MECHANICAL BEHAVIOR OF ELECTROVISCOUS NONAQUEOUS DISPERSE SYSTEMS IN SHEAR FLOW IN A TRANSVERSE ELECTRIC FIELD

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UDC 532.135:537.29

The features of the electrorheological effect in disperse systems are considered, and experimental data are presented on the influence of the concentration and moisture content of the disperse phase on the magnitude of this effect in the case of silica suspensions.

Until recently, the purpose of the investigation of the flow of a disperse system in an external electric field was mainly to study the structure formation and the influence of the latter on the mechanical behavior of the system. On this basis, a new interesting phenomenon was revealed, inherent in certain nonaqueous disperse systems, namely, the reversible increase of the apparent viscosity following application of an external electric field oriented normal to the shear surfaces of the flow. This phenomenon was named the electrorheological effect. A review of the main research on the electrorheological effect is contained in [1, 2]. The continuous phase in such a disperse system is a nonconducting liquid (mainly a nonpolar hydrocarbon). It was established that the viscosity of sufficiently well purified nonpolar liquids does not increase in a transverse electric field, whereas the apparent viscosity of a polar liquid under analogous conditions increases somewhat, initially in direct proportion to the square of the field intensity [3-10]. With further increase of the field, the viscosity ceases to depend on the intensity (saturation viscosity, usually not exceeding 0.2%). Insufficient purification or artificial contamination of the liquid (polar or nonpolar) may be the cause of an increase of 100% and more in the apparent viscosity in an electric field [6].

The electrorheological effect appears in suspensions in which the dielectric constant of the disperse medium is smaller than that of the discrete-phase particles. At the present time there are three principal opinions concerning the nature of this phenomenon.

I. The change of the viscosity of the suspension in the electric field is attributed to the simultaneous action of the electric and hydrodynamic orientations on the particle, i.e., to the restriction on the freedom of the particle to rotate when it becomes polarized, and to the corresponding increase of the dissipation of the mechanical energy of the flow. Tolstoi [11] and Demetriades [12] used a birefringence method to study the influence of simultaneous application of an electrical and a hydrodynamic field on the flow of suspensions of particles with anisotropic polarizability, but without a constant dipole moment. On the basis of the data of these experiments, Mason and co-workers, calculated the effective viscosity of such suspensions [13]. The motion of isolated particles of different shapes in the combined field was first described, after which the flow perturbation due to one particle was generalized to include the entire suspension. The measured viscosity turned out to depend only on the dielectric constants of the medium and of the particles, on the field intensity, and on the shear-velocity gradient.

II. The increase of the apparent viscosity is ascribed to the formation of a structure in the disperse phase, i.e., to the appearance of filament-like aggregates made up of particles of the disperse phase and directed along the force lines. The increase of the hydrodynamic resistance is due in this case to the stretching, blocking, and disintegration of the aggregates.

Winslow observed a considerable electrorheological effect in suspensions of nonconducting and semiconducting particles (activated moistened silica gel) in a nonconducting medium (kerosene fraction) to which

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Institute of Heat and Mass Exchange, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 18, No. 6, pp. 979-986, June, 1971. Original article submitted November 20, 1969.

surface-active substances were added [14]. The difference between the mechanical resistance of simple shear flow of the suspension in a transverse electric field and without the field turned out to be proportional to the square of the field intensity. Winslow related the appearance of the electrorheological effect to induced filament formation by the particles of the disperse phase.

The processes whereby structures are made up of solid particles suspended in a dielectric (liquid or gas) are varied and their nature has hardly been investigated. Pohl observed dielectrophoresis, or migration of particles of polar material towards the region of largest field intensity (i.e., displacement of the particles relative to the medium) in sharply inhomogeneous fields [15-17].

