Measurement and study of thermophysical properties of nanofluids with carbon nanotubes

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Abstract. This article is devoted to the study of the thermophysical properties of nanofluids with single-walled and multi-walled carbon nanotubes (CNT). Their weight concentration varied from 0.05 to 0.2%. Nanofluids, based on ethylene glycol and water, were studied. Dispersants were also used. The diffusion of CNT had been systematically investigated by the method of dynamic light scattering and their effective hydrodynamic dimensions were determined. The rheology and viscosity of all nanofluids were studied. It is shown that nanofluids are either pseudoplastic or viscoplastic. Their rheology changes with increasing CNT concentration and temperature. However, in all cases, the viscosity of nanofluids with single-walled CNTs is significantly higher than that of nanofluids with multi-walled CNTs. In the last part, the electrical conductivity of all these nanofluids and the dispersants effect on it are investigated.

1. Introduction
Carbon nanotubes (CNT), discovered about thirty years ago, have unique mechanical, optical, and thermophysical properties [1, 2]. Naturally, therefore, they are already actively used in a variety of applications [2-4], and primarily in new materials creation. In almost all applications, the CNTs use requires preliminary creation of the corresponding nanofluids. The unique thermal conductivity of CNTs indicates prospects of using nanofluids with them in various thermophysical applications. For this reason, the thermophysical properties of nanofluids with CNTs have been actively studied for about twenty years [4-10]. Nevertheless, the experimental data obtained are extremely contradictory and not universal. This is due to the fact that in most of the works, various nanofluids with different base fluids and dispersants were studied. In addition, CNTs used could be either single-walled (SWCNT) or multi-walled (MWCNT) and had significantly different properties (chirality, diameter, number of graphene layers, etc.). Therefore, in order to reveal the characteristic thermophysical properties, it is necessary to consider and analyze them for quite definite classes of nanofluids. The first step in this direction was made in [11-13]. The diffusion of SWCNTs in two base fluids and the rheology of the corresponding nanofluids were studied. SWCNTs produced by OCSiAl company (Novosibirsk) were used.

The aim of this paper is to experimentally study the SWCNTs diffusion, rheology, viscosity and electrical conductivity of nanofluids based on ethylene glycol (EG) and water (W) with SWCNTs. The weight concentration of SWCNTs varied from 0.05 to 0.2%. Sodium dodecylbenzenesulfate (SDBS), \( \text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na} \), and polyvinylpyrrolidone, \( (\text{C}_6\text{H}_9\text{NO})_n \) (PVP) were used as surfactants.
Nanofluids with SWCNTs based on the following base fluids have been systematically studied: EG, EG+PVP, EG+SDBS, W+PVP, W+SDBS. In the last part of the paper, the data on the above-mentioned thermophysical properties of nanofluids with MWCNTs (Taunit-M nanotubes, Nanotechsentr, Tambov) are presented and compared with the corresponding data for nanofluids with SWCNTs.

2. Diffusion coefficients of SWCNTs
All nanofluids studied were prepared by the standard two-step method [14]. In the first step, the required amount of CNTs powder was added to the initial base liquid, after which the resulting suspension was thoroughly mechanically mixed. Then, the obtained primary nanofluid was subjected to ultrasonic treatment (UST). UST was more effective procedure if the surfactants were simultaneously with UST used. USTA-0.8/22-OM device with a maximum power of 800 W and an ultrasonic vibration frequency of 22 ± 1.65 KHz was used for UST. The UST time was varied from 10 to 90 minutes at the maximal power.

The carbon content of SWCNTs, used in this work, is 86±1% by weight (according to thermogravimetric analysis), the rest is metal impurities. The mass content of SWCNTs is 75±1%, and their diameter is 1.6±0.4 nm, determined by Raman spectroscopy. The total specific surface area according to the BET method is 500 m²/g, and their average density is 1.8 g/sm³. According to atomic force microscopy, the length of SWCNTs was more than 4 µm. SWCNTs interact with each other very intensively. Such strong interactions lead to the formation of agglomerates. For this reason, the study of the SWCNTs’ real size in nanofluids is an extremely important task of their characterization. In this work, the size of nanotubes and their bundles was determined by the method of dynamic light scattering (DLS). For this purpose the Malvern Zetasizer ZSP device was used. The range of particle sizes, that this device is capable of measuring, is from 0.3 nm to 10.0 microns. For measurement, 1 ml of nanofluid was diluted to the required concentration of CNTs. Then, the sample was thermostated at a temperature of 25°C. Each measurement was performed several times, after that the results were averaged.

