Dynamic viscosity of dispersion of silica dioxide nanoparticles

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Abstract. Dynamic viscosity of silica dioxide suspensions in oils was investigated by acoustical, rotary and capillary methods. An installation has also been created for measuring the viscosity of a liquid at low gradients of the flow velocity, when one can expect that the structure of the liquid change little during elementary acts of viscous flow. It is shown that at low flow rate gradients of the investigated suspensions, an increased value of viscosity is found (relative to the viscometric one), which indicates the structuring of these suspensions with the formation of a supramolecular structure. The observed phenomenon of increased viscosity can be of practical importance for all processes where slow flows prevail.

1. Introduction
Nanoscale objects significantly change the physical properties of both planar and bulk solid and liquid nanostructured systems. Nanoparticles as a dispersed phase lead to the appearance of a volumetric spatial structural network throughout the entire volume of the dispersed system. In this case, the structural and mechanical properties of the dispersed system change, and the relaxation processes occurring in them become more complicated.

2. Materials
Polyorganosiloxane PES-2 and castor oils are used as base liquids. The suspensions were prepared using silica dioxide nanopowder SiO₂ of Tarkosil trademark obtained by gas-phase synthesis [1]. Depending on the peculiarities of the method of obtaining, nanoparticles characterized by the presence on the surface of OH-groups with a concentration of the order of (0.5÷4) / nm² [2]. The properties of dispersed systems depend on the degree of dispersion of nano-incclusions. Nanoparticles have high surface energy and form agglomerates in a dispersed medium to several microns in size. Figure 1 shows SEM images of the powders obtained using a JSM-6510LV JEOL scanning electron microscope. It can be seen that with an increase in the specific surface of the particles, the sizes of the agglomerates grow, much exceeding the primary sizes of the particles of silicon dioxide. To obtain a stable suspension, it is important to thoroughly disperse it, which allows the nanoparticle agglomerates to be destroyed as much as possible. In addition, during dispersing, a uniform distribution of nanoparticles in the volume is established. Our suspensions were prepared by the ultrasonic method, the optimal dispersing time of 30 min for SiO₂/PES-2 has been determined experimentally. As shown by the Nano Particle Size Analyzer SALD-7500nano the average size of particles in the suspension is 78 nm.
3. Measurement of dynamic viscosity by rotary and capillary methods

The study of the dynamic viscosity coefficient of suspension of T-0.5 silica dioxide particles in PES-2 liquid was carried out on an Anton Paar MCR 52 rheometer with the use of a cone-plane measuring system with a gap of 0.1 mm. The cone diameter was 50 mm, the angle between the generatrix of the cone and the measurement plane was 1°. The measurements were carried out at a temperature of 23 °C. A linear dependence of the shear stress $P$ on the rate of shear strain $\dot{\gamma}$ was obtained, indicating the Newtonian behavior of the viscosity of these suspensions (figure 2).

The viscosity coefficients of the studied liquids were measured with a VPZh-2 capillary viscometer at a constant temperature of 23 °C. Table 1 shows the values of the suspension viscosity coefficients obtained using Anton Paar MCR 52 rheometer and VPZh-2 viscometer. It can be seen that the results of measuring the viscosity of suspensions by these methods are in good agreement with each other within the measurement accuracy. It can also be noted that the viscosity of 1.25 wt.% suspension is slightly higher than the viscosity of the 1.0 wt.%. Numerous works [3, 4] have shown that the viscosity of the suspension increases with an increase in the concentration of nanoparticles.

Table 1. The values of the viscosity coefficients of suspensions SiO$_2$/PES-2.

| Viscometer       | $t$, °C | $\eta$, mPa·s | SiO$_2$/PES-2, 1.25 wt.% | SiO$_2$/PES-2, 1.0 wt.% |
|------------------|---------|---------------|------------------------|------------------------|
| Anton Paar MCR 52| 23      | 12.92         | 11.48                  |
| VPZh-2           | 23      | 11.74         | 11.82                  |
4. Investigation of the viscoelastic properties of suspensions by acoustic resonance method

Low-frequency viscoelastic properties of suspension of silica dioxide nanoparticles in PES-2 are studied by the acoustic resonance method using a piezoelectric quartz resonator. Piezoquartz crystal makes oscillations on the main resonance frequency, 73.2 kHz. One end of the piezoquartz horizontal surface contacts with liquid layer covered by quartz cover-plate. The liquid layer tests only shear deformations and the stagnant shear waves are installed in it. Depending on a thickness of the layer, the parameters of the resonance curve of the piezoquartz vary. The theory of the method gives the following expression for complex shift of the resonant frequency:

\[
\Delta f^* = \frac{S k^* G^*}{4\pi^2 M f_0} \frac{1 + \cos(2k^* H - \varphi^*)}{\sin(2k^* H - \varphi^*)},
\]

where \( G^* = G' + iG'' \) – is the complex shear modulus of the liquid, \( S \) – is the cover-plate base area, \( H \) – is the thickness of liquid interlayer, \( M \) – is the resonator mass, \( f_0 \) – is its resonance frequency, \( k^* \) – is the complex wave number; \( \varphi^* \) – complex phase shift in the reflection of a shear wave from the liquid – cover-plate interface.

