

# The Effect of Silver Ions Electrolytically Introduced into Colloidal Nanodiamond Solution on Its Viscosity and Thermal Conductivity

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**Abstract**—Experimental data have been presented on the influence of silver on the viscosity and thermal conductivity of a dispersion of diamond nanoparticles. A stable dispersion (5 wt %) of detonation nanodiamond particles has been used in the experiments. Silver ions have been introduced electrolytically into the dispersion of diamond nanoparticles. Silver concentration was not higher than 0.05 wt %. It has been shown that the introduction of silver ions significantly affects the thermal conductivity and viscosity of the dispersion.

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## INTRODUCTION

The thermal conductivity of fluids is of importance for the operation of heat-generating equipment. The introduction of particles with high thermal characteristics into a fluid is a method for improving its thermal conductivity. At present, research is being carried out in the field of using fluids with micro- and nanosized particles in heat exchangers. A method for improving the efficiency of heat exchangers by increasing the thermal conductivity of a fluid with the use of millimetric and submillimetric metal particles has been known for more than a century. However, such fluids have not been widely used in practice because of a number of negative factors, such as sedimentation, erosion, contamination, and pressure loss. The latest achievements in the production of new materials make it possible to obtain submicron metal particles. Liquids containing nanosized particles are referred to as “nanofluids” [1]. It has been shown that the thermal conductivity of nanofluids is several tens of percent higher than that of the carrier liquids [1–13]. In spite of the numerous works devoted to this field, a number of problems remain to be studied. In particular, the dependences of the thermal conductivity and viscosity of nanofluids on a number of parameters, such as concentration, size, and material of particles, are not quite

clear [2–6]. The mechanism of the thermal conductivity in nanofluids also remains to be established. In particular, it is still unclear if there is a single mechanism or several factors act simultaneously. Experimental data are often contradictory and even mutually exclusive. For example, it has been reported in [2–4] that the thermal conductivity of nanofluids increases with a reduction in nanoparticle sizes. On the contrary, the authors of [5, 6] have indicated that the thermal conductivity of nanofluids increases as the particle sizes grow. Moreover, some studies have shown that, as a rule, the available theoretical models inadequately predict the behavior of transfer coefficients of nanofluids. In particular, as opposed to coarse suspensions, their viscosity cannot be described by universal relations, such as the Einstein, Batchelor, and similar formulas. At equal volume concentrations, the viscosity of nanofluids is much higher than that of fluids containing dispersed particles of millimetric and submillimetric sizes. Therefore, to gain a deeper insight into the mechanisms of heat and pulse transfer, additional experimental investigations of the effects of different factors on the viscosity and heat conductivity of nanofluids are required.

Some studies have dealt with the use of nanodiamonds, along with particles of metals (gold, copper),

**Table 1.** Sizes and zeta potentials of nanoparticle clusters

Sample	Effective cluster diameter, nm	Zeta potential, mV
Nanodiamond dispersion	114 ± 3.0	−49.7
Nanodiamond/silver dispersion	108 ± 1.1	−51.3

metal oxides (aluminum and copper oxides), and silicon carbide [2, 3, 5, 8, 9], to improve the thermal conductivity of heat-transfer liquids, such as water [10], oil [11], and ethylene glycol [12, 13].

This work presents data on the thermal conductivity and viscosity of aqueous dispersions containing detonation diamond nanoparticles and silver.

## EXPERIMENTAL

A powder of detonation diamond nanoparticles was obtained by the procedure described in patent [14]. The thermal conductivity and viscosity of a stable dispersion of nanoparticles (5 wt % or 1.4 vol %) were experimentally determined. The dispersion was prepared by adding deionized water (Milli-Q system, Millipore, United States) to the nanodiamond powder (15 g), thus bringing the system volume to 300 mL. Silver ions were electrolytically introduced into the diamond-nanoparticle dispersion [15]. Silver plates supplied with an LK-27 ionizer served as a source of Ag<sup>+</sup> ions. The nanodiamond dispersion was used as an electrolyte.