Strictly speaking, in these experiments the diffusion coefficient of CNTs was measured. Then, using the Stokes–Einstein formula

\[ D = \frac{kT}{6\pi\eta R}. \]  

the effective hydrodynamical radius \( R \) of CNTs is determined (here \( \eta \) is the viscosity coefficient of the carrier fluid, \( T \) is the temperature, and \( k \) is the Boltzmann constant). The weight concentration of SWCNTs varied from \( 10^{-1} \) to \( 10^{-5} \%). The weight concentration of surfactants (if it was used) was equal to or twice the concentration of SWCNTs.

![Figure 1](image-url)  

**Figure 1.** The diffusion coefficients distribution of SWCNTs in EG at weight concentration dependence \( 10^{-5} \), \( 10^{-3} \), and \( 10^{-2} \).

A typical example of the distributions of the SWCNTs diffusion coefficient in ethylene glycol at three weight concentrations is shown in Fig. 1. This Figure shows the diffusion coefficient dependence
on the intensity of the scattered light. The maximum values of the diffusion coefficient distributions are $0.22 \times 10^{-12}$, $0.79 \times 10^{-13}$ and $0.59 \times 10^{-13}$ m$^2$/s, respectively. As the concentration of SWCNTs increases, the diffusion coefficient naturally decreases. The obtained values are in agreement with those measured earlier in [12], but less than the latter by almost an order of magnitude. But it should be so (see (1)), since the viscosity coefficient of EG is almost twenty times higher than that of water. Using (1), the measured values of the diffusion coefficient can be used to determine effective hydrodynamic sizes of SWCNTs. They are respectively equal: 592, 724 and 985 nm. It should be noted that relation (1) significantly underestimates the real length of nanotubes.

These experiments were carried out both, on pure ethylene glycol and also in nanofluids EG+PVP and EG+SDBS. Since data on the sizes were needed in all cases, the corresponding DLS measurements were carried out for all the above nanofluids. The distributions of the diffusion coefficient and size of SWCNTs in nanofluids based on EG+SDBS are shown in Fig. 2. The weight concentration of SWCNTs here is 0.1%, and SDBS is twice as much. A characteristic feature of the diffusion coefficient distributions is the presence of two substantially different maxima. The maxima of the diffusion coefficients differ by an order of magnitude. Since the intensity of the scattered light is proportional to the size of nanotubes, the presence of two maxima indicates two groups of nanotube bundles. The first is with a characteristic size of about 2 microns and the second is with an average size of about three hundred nanometers (see Fig. 2 on the right). The comparison in Figs. 1 and 2 shows that the use of a surfactant has a double effect on the diffusion and size of nanotubes. On the one hand, the presence of a surfactant makes it possible to obtain, along with bundles of SWCNTs, isolated nanotubes (a small peak in Fig. 2 on the left). On the other hand, the diffusion coefficient of large nanotube bundles in EG+SDBS nanofluid turns out to be almost five times lower. This is connected, of course, with the fact that the concentration of SWCNTs is higher here, but not only. The viscosity of the base fluid EG+SDBS at the considered weight concentration of the surfactant is higher than the viscosity of EG by almost 15.5%.

![Figure 2. Diffusion coefficient (left) and size (right) distributions of SWCNTs in EG+SDBS-based nanofluid.](image)

3. Rheology and viscosity of nanofluids with CNTs
The viscosity coefficient of nanofluids and their rheology were measured using LVDV-II+Pro Brookfield rotary viscometers with replaceable spindles. In all cases, thermostatic control was used, so that the viscosity coefficient and its dependence on temperature and shear rate were determined at a given temperature. The accuracy of the viscosity coefficient measurement was determined by measuring the viscosity of water and ethylene glycol and comparing the data obtained with those available from the literature. In all cases, the accuracy was about 1–2%. The rheology of all nanofluids mentioned in the introduction was studied. Below some examples will be presented only.

An important element in the preparation of nanofluids is UST. It is clear that efficiency of tube de-agglomeration and stability of the resulting nanofluid depend, at given UST power, on the processing time. The viscosity dependence of EG+SWCNT nanofluid (weight concentration of SWCNTs is 0.1%) on the shear rate at different UST times is shown in Fig. 3. Here rhombuses correspond to 10, and circles correspond to 40 minutes of UST at a maximum power of 800 W. It is important to note that the viscosity
value decreases with an increase in UST time, and the viscosity reaches a certain constant value at high shear rates. On the other hand, with an increase in UST time, the size of CNTs (or their agglomerates) decreases. This once again confirms conclusion made in [13] that the greater the viscosity, the larger the size of CNTs (or their agglomerates).