Studies of the low-frequency shear elasticity of colloidal suspensions of nanoparticles have shown that a region of linear elasticity is observed at low oscillation amplitudes. The ratio of the amplitude of the piezoquartz oscillation to the thickness of the liquid layer can be a measure of the angular deformation for small angles. At small deformation angles, the components of the complex shear modulus are constant, then, with an increase in the shear angle, the real modulus decreases, and imaginary one passes through a maximum. It can be assumed that the liquid has an equilibrium supramolecular structure and, at small angles of deformation equilibrium structure remains unchanged, and a region of linear elasticity is found [8]. At a critical shear angle, which corresponds to a certain critical shear stress, the equilibrium structure of suspension begins to break and its viscoelastic properties change. Other liquids, such as glycols, alcohols, acids, exhibit similar behavior [9-11].

Figure 3 presents dependences of the effective viscosity calculated using Maxwell's rheological model on the shear stress for suspensions SiO\(_2\)/PES-2 of 1.25 wt.%. At small stresses not exceeding the critical value, a constant increased viscosity characterizes effective viscosity and its value is higher for smaller particles size in suspension. When the structure is destroyed with shear stress increasing, the viscosity decreases to the smallest value. Therefore, it is of great interest to directly measure the increased viscosity of suspensions of nanoparticles with an intact equilibrium structure.

![Figure 3](image)

**Figure 3.** Effective viscosity versus shear stress: (a) SiO\(_2\)/PES-2, 50 nm; (b) SiO\(_2\)/PES-2, 100 nm.

5. Viscosity measurement at low flow rate gradients

An experimental setup has been created that makes it possible to study the flow of liquid in a capillary at low pressure differences at the ends of the capillary, when it can be expected that the liquid structure changes little during elementary acts of viscous flow. The use of conventional viscometers is impossible, because they fail to create extremely low flow velocity gradients. Figure 4a shows a diagram of the
measuring setup. Liquid from one vessel flows to another through a capillary. The liquid level in Vessel 1 is determined by the shift in the reflection of the laser beam from its surface using the photodiode. The change in the level determines the rate of liquid flow through the capillary. The process of measuring is carried out in an automatic mode at a constant temperature.

A capillary connects two vessels with liquid with the initial difference in liquid levels $h_0$, the current liquid level difference is equal to $h = h_0 - h_1 - h_2$ (figure 4b). The pressure difference at the ends of the capillary is equal to the expression $\Delta p = \rho gh = \rho g(h_0 - h_1 S_1 \alpha)$, where $\rho$ is the density of the liquid, $S_1$ and $S_2$ are the areas of the vessels and $\alpha = (1/S_1 + 1/S_2)$. When equilibrium is reached, the level difference will be equal to zero: $h_0 - h_{1,\text{end}} S_1 \alpha = 0$, where $h_{1,\text{end}}$ is the equilibrium liquid level of the in Vessel 1.

The volume $v$ of the liquid flowing in $t = 1$ s through a cylindrical capillary of radius $R$ and length $l$ at a pressure difference at its ends $\Delta p$ is [12]:

$$v = \frac{\pi R^4 \Delta p}{8 \eta l} = \frac{\pi \rho g R^4}{8 \eta l} h,$$

(2)

where $\eta$ is the dynamic viscosity of the liquid. Denoting $\gamma = \pi \rho g R^4 \alpha / (8 \eta l)$, after transformations we obtain

$$\ln\left(h_{1,\text{end}}(h_{1,\text{end}} - h_1)^{-1}\right) = \gamma t.$$

(3)

From expression (3) it follows that if the viscosity of the liquid at any pressure difference, or at all gradients of the flow velocity remains constant, then the dependence of $\ln\left(h_{1,\text{end}}(h_{1,\text{end}} - h_1)^{-1}\right)$ on time $t$ should be linear. If the viscosity increases at low gradients of the flow rate, then a deviation from this dependence will be observed. The absence of the effect of evaporation was checked by liquid level conservation in the Vessel 1 in the absence of a capillary for a period equal to the measurement time.

