6. J. E. Rizzo and N. A. Halliwell, "Multicomponent frequency shifting self-aligning laser velocimeters," Rev. Sci. Instrum., 49, No. 8, 1180-1185 (1978).
7. G. L. Grodzovskii, "Motion of fine particles in a gas stream," Tr. Tsentr. Aerogidrodin. Inst., Issue 1755, No. 2, 3-12 (1972).

CHARACTERISTICS OF CHARGE TRANSPORT IN THE DISPERSE PHASE OF ELECTRORHEOLOGICAL SUSPENSIONS

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The role of proton mobility in the polarization and conductivity of electrorheological suspensions is estimated on the basis of measurements of the shearing stress and conductivity of aluminum dihydrotripolyphosphate (AlTP) in transformer oil and of thermal changes in NMR spectra for AlTP.

The mechanical characteristics of suspensions of some substances in dielectric liquids to which an electric field is applied vary in relation to the specifics of development of the disperse phase structure, which, in turn, are determined by the nature of polarization of individual particles and the conditions of charge transport along interelectrode bridges [1-4]. The criteria for deciding upon the disperse phase of electrorheological suspensions have not yet been elaborated; however, it has been noted that variation of the suspension characteristics that have practical importance (e.g., a marked increase in the effective viscosity) at moderate (of the order of $(1\text{-}5) \cdot 10^6$ V/m) field strengths is observed in systems whose disperse phase has proton conductivity.

At the present time, the active components used in electrorheological suspensions comprise mainly dielectric materials with a highly developed external surface (Aerosil, diatomite, clays, etc.) carrying an adsorbed protogenic activator (water, amine, or an organic acid) [1]. In correspondence with this, it is assumed that the basic contribution to the polarization of such particles is provided by directional diffusion of protons in the adsorbed layer at the interphase boundary [4]. The principal disadvantage of such suspensions is that the amount of activator adsorbed by the particles depends heavily on the external conditions, which makes it difficult to ensure reproducible suspension characteristics.

It can be assumed that substances with a steady composition and marked proton conductivity are free from this disadvantage. The requirements imposed on the disperse phase of electrorheological suspensions should also be met by weakly hygroscopic layered hydroxides, where charge transport within individual microcrystals can occur in the interlayer space at a rather high rate, since it is not accompanied by diffusion of the basic structure-forming elements of the material. In correspondence with this, our aim is to elucidate the role of proton transitions in the conductivity and polarization of certain hydrated substances of constant composition.

We investigated aluminum dihydrotripolyphosphates with the composition $H_2AlP_3O_{10} \cdot 2H_2O$ (AlTP) and a layered structure, which were synthesized in accordance with [5], and also some simple hydrates — aluminum and iron dihydrophosphates and nickel and cobalt selenites. The suspensions based on mineral oils (in particular, transformer oil) with mass concentrations of particles equal to 5 and 10% were prepared by mechanical grinding with subsequent ultrasound dispersion. The mean size of microcrystals in the suspension was equal to 5 μm, while the theoretical external surface area was equal to 0.2 m²/g. The surface area of AlTP specimens dehydrated at 473°K, determined with respect to low-temperature adsorption of nitrogen, was approximately equal to 5 m²/g. Specimens characterized by an intermediate degree of hydration in comparison with the above formula unit were obtained by moistening to the re-

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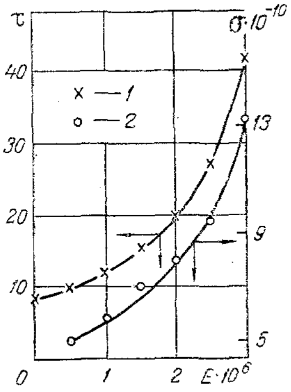

Fig. 1

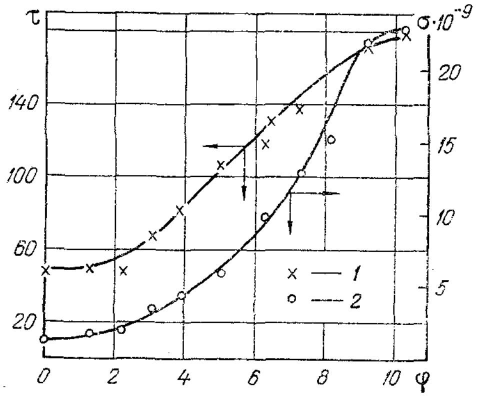

Fig. 2

Fig. 1. Shearing stress τ (N/m^2) (1) and conductivity σ ($\Omega^{-1} \cdot m^{-1}$) (2) as functions of the constant electric field strength E (V/m) for a 10 mass % suspension of aluminum dihydrotripolyphosphate in transformer oil. The shearing rate is equal to 251.4 sec^{-1}; the moisture content in AlTP is 0.6%.