In this paper, the rheology of five different nanofluids based on EG, EG+PVP, EG+SDBS, W+PVP, W+SDBS was studied. The specified base fluids are Newtonian. In the last four, the surfactants were used to create nanofluids. Their weight concentration was either equal to the weight concentration of carbon nanotubes, or it was twice as much. In all cases, it was found that nanofluids with SWCNTs had a non-Newtonian rheology, which was well described either by the power-law fluid model

\[ \mu = k_\nu \dot{\gamma}^{n-1}. \]  

(2)

or by the Herschel-Bulkley model with yield strength \( \tau_0 \)

\[ \mu_f = \tau_0 + k_\nu \dot{\gamma}^{n-1}. \]  

(3)

In formulas (2) and (3) \( n \) is the fluid index and \( k_\nu \) is the consistency factor.

**Figure 3.** Influence of UST treatment time on the dependence of viscosity on shear rate.

**Figure 4.** Viscosity (left) and shear stress (right) of EG+SWCNTs nanofluids versus shear rate.
As an example, the viscosity dependences and shear stresses on the shear rate for the nanofluid EG+SWCNTs are shown in Fig. 4. Concentrations of SWCNTs take values from bottom to top equal to 0, 0.05, 0.1 and 0.2%, respectively. At the minimum concentration of nanotubes (0.05%), rheology of the nanofluid is described by model (2); however, the fluid acquires a yield point with its growth (see formula (3)), which value increases with an increase in the concentration of nanotubes. In addition, with an increase in the concentration of SWCNTs, the fluid index $n$ decreases, while the consistency factor $k_v$ increases (see Fig. 5).

![Figure 5. Dependence of the fluid index (left) and the consistency factor (right) of the EG+SWCNTs nanofluids on the weight concentration (%) of carbon nanotubes.](image)

The measurements, shown in Fig. 5, were carried out at a temperature of 25 °C. The viscosity of that nanofluid (as well as others) decreased with an increase in temperature, but all nanofluids remained non-Newtonian. This is well illustrated in Fig. 6, which presents data for three temperatures, 25, 35 and 45 °C (top to bottom). The same EG+SWCNTs nanofluid was considered, where the nanotube concentration was 0.1%. It is also important to note that the degree of non-Newtonian nanofluid decreases with an increase in temperature, so the yield stress decreases by about 40%, and the consistency index decreases approximately also. On the other hand, the liquid index increases by 11%.

![Figure 6. Viscosity (left) and shear stress (right) of nanofluids versus shear rate at different temperature.](image)

In present paper, nanofluids with MWCNTs were also studied along with nanofluids with SWCNTs. The main goal was to compare the measured thermophysical characteristics of these two different types of nanofluids. Nevertheless, the limited scope of this article does not allow for systematic comparisons. We will restrict ourselves here to only comparing the viscosity of nanofluids, based on EG alone. The dependence of nanofluids viscosity EG+MWCNTs at three concentrations of nanotubes on the shear rate is shown in Fig. 7 on the left. Here the designations are the same as in Fig. 4. Nanofluids EG+MWCNTs at all concentrations as well as with SWCNTs are non-Newtonian. However, a
comparison of Figs. 4 and 7 shows that the viscosities of nanofluids with MWCNTs are significantly less than with SWCNTs. At high shear rates (185 s⁻¹), the viscosity of nanofluids with MWCNTs at the maximum concentration is more than an order of magnitude lower than that of nanofluids with SWCNTs. With a decrease in concentration, this difference decreases, and at a minimum concentration, the viscosity of nanofluids with MWCNTs is approximately five times lower. On the other hand, this difference increases with decreasing shear rates. When shear rates change from 9.3 to 186 s⁻¹, the viscosity of EG+SWCNTs nanofluids changes within 3000–180 cP, and for EG+MWCNTs nanofluids – 50–19 cP.

The second important circumstance is that nanofluids with MWCNTs are less non-Newtonian than with SWCNTs. At the same weight concentrations of nanotubes, the fluid index for EG+SWCNTs nanofluids varies within 0.52–0.24, and the consistency parameter is 9.84–140, while for EG+MWCNTs nanofluids n varies from 0.92 to 0.7, and k – from 0.28 to 0.7.

4. Electric conductivity of nanofluids with CNTs

In the paper [15], the electric conductivity of nanofluids, based on water and ethylene glycol with conventional spherical copper and aluminum nanoparticles, was studied. The weight concentration of nanoparticles varied from 1.68 to 20%. In all cases, the nanofluids had a significantly higher electrical conductivity compared to the electrical conductivity of the base liquid. The electric conductivity of nanofluid is practically described by the linear function of weight concentration. However, the electric conductivity significantly depended on the type of base fluid. For example, the gain in the specific electric conductivity of EG-based nanofluids with alumina nanoparticles was only 23%. On the other hand, the specific conductivity of W-based nanofluid increased by more than two orders of magnitude.

