Soviet-era science, translated into English

DEPENDENCE OF THE LOWER STRENGTH LIMIT OF THE STRUCTURE AND OF THE CRITICAL VELOCITY GRADIENT ON THE CONCENTRATION OF AN ALUMINUM NAPHTHENATE OLEOGEL

1958

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-195801.30404

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. A. FEDOTOVA and A. A. TRAPEZNIKOV

DEPENDENCE OF THE LOWER STRENGTH LIMIT OF THE STRUCTURE AND OF THE CRITICAL VELOCITY GRADIENT ON THE CONCENTRATION OF AN ALUMINUM NAPHTHENATE OLEOGEL

(Presented by Academician M. M. Dubinin, December 28, 1957)

In works (1,2) it was shown that many intermediate systems (in the rheological sense), which include the oleogels of aluminum soaps of naphthenic acids in decalin studied by us, are of particular interest because all the features both of fully flowing (liquid-like, non-Newtonian) systems and of practically non-flowing (plastic-solid or elastic-brittle) systems can be observed in them simultaneously. It was found (ˆ2) that in liquid-like systems, which exhibit flow under any arbitrarily small shear stress, it is likewise necessary to take into account the presence of a structural network. However, whereas in systems that behave practically as solids such a network is extremely slowly relaxing, in liquid-like systems it is mobile and is characterized by short relaxation times.

It was further established (ˆ2) that, among the large number of physicomechanical parameters needed for a complete characterization of the behavior of a structured system over wide ranges of the velocity gradient $\dot{\varepsilon}$ and shear stress P, the values of the lower strength limit of the structure P_k and of the corresponding critical $\dot{\varepsilon}_k$ are among the most important rheological constants of the system. The constants P_k and $\dot{\varepsilon}_k$ correspond to the transition from the region of constant true-relaxation viscosity $\eta_1 = \text{const}$, i.e., from the region of a statistically undestroyed structure (which has time to be completely restored during deformation), to the region of decreasing viscosity $\eta_2(P)$, which corresponds to the appearance of destruction of part of the structural bonds that do not have time to relax and be restored during deformation.

Investigation of the dependence of these constants on the concentration of the aluminum naphthenate oleogel led to the discovery of interesting regularities.

Processing the series of curves, obtained on a complex elastoviscosimeter (ˆ2), for the kinetics of development of deformation under constantly acting shear stresses $\varepsilon(\tau)_P$ (the method $P = \text{const}$) and the curves for the kinetics of development of shear stress at constant rotation rates of the outer cylinder $P(\tau)_\Omega$ (the method $\Omega = \text{const}$) led to the establishment of the dependence of the vis-

SovietRxiv

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

cosity of the system on the applied shear stress and velocity gradient, which in turn made it possible to determine P_k and $\dot{\varepsilon}_k$ for each gel concentration.

Figures 1 and 2 show the dependences $\eta(P)$ and $\eta(\dot{\varepsilon})$ for aluminum naphthenate gels in decalin in the concentration interval C from 6 to 20%*. If

* The study of the oleogels was carried out on the 20th day after their preparation. Data for $C < 6\%$ were published earlier (^2). In the present work aluminum naphthenate prepared by G. V. Belugina according to a formulation corresponding to 36% free NaOH and pH = 5 (^3) was used. This sample of soap was designated grade B in (^2).

systems with $C < 6\%$, while possessing elasticity, prove to be noticeably fluid, like liquids; systems with $C = 8$–20% already behave as true highly elastic gels with large shear moduli. At the same time, even in these gels, although slow, nevertheless quite measurable flow is observed at the smallest P, and, correspondingly, a fairly high viscosity of the order of 10^5–10^6 poise. In this respect, highly concentrated oleogels of aluminum naphthenate are close to systems belonging to the class of plastically solid bodies, for example hydrosuspensions of bentonite clays, in which recently (^{4}) the greatest constant viscosity was actually measured, and proved to be almost of the same order as that indicated above.

Fig. 1. Dependence $\eta(P)$ for 6-20% oleogels of aluminum naphthenate in decalin. The arrows indicate the values of the lower structural strength limit P_k

From Figs. 1 and 2 it is clearly seen that, for all the oleogel concentrations studied, in the range of the smallest P and $\dot{\varepsilon}$ the viscosity is constant; at somewhat larger P and $\dot{\varepsilon}$ it begins to decrease. Further, from Fig. 1 it follows that, with increasing gel concentration, the values of the maximum constant viscosity $\eta_1 = \text{const}$ and of the lower strength limit P_k increase markedly. At $P > P_k$, not all elements of the structure manage to relax at the given $\dot{\varepsilon}$, because of their inherent low relaxation rate Y_{rel} (^{5}), and are destroyed in the process of development of deformation along the curve $P(\tau)$ up to the moment when $P = P_s$ (^{2}). This, together with the factor of particle orientation in the flow, leads to a decrease in viscosity in the region $P > P_k$.

Fig. 2. Dependence $\eta(\dot{\varepsilon})$ for 6-20% oleogels of aluminum naphthenate in decalin. The arrows indicate the values of $\dot{\varepsilon}_k$ corresponding to P_k

The increase in the lower structural strength limit P_k with increasing C may be

SovietRxiv

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

explained by an increase in the number of local (transverse) bonds of the gel structural network, since an increase in concentration leads to a strong increase (per unit volume of the system) in the number of entanglements and in the degree of interaction between the threadlike high-polymer particles of aluminum naphthenate. Naturally, an increase in the number and strength of the bonds between the structural elements of the gel network requires an increase in the shear stress causing the onset of destruction of the structural bonds of the system.