The absorption spectra of the dispersions diluted 200 times with deionized water were recorded using a UVIKON 943 UV/VIS spectrophotometer (Kontron Instruments, Italy).

The sizes and electrokinetic potentials of nanoparticles in the aqueous dispersions were measured by dynamic light scattering with a Zetasizer Nano ZS analyzer (Malvern Instruments, United Kingdom). The particle concentration in the dispersions subjected to the measurements with the analyzer was nearly 0.1 wt %.

The microstructure and phase and elemental compositions of dispersion particles were studied by transmission electron microscopy (TEM) using a JEM-2100 high-resolution electron microscope (JEOL, Japan) equipped with an Oxford Inca X-sight energy-dispersive spectrometer. The content of silver was determined from the X-ray spectra with the use of a TM 3000 scanning microscope (Hitachi, Japan).

The EPR spectra of the dispersion samples were recorded in capillary tubes using an ELEXYS E-580 spectrometer (Bruker, Germany) operating in the continuous mode at room temperature and after freezing in liquid nitrogen at 85 K.

The setup used to measure the thermal conductivity and its testing have been described in [16]. The procedure for measuring the thermal-conductivity coefficient

was based on the nonstationary hot-wire method [17]. In the experiments, a copper wire 150 mm long and 75 μm in diameter was placed into a heat-insulated vessel 3 cm in diameter, which contained an examined fluid (200 mL). To balance the measuring circuit, a GWInstek GPC-3060D laboratory power supply was used to apply a voltage of 0.1 V for a short period of time. Voltage was measured using a GWInstek GDM-78261 precision voltmeter operating with time intervals of 10 ms. The temperature was measured with chromel–copel thermocouples connected with a TRM-138 measuring unit. The resultant relative error in the measurement of the thermal-conductivity coefficient was about 2%.

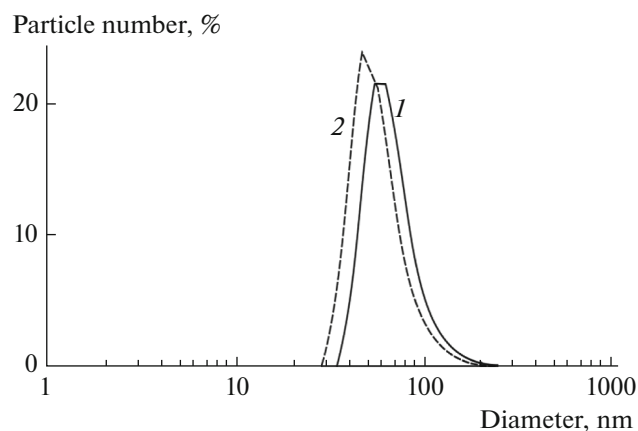
Dispersion viscosity was determined using a Brookfield DV2T rotational viscometer equipped with a ULA(0) adaptor designed for low-viscosity measurements. The setup and its tests for measuring viscosity of nanodispersions have been described in [18]. The error in measurement of the viscosity coefficient was no larger than 2%. The thermal conductivity and viscosity of the dispersions were measured at 25°C.

## RESULTS AND DISCUSSION

Table 1 lists the sizes and zeta potentials of diamond nanoparticles measured at 25°C in dispersions with and without silver. These data are the results of averaging 20 measurements each repeated three times.

The data in the table show that there are no fundamental differences in either the zeta potentials or the average effective sizes of nanoparticles for the studied dispersion samples. However, the particle-number size-distribution densities shown in Fig. 1 indicate that, in the presence of silver, the dispersion contains a much larger number of particles with sizes smaller than 100 nm. The X-ray spectral data have shown that, after the introduction of silver, the dispersion contains (wt %) carbon, 72.88; oxygen, 27.07; and silver, 0.05 (Fig. 2).