In this work we studied the electrical conductivity of nanofluids, based on EG, EG+PVP, EG+SDBS, W+PVP. The measurements were carried out using a simple stand, which was a 12 ml cuvette with the test liquid. Flat electrodes were attached to the cuvette’s ends, to which the source was connected. Bayonet electrodes were used as meters. Specific electric conductivity σ was determined by the formula \( \sigma = 4L/(\pi r d^2) \). Here \( r \) is measured resistance, \( L \) is the length of liquid volume, and \( d \) is the diameter of its section.

Since surfactants were used in the last three nanofluids preparation, it was necessary to first find out the electric conductivity of the base fluid and the effect of surfactant on the electric conductivity of the initial base fluid (W or EG). The specific electric conductivity of ethylene glycol was 0.35 \( \mu \)S/cm. The electric conductivity of base fluids with surfactants depended significantly on the concentration of the latter one. This is illustrated in Fig. 8, where the lower line is EG+PVP, the upper line is EG+SDBS, and the middle line is W+PVP. Both surfactants significantly alter the electric conductivity of the initial
base fluids. At PVP concentration of 0.4%, the specific conductivity of EG+PVP solution increases four and a half times (up to 1.6 $\mu$S/cm), and that of W+PVP solution, almost three times (up to 7.3 $\mu$S/cm). On the other hand, SDBS has a much larger impact. The electric conductivity of EG+SDBS solution increases by more than two orders of magnitude (up to 79 $\mu$S/cm).

![Figure 8](image1.png)

**Figure 8.** Effect of dispersants on the electrical conductivity of base fluids.

![Figure 9](image2.png)

**Figure 9.** Comparison of the SWCNT and MWCNT effect on the electrical conductivity of nanofluids.

The main data obtained of electric conductivity measurements are integrated in Fig. 9. Here the lines and marks 1, 2, 3, and 4 correspond to following nanofluids, EG+PVP+SWCNTs, EG+PVP+MWCNTs, W+PVP+MWCNTs and W+PVP+SWCNTs, respectively. First of all, it should be noted that nanofluids have significantly higher values of specific electric conductivity even at such low concentrations of CNTs. At these concentrations, the increase in electric conductivity is almost proportional to CNTs concentration. The conductivity of EG+PVP+SWCNTs nanofluid at maximum concentration is almost thirty times higher than that of the base fluid. The electric conductivity of W+PVP+SWCNTs nanofluid
at the maximum concentration exceeds the corresponding value for the base fluid by almost an order of magnitude. The second important circumstance is that nanofluids with multi-walled nanotubes have a 2–3 times lower electrical conductivity than nanofluids with SWCNTs.

5. Conclusion
The DLS method used in this work quite effectively allows to measure the diffusion coefficient of CNTs. The value of the measured diffusion coefficient naturally depends on SWCNT concentration. Using the data, founded by DLS method, one can obtain information on the dimensions of SWCNTs or their bundles. Of course, CNTs have a significant ratio of the tubes’ length (or their bundles) to their diameter. The aspect ratio can reach hundreds or even thousands. Therefore, the use of relation (1) for interpretation makes it possible to determine only the effective so-called hydrodynamic radius (diameter) of CNTs. This radius is several times less than the actual length of the tubes. Therefore, it is necessary to use alternative methods simultaneously with DLS to determine the size of CNTs in nanofluids.

The experimental data, presented in this work refer to nanofluids with SWCNTs and MWCNTs. Both nanofluids, prepared with the use of surfactants and without them, are considered. In all cases, the base fluids are Newtonian, regardless of whether dispersants are used or not. It is important to note that the viscosity of the initial base fluids (EG and W) differs by almost twenty times. At the same time, all the studied nanofluids have a non-Newtonian rheology. In all cases, the nanofluids are either pseudoplastic or viscoplastic, which rheology is well described by relations (2) and (3), respectively. In all cases, the fluid index decreases with increase in CNT concentration, and the consistency factor increases. In the general case, rheology of nanofluids also changes with an increase in temperature, and with its increase, the degree of non-Newtonianness of nanofluids decreases.

In all cases, nanofluids with SWCNTs have significantly higher viscosities than nanofluids with MWCNTs. The last are also non-Newtonian; however, at the same CNT concentrations, nanofluids with MWCNTs have significantly lower fluid indices and consistency factors than nanofluids with SWCNTs.