Figure 5a shows the dependences $\ln(h_{1,\text{end}}(h_{1,\text{end}} - h_1)^{-1})$ on time $t$ for PES-2 and a suspension of nanoparticles of silicon dioxide T-05 with a concentration of 1.25 wt.%. In the experiment, a capillary with a radius of 0.5 mm and a length of 955 mm was used for PES-2, and a capillary with a radius of 0.775 mm and a length of 174 mm was used for the suspension. It can be seen from the figure that at high gradients of the flow velocity, the dependence is linear. However, starting from a certain value of the level difference, for the suspension and for the base liquid increasing deviations from the linear dependence are observed, which indicates an increase in the viscosity.
It can be seen from formula (3) that the viscosity is inversely proportional to the tangent of the slope of the curve, figure 5a. Thus, the viscosity $\eta = \eta_0 \tan \varphi_0 (\tan \varphi)^{-1}$, where $\eta_0$ and $\tan \varphi_0$ are the initial viscosity and the tangent of curve slope angle respectively. As the gradient of the flow velocity decreases by the end of the experiment, the viscosity increases by two times for PES-2 and by ~ 6.2 times for the suspension.

To measure the increased viscosity of castor oil, which was chosen as a polar liquid, a capillary of 765 mm length and 3.01 mm in diameter was used. The viscosity of castor oil measured with the capillary viscometer VPZh-2 is 0.98 Pa·s. Figure 5b shows the change in the viscosity of castor oil and suspension of T-05 silicon dioxide particles in castor oil with a concentration of 1.25 wt.%. By the end of the experiment lasting more than six hours, the viscosity of castor oil increased by 2.7 times, for suspension it increased by 4 times.

6. IR spectroscopy investigation
Spectrometric studies of functional groups of investigated liquids in the mid-infrared region were carried out. The Bruker FTIR Spectrometer ALPHA obtained the IR spectra of suspensions of SiO$_2$/PES-2 and SiO$_2$/castor oil, nanoparticles of silica dioxide and hydrophobic base liquids.

Characteristic absorption peaks of siloxane and silanol groups are found in the IR spectra of silica dioxide nanoparticles, which are explained by the presence of OH groups on the particle surface. In the spectra of SiO$_2$/PES-2 suspensions, some changes are observed in comparison with the control spectrum of the base liquid, strengthening of the valence bonds Si–C and C–H, which indicate the interaction of nanoparticles with molecules of polyethylsiloxane liquid.

The figure 6a and the figure 6b show fragments of the IR spectrum of a SiO$_2$/PES-2 with particle concentration of 1.25 and 5 wt.% taking into account the background spectrum. Wide absorption bands were obtained in the frequency range associated with the absorption of the hydrogen bonds. At a higher concentration of nanoparticles in the suspension, the band is more pronounced.

The IR spectrum of castor oil shows a broad band in the region of hydrogen bond. In the IR spectrum of a suspension of SiO$_2$ particles in castor oil, there is also an absorption band in the region of OH group vibrations, associated with the formation of hydrogen bonds because of the interaction of nanoparticles and the base liquid, figure 6c.

7. Conclusion
Thus, the study of dynamic viscosity of colloidal suspensions of silica dioxide nanoparticles SiO$_2$ in polyethylsiloxane liquid (PES-2) and castor oil investigated by rotary and capillary methods showed the Newtonian behavior of the viscosity of studied suspensions. An increased value of the viscosity
coefficients are found at small shear deformation angles and low flow rate gradients, which indicate the structurization of the studied liquids with the formation of a supramolecular equilibrium structure. With a decrease in the flow rate gradient, the viscosity of the suspensions increases more strongly than the viscosity of the base liquids, which characterizes a higher degree of suspension structuring by the end of the experiment. Moreover, the effect is more pronounced for a polar base liquid.

![Figure 6. IR spectra of: (a) SiO₂/PES-2, c = 1.25 wt.%; (b) SiO₂/PES-2, c = 5 wt.%; (c) 1 - castor oil; 2 - suspension SiO₂/castor oil, c = 1.25 wt.%](image)

Spectrometric studies of suspensions of silica dioxide nanoparticles in polyethyilsiloxane liquid and castor oil revealed the presence of absorption bands in the region of hydrogen bond vibrations that form a supramolecular structure. With an increase in the liquid flow rate gradient, the bonds that determine the supramolecular structure are destroyed like thixotropic structures under mechanical action. It leads to viscosity values measured by traditional methods, which can be assumed to refer to a liquid with a destroyed spatial structure.

The considered phenomenon of increased viscosity can be important in all processes where slow flows prevail, for example, when filtering liquids through artificial and natural membranes.

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