The absorption spectrum (Fig. 3) of the dispersion of diamond nanoparticles (curve 1) differs from that of the nanodiamond/silver dispersion (curve 2) prepared by electrolysis. Since diamond nanoparticles were not deposited onto the electrodes during the electrolysis, as follows from their clean surface, it is reasonable to assume that the change in the optical density of the nanodiamond/silver dispersion has resulted from the effect of silver alone, which slightly alters the spectrum of nanoparticle sizes (Fig. 1). Moreover, the electron-microscopy data have shown that the dispersion sub-

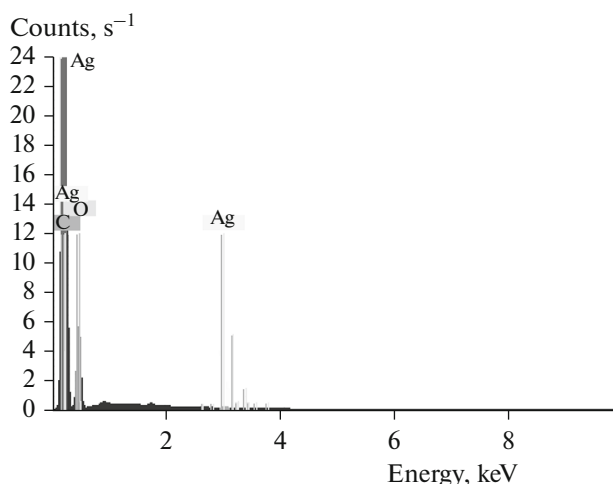


**Fig. 1.** Particle-size distributions in (1) initial dispersion and (2) nanodiamond/silver dispersion.

jected to electrolysis contains not only diamond nanoparticles with sizes of 3–8 nm, but also silver nanoparticles with sizes of 5–30 nm (the average size is about 15 nm). In the TEM image (Fig. 4a), silver nanoparticles appear to be more electron-dense formations, while diamond nanoparticles exhibit a substantially smaller contrast. The inset in Fig. 4a depicts the diffraction pattern obtained from an area of about 0.15  $\mu\text{m}$  in diameter. The diffraction reflections correspond to the phases of Ag (the  $Fm-3m$  spatial group; lattice parameter is  $a = 4.086 \text{ \AA}$ ) and diamond (the  $Fd-3m$  spatial group; lattice parameter is  $a = 3.567 \text{ \AA}$ ) [19]. Figure 4b shows the high-resolution TEM image, which indicates that diamond and silver nanoparticles are separate structures. No diamond nanoparticles entirely coated with silver are observed.

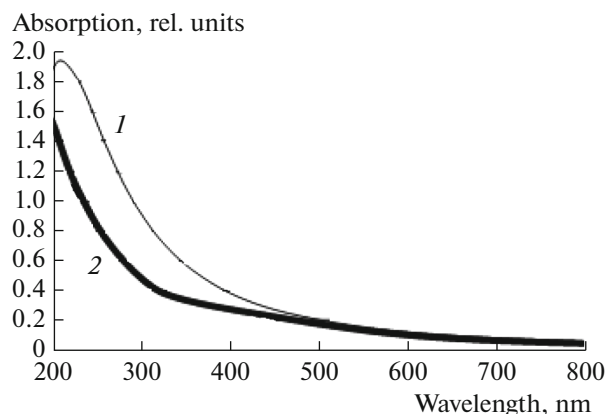
A disagreement should be noted between the data in Figs. 3 and 4. Figure 3 shows that no pronounced peak recorded for silver-nanoparticle dispersion arises as a result of the electrolysis. Only a faint shoulder is observed in the region corresponding to it. The data in Figure 4 unambiguously attest to the presence of silver particles after the electrolysis. This discrepancy in the results may be explained by a low content of silver particles as compared with diamond nanoparticles. The dispersions were diluted with water by 200 times to record the optical-absorption spectra; therefore, the contribution from silver particles to the spectrum was too small to be recorded reliably. Dilution was carried out to provide the required optical density of the dispersions. In the course of sample preparation for electron microscopy, the dispersions were concentrated due to water evaporation; therefore, particles of different natures are observed in the TEM images.