Fig. 2. Shearing stress τ (1) and conductivity σ (2) in 10 mass % suspensions of aluminum dihydrotripolyphosphate in transformer oil as functions of the content of water of crystallization in the dispersed phase φ (as a percentage of the mass of particles). The shearing rate is equal to 502.9 sec^{-1}; the strength of the constant electric field is equal to $3 \cdot 10^6$ V/m.

quired degree specimens that were dehydrated at 413°K to a constant weight. As has been shown in [6], hydration—dehydration cycles do not alter the structural pattern of dihydrotripolyphosphates.

The shearing stress in the suspension τ and the conductivity σ were measured by means of a Reotest-2 rotary viscosimeter incorporating a measuring cell in the form of a coaxial cylindrical capacitor in the dc intensity range of $(0\text{-}3) \cdot 10^6$ V/m and the temperature range from 293 to 423°K. Moreover, in the cell for determining the electrophysical parameters of the suspension at rest, we determined the relative permittivity (ε) and the dielectric loss tangent (tan δ) at a frequency of 1 kHz and the dc conductivity. For the solid phase, the NMR spectra, recorded by means of a broadline instrument operating at a frequency of 15 MHz, were analyzed in the same temperature range.

Discussion of the Results. The field dependences of the shearing stress and the conductivity of AlTP suspensions (Fig. 1) exhibit a behavior qualitatively similar to that observed in the case of activators deposited on the surface of the adsorbent [1], i.e., layered hydrates with volume conductivity constitute the active components of electrorheological suspensions. However, the differences in charge structure and the character of charge transfer predetermine the fundamental differences in a number of characteristics of the suspensions in question. This pertains primarily to the behavior of τ and σ as functions of the percentage of water of crystallization (Fig. 2). This dependence is usually extremal [1], and the position of the maximum for any particular adsorbent is determined only by the activator percentage, while the height is determined by the voltage applied.

The descending branch of the curve is usually related to the increase in the mobility of adsorbate molecules for high values of the adsorbent fill factor: When an electric field is applied, the molecules gather in the region of elevated strength, viz., at the places of contact between particles, as a result of which the cohesive force between particles decreases [2, 4]. In the system under consideration, the dependence of the shearing stress on moisture is much less pronounced, while it exhibits a rising tendency up to a moisture content corresponding to the stoichiometric amount of water in the specimen (11.3% for AlTP). Generally, this is to be expected since the charge (proton) in the interlayer space is transferred primarily by the relay mechanism, while the intracrystalline water is fairly rigidly bound by the surrounding lattice elements as a result of coordination and hydrogen bonds. These differences are not related to substantial changes in the molecular parameters of water in the systems under consideration, since the dependences of ε and tan δ on the moisture in the disperse phase display qualitatively the same behavior for both these systems.

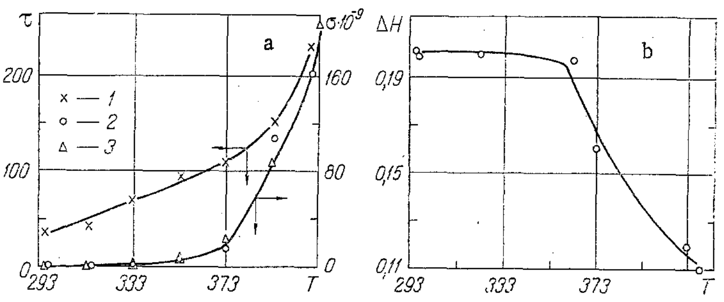

Fig. 3. Shearing stress τ (1) and conductivity σ as functions of the temperature in the case of displacement (2) and at rest (3) for 20 mass % suspensions of aluminum dihydrotripolyphosphate (a) and the ΔH (G) line width in the NMR spectrum of AlTP (b). The shearing rate in (a) is equal to 251.4 sec^{-1}, while the field strength is equal to $2 \cdot 10^6$ V/m; the temperature is given in °K.

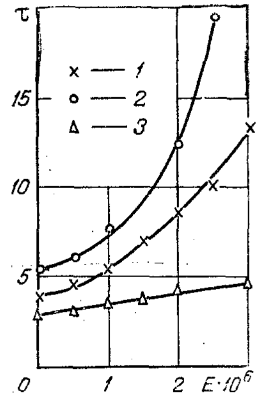

Fig. 4. Shearing stress τ as a function of the constant electric field strength E for 5 mass % suspensions of $AlPO_4 \cdot 2H_2O$ (1), $FePO_4 \cdot 2H_2O$ (2), $NiSeO_3 \cdot 2H_2O$ (3) in transformer oil.

