Reports of the Academy of Sciences of the USSR

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1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1962. Volume 143, No. 4

PHYSICAL CHEMISTRY

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THE EFFECT OF STRONG ELECTRIC FIELDS ON THE STRUCTURE OF NON-AQUEOUS PLASTIC DISPERSE SYSTEMS

(Presented by Academician V. A. Kargin, 23 IX 1961)

Plastic disperse systems (greases, clay pastes, etc.) are characterized by a very high rate of structure formation—the formation of a three-dimensional structural framework that imparts to them the properties of solids. Since the disperse phase in such systems is formed by particles of relatively large size, at room temperatures thermal motion acts on them only weakly. Therefore, the rapid stopping of the flow of plastic disperse systems is accompanied by practically instantaneous cementation of the structure that exists in the flow. The solidified flow structures may correspond to various, including high, rates of deformation. At room temperatures they persist for a long time without change (weeks, months). In the case of anisodiametric particles of the disperse phase, solidified oriented structures are readily formed. If these particles possess intrinsic birefringence, then in dynamic and solidified flows a considerable polarization-optical effect is sometimes observed, making it possible to study plastic disperse systems by the photo-viscosity method (1,2). The orientational effect and the formation of solidified anisotropic structures are also detected by measuring the dielectric permittivity and the tangent of the loss angle (2,3). Both methods make it possible to follow changes in the structure of disperse systems under the influence of various external actions. The polarization-optical method is especially simple and illustrative.

In a systematic study of the electrical properties of nonaqueous pseudogels of soaps (greases), electrokinetic phenomena—electrophoresis and electroosmosis in strong electric fields—were found in some of them (⌒4). Consequently, in non-aqueous disperse systems as well, at the interface between the phases there may exist a double electric layer, including a diffuse layer, which must undoubtedly affect the processes of structure formation. The presence of a double electric layer on the surface of the disperse phase makes the structure of the systems

Fig. 1

Figure 1: Fig. 1

under consideration sensitive to the action of an electric field. This can conveniently be observed by using the polarization-optical method.

On a glass plate measuring 50×70 mm^2, two capacitor plates—electrodes consisting of strips of aluminum foil 0.1 mm thick—are glued or fixed. In the gap between the electrodes, 0.6 mm wide, is placed the system under investigation, which was a hydrated Ca grease (fatty solidol). The capacitor was placed on a flat ebonite ring mounted on the stage of a universal polarizing microscope. Spring contacts fastened in the ebonite ring supplied high voltage to the electrodes. The source of direct current was an apparatus consisting of a laboratory autotransformer, a high-voltage transformer, and a full-wave rectifier assembled on 2Ts2S tubes. An electric field with a gradient of 15 kV/cm was applied to the grease.

To obtain a solidified structure of solidol in which the lines of flow are perpendicular to the direction of the electric field, the following procedure was used. Ma

a small lump of grease was placed at the edge of the gap between the electrodes. Pressing it down with a cover glass and rapidly moving the glass along the gap, the latter was filled with grease having a structure oriented in the slow flow. When the cover glass is stopped, a solidified anisotropic plastic system is formed. It is convenient to observe it in plane-polarized light, using a plate of sensitive tint.

When an electric field is applied, an intensive transfer of the dispersion medium (mineral oil) to the cathode takes place, where a layer of it of considerable thickness may be formed. Simultaneously with this, compression of the structural framework is observed. This is illustrated by the microphotographs shown in Fig. 1, taken in polarized light at

Fig. 1. Change in the structure of a hydrated calcium grease under the action of a high-voltage electric field. 1 —initial system; 2, 3 —after 1 and 5 min after application of the electric field; 4–6 —after 1, 2, and 5 min after reversal of the sign of the poles

low magnification and with the greatest clearing of the grease. The air bubbles present in the grease give it a certain nonuniformity, which, however, facilitates observation of the changes occurring in it. The dispersion medium does not possess birefringence. Therefore its displacement toward the cathode is accompanied by the formation at its surface of a dark near-wall layer, the thickness of which increases with increasing duration of the action of the electric field. In the lower part of the photographs an arrow indicates one of the air bubbles in the grease. The figure clearly shows how it moves relative to the vertical line of the stationary coordinate cross. The formation of a layer of dispersion medium at the surface of the cathode causes the structural framework of the grease to be squeezed toward the anode; this is promoted by the strong interaction, accompanying cataphoresis, between the anode and the negatively charged particles of the disperse phase. Reversal of the sign of the electrodes causes the layer of dispersion medium separated at one of them to move to the other. In this process the layer of liquid may be washed out, as is clearly seen in Fig. 1, 4, 5. If the layer of dispersion medium at the cathode has been well formed by prolonged holding of the grease (30 min and more) in the electric field, then upon reversal of the sign of the electrodes it moves through the grease, becoming only slightly washed out. In one way or another, after some time a layer of dispersion medium again forms at the cathode. This process can be repeated many times.

Experiments with a grease in which a solidified flow structure had been obtained, coinciding in direction with the electric field, showed that in this case the intensity of transfer of the dispersion medium to the cathode was considerably lower.