Figure 5 shows symmetric signals due to paramagnetic defects observed in the EPR spectra of the diamond nanoparticle dispersions in the absence and presence of silver.

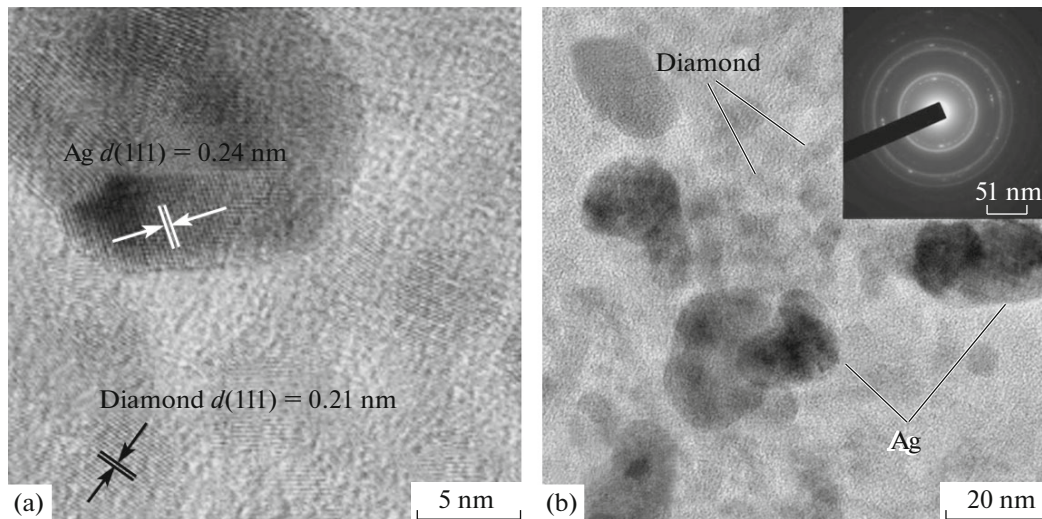


**Fig. 2.** Elemental composition of nanodiamond/silver sample.

The noticeable differences between the  $g$ -factors (the error in their determination was smaller than 0.00003) and the linewidths in the EPR spectra for these samples (Fig. 5) indicate the presence of cations (or positively charged particles) of silver on the surface of diamond nanoparticles. Previously, similar results were obtained for a gadolinium/diamond nanoparticles system [20]. The influence of the surface state on the resonance characteristics of paramagnetic defects in the bulk of detonation diamond nanoparticles is associated with the exchange interactions between the paramagnetic centers and components that are present in large amounts on the surface [21]. This enables us to consider the contribution to the changes in the EPR signals due to the defects of diamond nanoparticles as depending on the state of silver present on the surface of the nanoparticles. It is known that the  $g$ -factor of an EPR signal grows with an increase in the positive charge of cations or cationic forms of silver parti-



**Fig. 3.** Absorption spectra of (1) initial dispersion and (2) nanodiamond/silver dispersion.



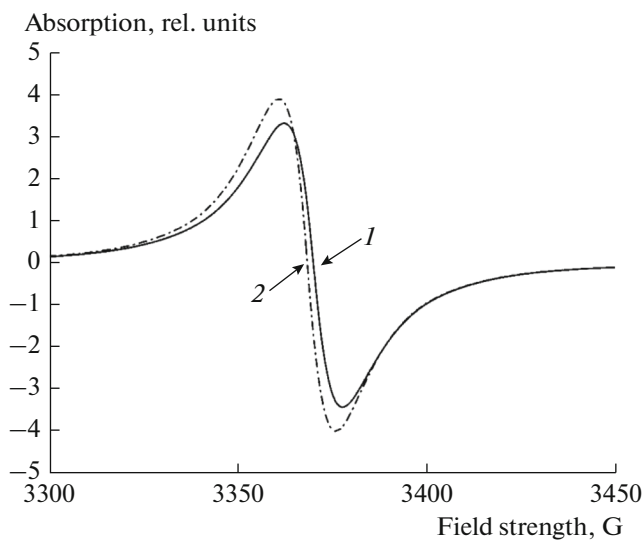
**Fig. 4.** Panel (a): TEM image taken from silver-containing dispersion of diamond nanoparticles (inset shows the X-ray diffraction pattern) and panel (b): high-resolution TEM image of individual nanoparticles.

cles [22]. Therefore, a positive shift of the  $g$ -factor (Table 2) is indicative of cations or cationic forms of silver particles present directly on the surface of diamond nanoparticles; i.e. the surface of the nanoparticles is modified.