The temperature dependences of τ and σ also are different from each other (Fig. 3). The maximums on the corresponding curves for the adsorbent—activator system are related either to a partial activator loss in the case of a high activator percentage or an increase in the mobility of its molecules caused by heating [1]. In hydrates with a steady composition there should be no extremal dependences in the temperature range of thermodynamic stability of the material, which is actually observed in experiments. The behavior of the temperature dependences (Fig. 3) along with spectroscopic data on the proton structure of the compounds under investigation allows us to draw certain definite conclusions concerning their proton polarization mechanism, with the aim of determining the active components of electrorheological suspensions.

Generally, the conductivity of a solid particle depends on the density of charge carriers and their mobility, while the conditions and the chemical nature of the material determine which of the above parameters is the limiting one. In metal dihydrotripolyphosphates, the basic charge carriers are hydrated protons, which are generated as a result of dissociation of phosphohydryl groups and proton transfer to a water molecule along the line of a rather strong hydrogen bond. According to NMR data in [7], the density of the thus-generated oxonium ions increases approximately by a factor of five in the temperature range 293-423°K, while the activation energy of this process amounts to ∿ 8.4 kJ/mole. At the same time, in the above temperature range another process occurs in the proton sublattice of the crystal, which is connected with the fact that some of the water molecules or oxonium ions acquire rotational and diffusion mobility, which manifests itself in a narrowing of the NMR line in a certain temperature range (curve in Fig. 3b). With respect to its scope and the character of temperature variations in the NMR spectrum, this process is similar to the order—disorder phase transition, which makes it possible to estimate its activation energy in accordance with [8] as approximately equal to 62.8 kJ/mole.

Thus, charge carriers are formed as a result of the dissociation of P—OH groups in the system, and this process characterizes to a certain extent their mobility. The fact that the temperature ranges of NMR line contraction and of sharp increase in the conductivity of the suspension coincide suggests that the basic contribution to the polarization of AlTP particles caused by proton transfer is provided by their mobility. This is also confirmed by the fact that the activation barriers of motion of proton-containing groups are close to the suspension's activation energy of conductivity, calculated on the basis of the experimental exponential curve (Fig. 3a) and found to be equal to 71.1 kJ/mole. This conclusion is also supported by a comparison between the results of experimental investigations of dihydrotripolyphosphates and aluminum orthophosphate and metal selenite dihydrates (Fig. 4). According to NMR data given in [9, 10], the density of "free" protons as charge carriers in the above hydrates is comparable to that in AlTP. However, their transport in materials with tighter packing requires the transfer of basic structural elements of a crystal. Since the latter process is characterized by low values of the diffusion factor, the proton conductivity of such hydrates is much lower (by three to five orders of magnitude), while the line width in NMR spectra is constant in the temperature range of hydrate stability [10]. Correspondingly, their activity as components of electrorheological suspensions is low.

Consequently, in order to ensure the optimum (in the sense of electrorheology) proton conductivity of AlTP, it is first necessary to regulate the mobility of charge carriers. For proton transfer involving the relay mechanism, it is sufficient to have a relatively small amount of residual water in the interlayer space of a crystal; according to NMR data, a marked reduction in mobility is observed only at intense dehydration stages. The conductivity can also be regulated by substituting ligands possessing a weaker affinity to protons for a portion of the water or by changing the limiting stage of the process, e.g., replacing a part of the protons with the heavier cations.

Thus, constant-composition hydrates with volume proton conductivity belong to a class of promising substances to be used as the disperse phase of electrorheological suspensions. Among the criteria for their suitability are protogenic groups and transport paths determined by the structure and containing ligands — intermediaries — that are necessary for proton transfer. The number of promising substances from among the vast number of hydrated compounds can be reduced on the basis of data on the compound structure and the experimentally measured mobility of proton-containing groups, using, e.g., the NMR method. Besides the aluminum dihydrotripolyphosphates considered in the present article, other types of inorganic ion exchangers should also possess these properties.

NOTATION

τ, shearing stress; σ, electrical conductivity; ε, specific permittivity; $\tan \delta$, dielectric loss tangent; E, strength of the electric field.

