.

The concentration of CNTs in emulsions varied from 0.01 to 0.1 wt.%. Preliminary experiments have demonstrated that emulsions turn into gels at higher SWCNT concentrations and become inapplicable as drilling fluids. A DT1202 (Dispersion Technology, Bedford, United States) acoustic and electroacoustic spectrometer was used to measure the mean size of nanotubes directly in the fluid. The distribution of the mean size of CNTs in water is shown in Fig. 2. The mean hydrodynamic size of multi-walled and single-walled nanotubes in suspensions was $0.30\,\mu$m and $0.43\,\mu$m, respectively. Note that while the mean hydrodynamic sizes of nanotubes in the fluid are similar, the aspect ratio of SWCNTs is an order of magnitude greater than the one for MWCNTs. An Ofite 900 (United States) cylinder rotational viscometer was used to examine the viscosity and rheology of emulsions. This viscometer provides an opportunity to measure the viscosity coefficient within a wide range of shear rates from 5.1 to $1024\,s^{-1}$. The rheological properties of emulsions were studied under normal conditions (a temperature of 25°C and a pressure of 1 atm). The confidence error of measurements did not exceed 5%.

Dependences of the viscosity of drilling emulsions on the shear rate were obtained. The measurement results are shown in Fig. 3, *a*. It is evident that all the examined drilling emulsions are non-Newtonian, their viscosity depends on the shear rate, and they have a yield point. The effective viscosity of the emulsion increases approximately by 80% throughout the entire range of shear rates after the addition of 0.1 wt.% of single-walled nanotubes. The effect of the same amount of added MWCNTs is much weaker: the effective viscosity increases by 25% on the average at an additive concentration of 0.1 wt.%. This is largely attributable to the significant difference in specific surface area and aspect ratio of SWCNTs and MWCNTs. Comparing these data with the results of our studies into the modification of properties of drilling fluids by the addition of spherical nanoparticles [8,9], one finds that nanotubes are an order of magnitude more efficient in adjusting the rheology of fluids. Specifically, the effective viscosity of an emulsion with 2 wt.% of added spherical silicon oxide nanoparticles (80 nm) increased by approximately 20%. Thus, the amount of added nanotubes needed to achieve comparable effects is tens of times lower than the amount of spherical nanoparticles. It is well known