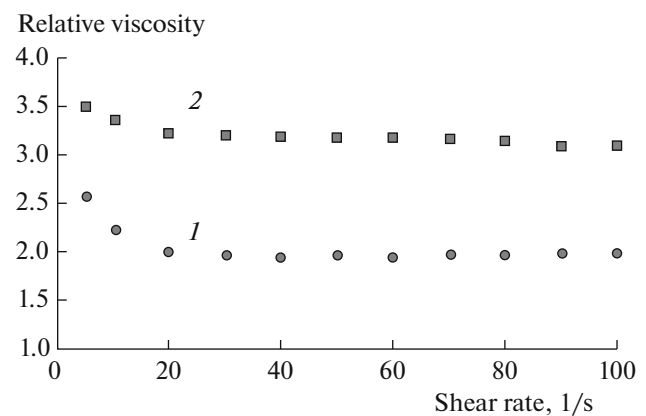
Figure 6 illustrates the effect of silver on the viscosity of the diamond-nanoparticle dispersion. Here, the relative viscosity coefficient should be read as a dispersion-to-water viscosity ratio. The procedure entails the measurement of the viscosity within a wide range of shear rates from 1 to 200  $\text{s}^{-1}$ . The presented data

show that, at low shear rates (lower than 20  $\text{s}^{-1}$ ), both of the dispersions are non-Newtonian fluids, because their viscosities depend on the shear rate. At high shear rates, the dispersions are Newtonian fluids (the viscosity is independent of the shear rate). This difference between the behaviors of the viscosities at low and high shear rates may indicate that aggregates of weakly bonded particles formed in the dispersions are disrupted at high shear rates.

After silver was introduced into the dispersion, its viscosity increased by a factor of nearly 1.64. As has been shown above (Table 1, Fig. 2), the introduction of silver ions caused no significant changes in the effective average size of the dispersed phase, but resulted in narrowing of the particle-size distribution. It was shown in [18] that a decrease in the particle sizes was accompanied by an increase in the viscosity of a



**Fig. 5.** EPR spectra of frozen dispersions of diamond nanoparticles: (1) initial sample and (2) silver-containing sample. Data have been recorded at 85 K and modulating-field strength and power of 0.1 mT and 0.23 mW, respectively



**Fig. 6.** Relative-viscosity vs. shear-rate dependences for (1) initial dispersion and (2) nanodiamond/silver dispersion.

**Table 2.** EPR signal parameters of intrinsic defects of diamond nanoparticles

Sample	$T, K$	$\Delta H, G$	$g$ -Factor
Nanodiamond dispersion	85	15.4	2.00315
	300	11.6	2.00258
Nanodiamond/silver dispersion	85	14.9	2.00324
	300	11.4	2.00267

**Table 3.** Dispersion-to-water thermal-conductivity coefficient ratios

Sample	Experimental data	Calculation by the Maxwell model
Nanodiamond dispersion	1.035	1.043
Nanodiamond/silver dispersion	1.075	–
Dispersion of silver nanoparticles (1 wt %)	1.009	1.003

dispersion. For example, as the average size of  $\text{SiO}_2$  particles in an aqueous dispersion decreased from 100 to 11.5 nm, the viscosity increased by a factor of 1.34. It is obvious that, in our case, an insignificant change in the average size cannot lead to such a dramatic increase in the viscosity and that the presence of 0.05 wt % silver particles cannot affect the viscosity. To check this hypothesis, the viscosity was measured for a colloidal silver solution with a particle concentration of 1 wt %, which was 20 times higher than that in the nanodiamond/silver dispersion under investigation. The measured relative viscosity coefficient of colloidal silver has appeared to be  $\mu/\mu_0 = 1.11$ . Here,  $\mu$  is the viscosity of the dispersion and  $\mu_0$  is the viscosity of the dispersion medium (water). Hence, the presence of 0.05 wt % silver in the dispersion of diamond nanoparticles could not, in itself, increase the viscosity by a factor of 1.64.