LITERATURE CITED

1. A. V. Lykov (ed.), Electrorheological Effect [in Russian], Nauka i Tekhnika, Minsk (1972).
2. Z. P. Shul'man, A. D. Matsepuro, and V. A. Kuz'min, "Formation of bridges of disperse phase particles accompanying the electrorheological effect," Vestsi Akad. Nauk BSSR, Ser. Fiz.-Energ. Navuk, No. 2, 130-134 (1974).
3. Z. P. Shul'man, A. D. Matsepuro, and B. M. Khusid, "Charge transfer by oscillating particles in electrorheological suspensions. 1. Experimental Investigation," Vestsi Akad. Nauk BSSR, Ser. Fiz.-Energ. Navuk, No. 4, 62-69 (1974).
4. Z. P. Shul'man, A. D. Matsepuro, and B. M. Khusid, "Structure formation in electrorheological suspensions in an electric field. 1. Qualitative Analysis," Vestsi Akad. Nauk BSSR, Ser. Fiz.-Energ. Navuk, No. 3, 116-121 (1977).
5. F. d'Yvoire, "Etudes des phosphates d'aluminum et fer trivalent IV. Les di- et triphosphates. Pouvoir d'echange cationique des triphosphates acides $H_2(AlP_3O_{10}) \cdot 2\text{-}3\ H_2O$ et $H_2(FeP_3O_{10}) \cdot 2H_2O$," Bull. Soc. Chim. France, No. 6, 1224-1236 (1962).
6. V. A. Lyutsko, M. V. Nikanovich, and K. N. Lapko, "Infrared-spectroscopic investigation of proton-containing groups of aluminum tripolyphosphate $H_2AlP_3O_{10} \cdot 2H_2O$," Neorg. Mater., 16, No. 9, 1613-1617 (1980).
7. K. N. Lapko, V. N. Makatun, and I. I. Ugolev, "Proton structure of crystalline aluminum dihydrotripolyphosphate dihydrate," Zh. Neorg. Khim., 25, No. 6, 1688-1691 (1980).
8. J. S. Uo and É. I. Fedin, "Determination of moderated rotation barriers in solids," Fiz. Tverd. Tela, 4, No. 6, 22-33 (1962).

9. I. I. Ugolev, A. K. Potapovich, and V. N. Makatun, "State and dynamics of water in polycrystalline dihydrates of aluminum phosphates," Dokl. Akad. Nauk BSSR, 21, No. 3, 232-235 (1977).
10. V. N. Makatun, R. Ya. Mel'nikova, V. V. Pechkovskii, and M. L. Afanas'ev, "Dissociation of coordinated water in solid hydrates," Dokl. Akad. Nauk SSSR, 213, No. 2, 353-355 (1973).
11. I. I. Ugolev, V. L. Shneerson, V. N. Makatun, A. K. Potapovich, and I. A. Shingel', "Nuclear magnetic resonance spectra of N aquo complexes with strong hydrogen bonds," Zh. Prikl. Spektrosk., 32, No. 5, 928-932 (1980).

KINETIC EQUATIONS FOR SUSPENSION SEPARATION

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A kinetic equation for description of suspension separation is proposed. Examples of determining effective rheological characteristics and phase separation surfaces during filtration are presented.

At the present time, various models are used to describe processes occurring in separation of suspensions — motion of a liquid through a porous layer of variable thickness with constant (or variable) porosity, motion through a set of capillaries which decrease in number (or diameter), or motion of particles in a suspension, precipitate, or filter pores, etc. [1-4].

The existing models are imperfect: several times deviations have been noted in theoretical expressions based on Darcy's law, the Hagen—Poiseuille or Stokes equations, etc., as compared to experimental data obtained by separation of real suspensions [3-6]; a number of modified equations and empirical expressions have been proposed [1-5, 7, 8]. Moreover, the differing dimensions of the parameters appearing in the equations do not permit comparison of suspension properties which determine the selection and productivity of equipment to be used. Thus, the basic characteristic of filtration with formation of a precipitate — specific resistance — cannot be applied to filtration of the very same suspension if the filter barrier pores are comparable in size to the dimensions of the precipitate particles and filtration occurs with the pore sealing process, etc.

The unsatisfactory state of suspension separation theory and technology has been evaluated several times [9, 10]. In reality, as Romankov noted, all suspensions are non-Newtonian liquids, and a theory of their separation should be developed from universal concepts [11].

One reason for the lack of a unified mathematical description of suspension separation is the insufficient development of theory in the rheology of two-phase flows in general, despite the large number of studies dedicated to this problem [12, 13]. The complexity of the phase interaction mechanism, especially when physicochemical processes on the interphase boundary are considered, eliminates the possibility of the early appearance of a unified description and compels us to seek new and better semiempirical models.

Below we will present a model, according to which as the suspension separates and the volume of liquid phase in the two-phase system decreases, there occurs a corresponding reduction in the mean distance between solid phase particles.

We assume that the suspension is isotropic, that external forces in separation are compensated by friction forces, that inertial forces are absent, and that motion is one-dimensional and laminar, and we will neglect the effect of the vessel (filter) walls. As is well known, due to phase interaction in the surface layer, the apparent viscosity of the suspension differs from the dynamic viscosity of the liquid, a fact which is considered by a quadratic dependence

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