In macroscopically homogeneous fields, two types of structures are possible: a) structures not connected with the surface of the electrodes, in systems where ε of the medium is larger than ε of the particles; b) structures connected with the surface of the electrodes, in systems where ε of the medium is smaller than ε of the particles. The structure-formation processes are determined by the dimensions (but not by the shapes) of the particles, by the viscosity and density of the medium, by the concentration of the disperse phase, and by the field intensity [18-19].

III. The change of the apparent viscosity of the suspension following application of a transverse electric field is connected with the deformation and the interaction of the electric double layers surrounding the disperse-phase particles. The increase of the viscosity of the suspension of particles with ionic electric double layers in comparison with the value predicted by Einstein's equation is defined as the electroviscous effect. There are three known types of electroviscous effects [20].

Application of a transverse electric field on shear flow of a suspension of charged particles leads as a rule to a change in the apparent viscosity.

Bjornstahl and Snellman observed an exponential increase of the viscosity of silver and nickel sols in benzene with increasing intensity of the alternating field [21].

Extensive material has been accumulated on the behavior of lubricants in electric fields. The most significant investigations in this field were made by Deinega and Vinogradov [22-25]. In their experiments with consistent lubricants containing soapy thickening agents, they established the ability of the soap crystallites to become oriented in a shear flow with formation of bonds that can be easily broken and restored. When the shear flow is stopped, a three-dimensional skeleton made up of the disperse-phase particles becomes fixed in the lubricant. An electric double layer exists on the separation boundary and, if the skeleton has predominantly a charge of one polarity, then compression of the structure skeleton at one electrode and segregation of the disperse phase at the other electrode (electrosyneresis) takes place in an electric field. The effect of slippage at the wall then increases, i.e., in a transverse electric field the resistance of the lubricant to deformation decreases. The relative displacement of the phases following reversal of the polarity of the field exerts a noticeable influence on the shear stress.

Lubricants with nonsoapy thickening agents (silica, bentonite), which were investigated by Klass and Martinek [26, 27] have an entirely different behavior. When a transverse electric field is applied, an instantaneous reversible increase of the apparent viscosity, which depends on the field intensity and on the shear velocity, is observed in these lubricants. Further investigations of specially produced electrorheological systems have permitted these authors, first, to present a relatively complete description of the electrorheological effect and, second, to prove the connection of this effect with the presence of ionic double layers (manifestations of the first and second electroviscous effects in an electric field) [1, 2].

In investigations of the suspension of silicon dioxide and calcium titanate in naphthene hydrocarbons to which surface-active substances of ionic and nonionic type were added, Klass and Martinek observed the following.

1. The apparent viscosity in the electrorheological effect is high at low shear viscosity $\dot{\gamma}$ and increases with increasing $\dot{\gamma}$.
2. The apparent viscosity first increases in proportion to the square of the field intensity, and then reaches saturation (if no breakdown takes place).
3. The electrorheological effect has a bulk character, and is not among the wall effects.
4. The effect is stronger at high concentration of the disperse phase (up to reversible apparent solidification).

5. The effect appears, other conditions being equal, more strongly in suspensions of silicon dioxide in comparison with suspensions of calcium titanate, whereas ε of the latter is larger than ε of silica. It is therefore concluded that the surface properties of the particles are much more important than their volume properties.
6. The electrorheological effect is more strongly pronounced at higher temperatures.
7. The effect is observed in constant and alternating fields; in the latter it depends on the frequency of the field and attenuates at high frequencies.
8. The systems exhibit a dispersion of the dielectric constant and of the tangent of the dielectric loss angle, as well as a dependence of ε, $\tan\delta$, and the resistivity ρ on the shear velocity. In the case of flow, an electrization potential appears in the suspensions.

For most investigated rheological systems (suspensions of nonconducting particles in hydrocarbons), the state of the interphase surface is of exceptional importance.

Winslow [14] pointed out the influence of the moisture content of nonconducting particles of the disperse phase on the apparent viscosity in an electric field, and also the possibility of acting on the electrorheological effect with the aid of adsorption of substance having large ε on the particle surface, in which case the electric conductivity of these substances should be minimal.