From the experiments considered it is evident how sharply electrokinetic phenomena can be manifested in nonaqueous destroyed pseudogels of the type

lubricants. The change in the concentration of the dispersion medium at the cathode, on the one hand, represents a method for forming and isolating a wall layer of liquid at the boundary between the conducting wall and the plastic system, and, on the other hand, a method for lowering the concentration of the liquid phase there. Regulation of the concentration of the dispersion medium at the surface of the electrodes, and of the thickness and position of its isolated layer, opens up entirely new ways of studying the effect of wall slip and its influence on the rheological properties of plastic dispersed systems. A layer with an increased concentration of the dispersion medium and with reduced shear strength may occupy different positions. Its displacement will model the continuously successive processes of destruction and thixotropic restoration of the structural framework of plastic dispersed systems ([5]). Everything stated here was confirmed experimentally in tests with a Na lubricant, a consistent grease obtained by thickening spindle oil with sodium soaps (20.6%) of castor-oil acids. The tests were carried out in a plastoviscosimeter, the rotor and housing of which constituted the electrodes—the plates of a capacitor ([6]). With a rotor diameter of 12.5, the gap between it and the housing was 0.25 mm. The potential difference was 100 V. The experiments were conducted at a rotor speed of 0.96 rpm.

Fig. 2. Change in shear stress (τ) with time during continuous deformation of a lubricant under conditions of absence and application of an electric potential to the working surfaces in a plastoviscosimeter-capacitor

The results of tests of the consistent grease, which exhibited strongly pronounced electrokinetic phenomena, are presented in Fig. 2. In view of the long duration of the test, which included several experiments, the time axis and the curves

Fig. 2. Change in shear stress (τ) with time during continuous deformation of a lubricant under conditions of absence and application of an electric potential to the working surfaces in a plastoviscosimeter-capacitor

Figure 2: Fig. 2. Change in shear stress (τ) with time during continuous deformation of a lubricant under conditions of absence and application of an electric potential to the working surfaces in a plastoviscosimeter-capacitor

$\tau(t)$ are given with breaks. Rotation of the rotor at a constant speed was begun in the absence of an electric field. As deformation increased, the shear stress rose, as shown by curve OA. At point A, a negative potential was applied to the rotor. This caused an influx of the dispersion medium to its surface and the formation of a wall layer with very low resistance to deformation. As a result, the shear stresses decreased by several tens of times. After a steady flow regime had been reached, at point B a positive potential was applied to the rotor. Simultaneously with the continuing deformation, the dispersion medium flows away from the rotor surface. Over a certain time the homogeneity of the system increases, which entails an increase in shear stresses. At a certain critical stress, transition through the strength limit occurs. It should be supposed that this process develops in the layer of lubricant with an increased content of the dispersion medium. Therefore the maximum (point C) is located at a low level. At the same time the wall layer at the housing becomes enriched

by the dispersion medium, and a zone with a greatly reduced resistance of the lubricant to deformation is created there. When the concentration of the dispersion medium directly at the working surface of the housing rises to a certain limiting value, a steady flow regime is attained.

The application at point D of a negative potential to the rotor again causes an increase and then a decrease in the shear stress. Under the influence of the recharging of the rotor and the housing (points B, D, F, H) and of displacements of the dispersion medium in the gap between them, the phenomena considered in connection with the experiment represented in Fig. 2 by curve BCD can be observed repeatedly.

It is evident from Fig. 2 that higher shear stresses in steady flow regimes are observed when the housing is negatively charged. Its working surface had a rougher finish (it had been turned). Therefore the flow of the lubricant at the housing surface is associated with the disturbing effect of its roughness on the flow and with a somewhat smaller influence of the wall effect, which greatly reduces the resistance of the system to deformation. This similarly explains why the maxima E and I lie above the maxima C and G. The point is that the transitions through the maxima E and I occur as a result of destruction of the lubricant structure at the rough surface of the housing.

If, under a steady flow regime, the electric field is removed, a rather rapid and very large increase in shear stress is observed. It is caused by the washing out of the wall layer during deformation of the microgranular system, which is connected with rotation of the grains and their mutual displacements. The shear stress increases until the limit of shear strength is reached. The maximum stresses attained after removal of the electric field have practically the same value as in the case of deformation of a lubricant that had not been subjected to the action of an electric field. Both in experiments in which the lubricant was in an electric field and the field was then removed, and in experiments without application of a field to it, after passage through the strength limit the stresses sharply decrease to the same values under steady flow regimes.

Thus, the present work shows that in nonaqueous plastic systems with a hydrophilic dispersed phase, electrokinetic phenomena can manifest themselves with high intensity. Phase transfer and changes in the structure of systems in strong electric fields are conveniently observed in polarized light. Under the influence of changes in the concentration of the dispersion medium inside the system and at the solid surfaces relative to which it is deformed, it is possible, as desired, to strengthen or weaken wall slip, changing the effective resistance of the system to deformation by tens of times.

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Received
19 IX 1961

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