The increase in P_k with increasing C of the system, analogous to that noted

by us (2) and described in detail above, was also found for hydrosuspensions of bentonite clays (4). This once again emphasizes the possibility of describing systems belonging to liquid-like and solid-like bodies by common parameters, as was proposed earlier (1,2).

From the curves in Fig. 2 it is seen that the dependence $\eta(\dot{\varepsilon})$ outwardly resembles $\eta(P)$; however, there is an essential difference between them. With increasing C, the values of $\dot{\varepsilon}_k$ do not increase, but decrease. The decrease of $\dot{\varepsilon}_k$ with increasing C is apparently a consequence of the fact that the rate of true relaxation of the elastic stresses of the system as a whole decreases with increasing concentration of the oleocolloid.

Fig. 3. Change in the lower strength limit of the structure P_k and the corresponding critical velocity gradient $\dot{\varepsilon}_k$ with the concentration of the oleogel

Fig. 4. Dependence of $\lg P_k$ on C and $\lg \dot{\varepsilon}_k$ on C for oleogels of aluminum naphthenate in decalin

The lower the relaxation rate possessed by the system, the smaller the probability that, at a given rate of deformation, all stressed bonds will have time to relax, and the smaller the $\dot{\varepsilon}$ it can withstand without destruction of the structure.

Of special interest is the regularity we obtained for the change of P_k and $\dot{\varepsilon}_k$ with C. In Fig. 3 the corresponding curves are shown. In Fig. 4 these same dependences are plotted in semilogarithmic coordinates.

As is seen from Fig. 4, both dependences ($\lg P_k$—C and $\lg \dot{\varepsilon}_k$—C) lie well on straight lines passing almost at the same angles of inclination to the horizontal. This means that their exponents are practically identical and differ only in sign:

$$P_k = P_{k1} e^{\alpha(C-C_1)} \quad \text{and} \quad \dot{\varepsilon}_k = \dot{\varepsilon}_{k1} e^{-\alpha_1(C-C_1)},$$

where C_1 is some arbitrary concentration and $\alpha \approx \alpha_1$. From such a relation it follows that there is an internal connection between P_k and $\dot{\varepsilon}$. Indeed, from the above equations it follows that the product of the corresponding values is a constant quantity, independent of C:

$$P_k \dot{\varepsilon}_k = P_{k1} \cdot \dot{\varepsilon}_{k1} = W_k = \text{const.}$$

The product of the value P, maintaining steady flow, by the corresponding value of $\dot{\varepsilon}$ represents the power of the flow per unit volume of the body, or the energy of dissipation. Consequently, the critical energy of dissipation does not depend on C of the gel (for the given aluminum naphthenate) in in-

in the concentration interval from 6 to 20%. As is seen from the data of Table 1, the values of W_k in fact increase slightly with increasing C, which is connected with the small differences between α and α_1; however, when P_k and $\dot{\varepsilon}_k$ change by a factor of 10-13, the change in W_k is very small.

Table 1

C, %	P_k, dyn • cm^{-2}	$\dot{\varepsilon}_k \cdot 10^3$, sec^{-1}	$W_k = P_k \cdot \dot{\varepsilon}_k \cdot 10^3$, erg • cm^{-3} • sec^{-1}
6	160	3.8	607
8	240	3.1	744
10	350	2.0	700
15	860	0.98	844
20	2160	0.40	864

It may be supposed that the observed independence of W_k from C is due to the fact that, when W_k is exceeded, identical bonds begin to break down in gels at different C. In other words, the increase in the total number of bonds per unit volume of the system with increasing concentration must be compensated by a corresponding decrease in $\dot{\varepsilon}$, so that, during deformation of the system in a steady flow, a quite definite number of bonds could have time to be completely restored per unit time. Consequently, the value of W_k can be used to determine the minimum rate of bond restoration. Earlier (^{5}), a concept was developed of a set of bonds in aluminum naphthenate gels possessing different ε_{k_i} and ϑ_i and different rates of restoration. It may be assumed that the constancy of W_k is determined by the shortest elements of the structure, possessing the smallest ε_{k_i} and restoring most slowly. The weak increase of W_k with C that is actually observed may probably be attributed to some strengthening of the interaction of aluminum naphthenate chains at short distances.

The concept of critical power was also used by Ramaya in treating the data he obtained on the viscosimetry of oils (^{6}). He noted the constancy of $P_k \cdot \dot{\varepsilon}_k$ with changes in the temperature of the oil. Although the nature of the objects studied by us and the methods of investigation differ very considerably from those used by Ramaya, the closeness of the results obtained independently deserves attention and emphasizes the importance of the concept of critical power.

Received
26 XII 1957

REFERENCES

1. A. A. Trapeznikov, *Kolloidnyi zhurnal*, **12**, 67 (1950); in: *New Methods of Physicochemical Investigation of Surface Phenomena*, **1**, 20, 1950; Proceedings of the 2nd All-Union Conference on Colloid Chemistry, Kiev, 1952.
2. A. A. Trapeznikov, V. A. Fedotova, DAN, **81**, 1101 (1951); **82**, 97 (1952); Proceedings of the 3rd All-Union Conference on Colloid Chemistry, Publishing House of the Academy of Sciences of the USSR, 1956.
3. A. A. Trapeznikov, G. V. Belugina, DAN, **87**, 635, 825 (1952); **94**, 97 (1954).
4. L. A. Abduragimova, P. A. Rebinder, N. N. Serb-Serbina, *Kolloidnyi zhurnal*, **17**, 184 (1955).
5. A. A. Trapeznikov, DAN, **102**, 1177 (1955); *Kolloidnyi zhurnal*, No. 3 (1958).
6. K. S. Ramaya, *Anomaly of the Viscosity of Oils and Its Influence on Friction in Machines*, 1949.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.