Bondi and Penther, in a study of the flocculation of thickener particles in lubricants with the aid of electric research methods (measurements of ρ, ε, and $\tan\delta$), observed a dependence of the electric parameters of lubricants on the presence in them of oxidation products or moisture on the soap–oil interface or on the silicon dioxide–oil interface. Corresponding changes take place in ε, ρ, and in the low-frequency $\tan\delta$, and the character of these changes is connected with the formation of fibrous structures made up of the disperse-phase particles, determined in turn by the surface conductivity [28]. The electric parameters of the investigated lubricants varied with the shear velocity.

A similar conclusion was obtained by Deinega and Vinogradov in their experiments with soapy consistent lubricants. The observed electrokinetic phenomena (e.g., electroosmosis) depends strongly on the moisture contents of the lubricants, i.e., the formation of the electric double layer around the soap crystallites is connected with adsorption of water.

Martinek and Klass developed a theory of the structure of consistent lubricants with inorganic thickeners, based on the electrostatic interaction of particles surrounded by ionic double layers [26, 27]. This theory refutes the previously proposed flocculation mechanism, which presupposes that the individual particles of the disperse phase in a nonpolar solvent are interconnected by ridges of water and form a porous structure. The authors assume that the structure of the nonsoapy lubricants is a result of interparticle electrostatic repulsion forces, which not only prevent flocculation of the particles, but also lead to a maintenance of a maximum distance between them [26]. The suspension particles are surrounded by ionic double layers, and the lubricant has a denser consistency if the diffuse parts of the double layers of neighboring particles overlap, and a more liquid consistency in the absence of such an overlap. The thickness of the diffuse part can be regulated by varying the surface properties of the particles (dehydration, adsorption of polar substances) or the properties of the medium (polarity, ion strength).

In a so-called "simple" system consisting of silica and oil without impurities, there is no dispersion of ε and $\tan\delta$ at frequencies 50-115 Hz. Introduction of polar impurities – the formation of a "complex" system – leads to a change in the consistency of the lubricant and depending on the amount of impurities, up to total loss of plasticity, to appearance of dispersion of ε and $\tan\delta$, and to the appearance of the electrorheological effect (the authors believe that the electrorheological effect can be observed also in "simple" systems).

The disperse phase used in most investigated electrorheological systems is silica, which has the ability of adsorbing polar molecules only on a hydrated surface, i.e., a surface containing silanol groups. The maximum content of OH groups on a surface of 1 $m\mu^2$ is eight, and each OH group can adsorb one molecule of water, i.e., not more than eight water molecules can be adsorbed on 1 $m\mu^2$ [29].

The electric activity of the suspensions is determined both by the choice of the type of silica and by the amount of chemically and physically adsorbed water. For example, Martinek, Leik, and Klass recommend, for operation only in short-duration electric fields, suspensions of silica gel with not less than