It should also be noted that calculation by the classical Einsteinian formula for the viscosity of dispersions  $\mu = \mu_0(1 + 5/2\varphi)$ , where  $\varphi$  is the volume fraction of particles, gives relative-viscosity coefficient  $\mu/\mu_0 = 1.035$  at  $\varphi = 1.4\%$ . This value is well below the experimental data for the nanodiamond dispersion ( $\mu/\mu_0 = 1.95$ ) and the nanodiamond/silver dispersion ( $\mu/\mu_0 = 3.19$ ). The data presented confirm once more that the classical theory does not describe adequately the viscosity of nanofluids.

The thermal conductivity coefficients measured for the dispersions of diamond nanoparticles with and without silver are listed in Table 3. The ratio of the thermal-conductivity coefficient of the initial dispersion to that of water is  $\lambda/\lambda_0 = 1.035$ , which is consistent with the data of [10, 13] and close to the prediction of the classical Maxwell theory

$$\lambda/\lambda_0 = \frac{(\lambda_p + 2\lambda_0 + 2\varphi(\lambda_p - \lambda_0))}{(\lambda_p + 2\lambda_0 - \varphi(\lambda_p - \lambda_0))},$$

where  $\lambda_p$  and  $\lambda_0$  are the thermal conductivities of the particles and the dispersion medium, respectively. For  $\varphi = 1.4\%$ , we obtain  $\lambda/\lambda_0 = 1.043$ .

It has been found that the introduction of silver ions into the dispersion significantly increases the thermal-conductivity coefficient (see Table 3). Note that the thermal-conductivity coefficient of the modified dispersion is considerably higher than that predicted by the Maxwell theory. The influence of silver on the viscosity of the nanodiamond dispersion is much weaker than that on its thermal conductivity.

The thermal conductivity of a 1 wt % colloidal silver solution was independently measured to assess an influence of silver particles on the thermal conductivity of the dispersion. The presence of 1 wt % silver increased the thermal conductivity of the dispersion by less than 1% (see Table 3). Hence, the presence of 0.05 wt % silver in the dispersion of diamond nanoparticles per se could not increase the thermal-conductivity coefficient by 4%.

## CONCLUSIONS

The work presents experimental data on the influence of electrolytically introduced silver on the viscosity and thermal conductivity of aqueous dispersions of diamond nanoparticles. It has been shown that the introduction of 0.05 wt % of silver influences the thermal conductivity and, especially, viscosity of the dispersions. After the introduction of even a small amount of silver, the dispersion viscosity increases by a factor of 1.64. It is well known [18] that the viscosity of dispersions depends on particle sizes; it increases as they decrease. However, the measurements have shown that the effective average size of nanoparticles in the dispersion has remained almost unchanged after silver ions were introduced. It has been established that diamond and silver nanoparticles form clusters with an average size of about 115 nm. Therefore, it may be supposed that the increase in the viscosity of the

dispersion is caused by the influence of silver on the structure of the clusters formed in the dispersion. The presence of cations or cationic forms of silver clusters bonded directly to the surface of nanodiamonds is confirmed by the positive shift in  $g$ -factor of the EPR signal.

Thus, it may be supposed that the interaction of nanoparticles in the clusters significantly affects the viscosity and thermal conductivity of nanodispersions. Since the sizes of the clusters remain almost unchanged, the strong influence of introduced silver cannot be described in terms of the available models. The discovered effect can be used in practice for producing nanofluids with controlled properties.

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