The reason for the non-Newtonian rheology of nanofluids in comparison with rheology of the base fluid is a significant change of its structure compared to the structure of the base fluid. The change of the nanofluid structure depends on CNT concentration and their size. As it is shown in the paper, a decrease in the effective size of CNTs also leads to a decrease in the viscosity of the corresponding nanofluid. In our opinion, the mechanism of the viscosity increasing with growth of the effective size of CNTs is associated with their percolation. CNTs form a solid space lattice, significantly changing the fluid’s structure. On the one hand, it leads to a change in the rheology of the nanofluid, and on the other, to an increase in its viscosity. However, these are mostly qualitative considerations, although the research of the nanofluid micro rheology [13] confirms them. Nevertheless, further experimental studies of the nanofluid structure, using different surfactants and the CNT concentration, are required.

The dependence of the studied nanofluids viscosity on the shear rate should be taken into account, studying real flows. Typically, flows contain regions with high and low shear rates. Therefore, a higher or lower viscosity will be fixed. There is one more effect. Nanotubes in a shear flow can be oriented along the flow.

The electric conductivity of the studied nanofluids turns out to be very significant. At such low mass concentrations of CNTs (and the bulk ones are even less), the relative electric conductivity of nanofluids with them is several times or even more than an order of magnitude higher than the electrical conductivity of nanofluids with metal nanoparticles (see [15]). It is important that nanofluids with MWCNTs have electric conductivity several times less than nanofluids with SWCNTs. The reasons for this should be sought, first of all, in the structure of these two nanofluids. The second important circumstance is the electric conductivity of both CNTs. There is still a lack of reliable data and understanding of the electric conductivity mechanisms of CNTs themselves. And if the ballistic mechanism of SWCNTs’ electric conductivity seems very likely, then it raises a number of questions for MWCNTs. Finally, an important circumstance is the dependence of relative electric conductivity on CNT concentration. In the present paper, it is found that it grows almost linearly with increasing concentration. However, it is clear that the presence of the percolation structure formation of CNTs will significantly change this dependence.
Electrical conductivity should reach a certain plateau value with an increase in the concentration of CNTs. Here everything will depend on the concentration limit of percolation, but there is practically no information at all. It is only clear that this limit is not universal; in addition to the fact that it depends on the type of CNTs and their length, the base liquid, in particular, the surfactants used, may also be an important circumstance.

The last thing worth mentioning is the dependence of the electric conductivity on the surfactants used. The appearance of high-molecular compounds in the base fluid, which can create numerous mobile ions in an electric field, certainly contributes to its electrical conductivity. In particular, this is evidenced by Fig. 8, the conductivity of EG+SDBS solution increased by two orders of magnitude compared to EG. Thus, the choice of the dispersant can have a noticeable effect on the electrical conductivity of nanofluid.

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References
[1] Treacy M M J, Ebbesen T W and Gibson G M 1996 Nature 381 678
[2] Ibrahim K S 2013 Carbon Lett. 14(3) 131
[3] Espinosa C, Ortiz-Trujillo I C, Carlos-Cornelio J A, Zapata-Hernández R D and Hoyos-Palacio L M 2017 DYNA 84(203) 24
[4] Saxena G and Raj J 2017 Int. J. Eng. Manag. Res. 7(1) 304
[5] Chen L, Xie H, Yu W and Li Y 2011 J. Disp. Sci. Tech. 32 550
[6] Baratpour M, Karimipour A, Afrand M and Wongwises S 2016 Int. Comm. Heat Mass 74 108
[7] Younes H, Christensen G, Li D, Hong H and Ghaferi A A 2015 J. of Nanofluids 4(2) 107
[8] Estellé P, Halelfadl S and Maré M 2015 J. Thermal Eng. 1(2) 381
[9] Tawfik M M 2017 J. Renewable and Sustainable Energy Reviews 75 1239
[10] Akhilesh M, Santarao K and Babu M V S 2018 Mechanics and Mech. Eng. 22(1) 207
[11] Rudyak V Ya and Tretiakov D S 2020 J. of Physics: Conf. Ser. 1677 012174
[12] Rudyak V Ya and Tretiakov D S 2020 Thermophysics and Aeromechanics 27 847
[13] Rudyak V, Minakov A and Pryazhnikov M 2021 J. Molecular Liquids 329(1) 115517
[14] Rudyak V Ya and Minakov A A 2016 Modern Problems of Micro and Nanofluidics (Novosibirsk: Science)
[15] Rudyak V Ya, Minakov A V and Pryazhnikov M I 2019 Technical Physics Lett. 45(5) 457