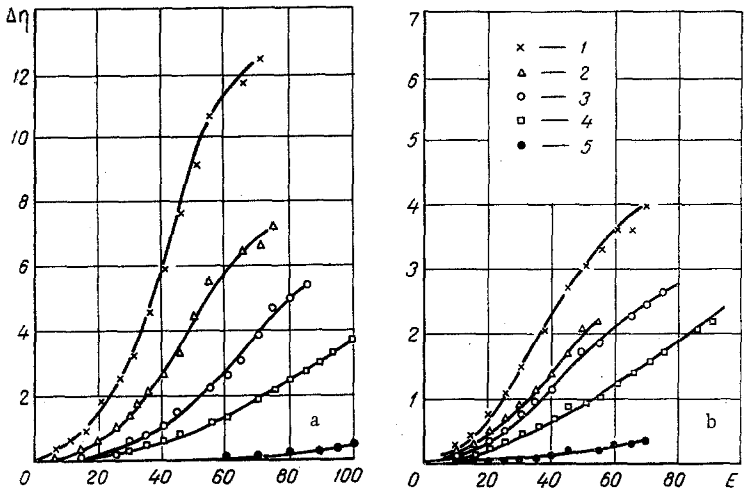


Fig. 1. Difference $\Delta\eta$ (nsec/m^2) between the apparent viscosity without a field versus the field intensity E (kV/cm) for suspensions of diatomite (a) and silicon dioxide (b) in a 1% solution of polyisobutylene in kerosene. The moisture content of diatomite is 3.8% and that of the silicon dioxide is 2.8%. The shear rate is 107.1 sec^{-1} and the concentrations are: 1) 10; 2) 5; 3) 1; 4) 0.5; 5) 0.1%.

six chemically bound hydroxyl groups (preferably eight) and from zero to four molecules (preferably 1-2) of physically adsorbed water on a surface of 1 mμ^2. Most suitable for operation in varying or constant fields is silica gel containing not less than five (preferably eight) chemically bound hydroxyl groups and from zero to four (preferably 1-2) molecules of free water on 1 mμ^2 surface.

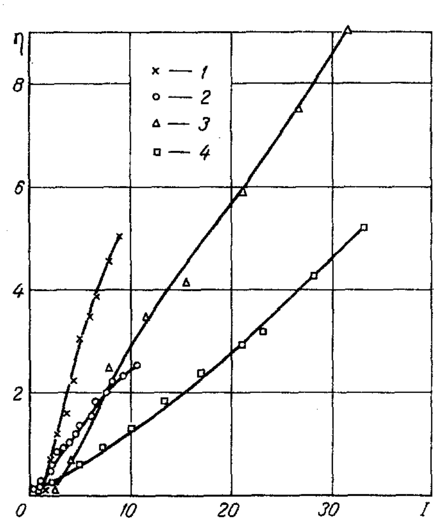
Methods for producing the required moisture content, and the types and amounts of additives ensuring electroactivity of the liquids are described in [30].

In our earlier papers [31, 32] we reported the results of electrorheological investigations of certain disperse systems. In a suspension of silicon dioxide (particle dimensions 0.1-0.2 μ) to which surface-active substances were added, we obtained a reversible increase of the apparent viscosity with increasing intensity of the transverse electric field, and we observed delay effects, aftereffects, and hysteresis. These properties were possessed also by other systems, namely suspensions of diatomite and of specially prepared silicon dioxide in a 1% solution of polyisobutylene brand 180 (thickener) and kerosene of brand TS-1. The rheological investigations of these systems have shown that when the intensity of the dc electric field is increased, the apparent viscosity changes at first slowly (activation section), and then increases abruptly (with an approximately parabolic dependence on E), after which a saturation plateau is reached. In addition, in all the investigated suspensions, the apparent viscosity depends on the shear rate; the larger γ, the smaller η. Examination of the behavior of the investigated systems in a gap between flat electrodes in a constant field with E up to 60 kV/cm, revealed intensive formation of fibrous structures made up of the disperse-phase particles and interconnecting the electrodes. If the resultant structures are mechanically broken up, the particles immediately form new structures.

Apparatus. The investigations were performed with a coaxial cylindrical rotary viscosimeter–capacitor based on the EVI-57P electroviscosity meter developed at the Physicotechnical Institute of the Gor'kii University. The rotor diameter was 62.5 mm, the gap was 1 mm, and the rotor was operated by a shaft of a miniature motor through a five-step pulley transmission. This ensured shear rates of 38.0, 72.5, 107.1, 142.5, and 210.7 sec^{-1}. The torque was measured with the aid of the same miniature motor and a measuring system containing a phase-sensitive indicator and a bridge. The viscosimeter was calibrated against water–glycerine solutions. The output was indicated by a milliammeter. The experiments were performed at a temperature 19-20°C in the room. The rotor was grounded and a voltage from a VS-23 high-voltage source was applied to the stator (intensity up to 100 kV/cm).