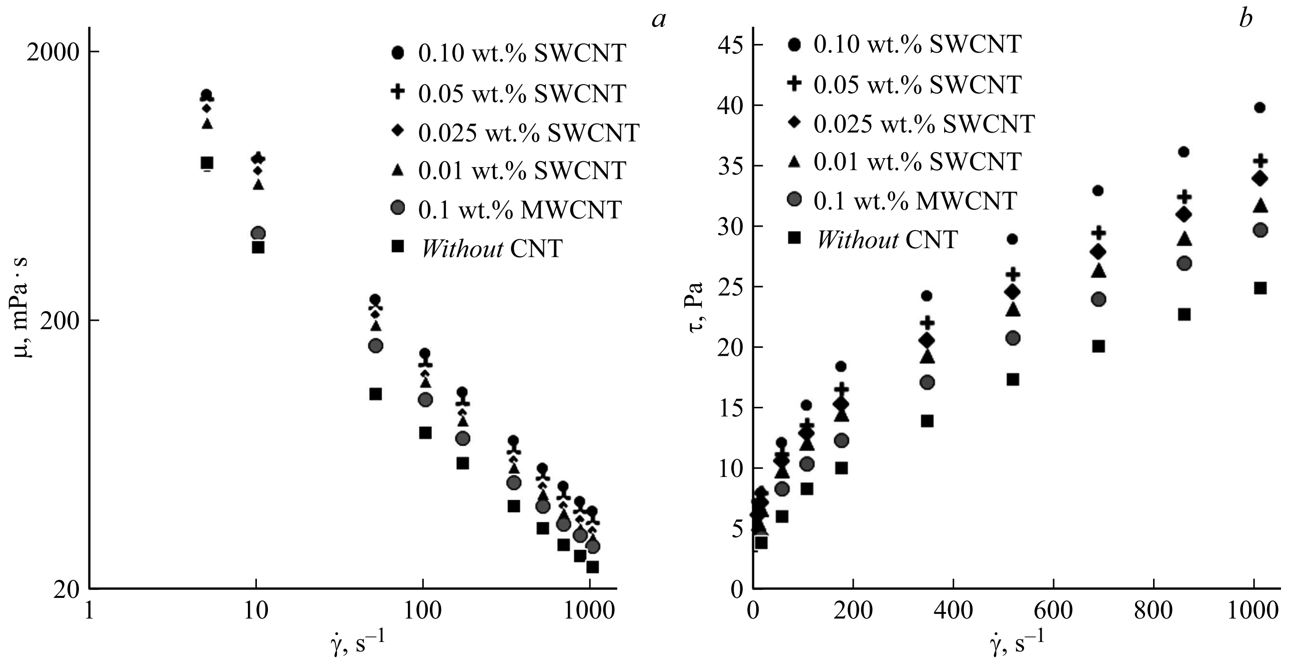

Figure 3. Dependences of the viscosity coefficient (a) and the shear stress (b) of inverse emulsions on the shear rate at different CNT concentrations. CNT — carbon nanotubes, SWCNT — single-walled carbon nanotubes, and MWCNT — multi-walled carbon nanotubes.

Rheological parameters of inverse emulsions with CNTs

w, wt.%	Power-law model			Bingham model			Herschel–Bulkley model			
	K, Pa · s^n	n	R^2	τ_0, Pa	k_ν, mPa · s	R^2	τ_0, Pa	K, Pa · s^n	n	R^2
0	1.657	0.3652	0.9511	4.820	22.07	0.9752	2.879	0.4411	0.5381	0.9991
					MWCNTs					
0.1	1.777	0.3886	0.9897	5.998	26.11	0.9612	3.475	0.5026	0.5503	0.9995
					SWCNTs					
0.01	2.715	0.3356	0.9840	7.613	26.95	0.9610	4.562	0.7140	0.501	0.9996
0.025	3.025	0.3286	0.9819	8.248	28.60	0.9634	4.972	0.786	0.495	0.9994
0.05	3.157	0.3374	0.9854	8.875	30.21	0.9595	5.292	0.851	0.491	0.9997
0.1	3.288	0.3415	0.9882	9.544	33.58	0.9542	5.676	0.878	0.505	0.9993

that the viscosity of nanofluids with spherical nanoparticles increases with a reduction in their size [9]. The pattern in reverse in the case of CNTs. The microrheology [5], electric conductivity, and data from electron microscopy studies [10] of such nanosuspensions suggest that a spatial structure of nanotubes forms in their bulk. The higher the aspect ratio of tubes is, the lower is the concentration at which this stable structure forms. This is the reason why SWCNTs exert a much greater influence on the emulsion viscosity. The table lists the rheological parameters of emulsions approximated by three most widely used rheological models: power-law model $\mu = K\dot{\gamma}^{n-1}$, Bingham model $\mu = (\tau_0 + k_\nu\dot{\gamma})/\dot{\gamma}$ and Herschel–Bulkley model $\mu = (\tau_0 + K\dot{\gamma}^n)/\dot{\gamma}$, where k_ν is the plastic viscosity [mPa · s], n is the nonlinearity index, τ_0 is the yield stress [Pa], and K is the consistency index [Pa · s^n]. The Herschel–Bulkley model provides the closest approximation of experimental data. It was found that the studied emulsions are nonlinear-viscoplastic fluids. The consistency index, the yield stress, and the plastic viscosity of emulsions increase significantly at higher SWCNT concentrations. In contrast, the nonlinearity index decreases slightly. All this suggests that added SWCNTs enhance the non-Newtonian properties of emulsions.

It was demonstrated above that added CNTs may exert a significant influence on the rheological characteristics of emulsions. The addition of 0.1 wt.% of SWCNTs results in a two-fold increase in the yield stress and the consistency index of a drilling fluid. SWCNTs are especially efficient in this respect. The amount of added SWCNTs needed to achieve a comparable influence on the viscosity of emulsions is hundreds of times lower than the amount of spherical nanoparticles. This is very important for their practical application.

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Conflict of interest

The authors declare that they have no conflict of interest.

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