EXPERIMENTAL METHOD

The kerosene, from which the impurities were removed, was treated with an adsorbent, filtered, and checked for conductivity in strong fields and for the dielectric strength (in the operating gap of the



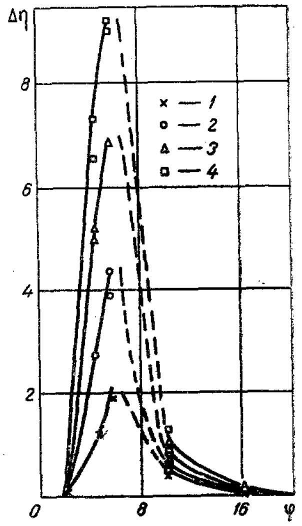


Fig. 2

Fig. 3

Fig. 2. Dependence of the apparent viscosity η (nsec/m^2) on the conductivity current I (μA) in the gap of the viscosimeter —capacitor for diatomite suspensions in a 1% solution of polyisobutylene in kerosene. The moisture content of the diatomite is 3.97%: 1) concentration C = 0.5%, shear rate $\dot{\gamma}$ = 38 sec^{-1}; 2) C = 0.5λ, $\dot{\gamma}$ = 141.6 sec^{-1}; 3) C = 5%, $\dot{\gamma}$ = 38 sec^{-1}; 4) C = 5%, $\dot{\gamma}$ = 141.6 sec^{-1}.

Fig. 3. Difference $\Delta\eta$ (nsec/m^2) between the apparent viscosity in a dc electric field and the viscosity without a field versus the moisture content of diatomite suspended in a 1% solution of polyisobutylene in kerosene. Diatomite concentration 2.3% by weight, shear rate 72.5 sec^{-1}, field intensity: 1) 30 kV/cm; 2) 40; 3) 50; 4) 60 kV/cm.

viscosimeter). One percent of polyisobutylene was dissolved in the kerosene by stirring (without heating). The moisture content of the diatomite was determined by a weight method: by drying the sample to a constant weight at a temperature 150°C. The diatomite was moistened by keeping the sample over boiling water in a closed flask (with a drain) and subsequently storing in a hermetically closed vessel. The suspension was prepared by thoroughly grinding the mixture of solid particles and the solution in a porcelain mortar.

The viscosity was measured immediately after the preparation of the suspension. At each shear rate we investigated a fresh batch, so as to exclude the influence of residual factors due to the action of the electric field. After the test, the system "rested" for 15 min, after which it was tested again with good reproducibility. The voltage was raised gradually in steps of 30 sec, and the milliammeter was read after its pointer settled.

Investigations of suspensions of diatomite and silicon dioxide at different concentrations (from 0.5 to 10% by weight) have shown that the apparent viscosity has a clear-cut dependence on the concentration, other conditions being equal (Fig. 1a, b). At low concentrations, the electrorheological effect is weak but becomes manifest at sufficiently high field intensities and does not reach saturation. The more concentrated (5-10 wt. %) suspensions show a near-parabolic dependence of the apparent viscosity on the intensity, and exhibit a tendency to saturation. The increase of the apparent viscosity with increasing field intensity is accompanied by an increase in the conductivity (Fig. 2).

The influence of the moisture content of the diatomite on the apparent viscosity of the suspension in a dc field is shown in Fig. 3. Up to 2% moisture, the change of the viscosity is small at all field intensities and is not detected by the instrument. An increase of the moisture content above this threshold causes an intense growth of the electrorheological effect. The maximum (which is different at each field intensity and at constant shear rate) is reached at $\varphi \approx 6\%$, after which the effect becomes progressively weaker, reaching zero value at $\varphi \approx 20\%$. The dependence of the apparent viscosity in the electric field on the shear rate, as expected, becomes more pronounced at lower shear rates, inasmuch as the mechanically destructive factors are weaker under these conditions.

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