A. A. TRAPEZNIKOV, A. S. MOROZOV, and G. G. PETRZHIK

1960

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. A. TRAPEZNIKOV, A. S. MOROZOV, and G. G. PETRZHIK

DEPENDENCE OF NORMAL AND SHEAR STRESSES ON THE MAGNITUDE OF DEFORMATION DURING THE TRANSITION FROM REST TO STEADY FLOW OF AN ALUMINUM NAPHTHENATE GEL

(Presented by Academician S. I. Volfkovich, 24 III 1960)

Weissenberg showed that, in a variety of colloidal systems and polymer solutions, stresses orthogonal to the streamlines develop under shear ([1]). One of the manifestations of these stresses indicated by Weissenberg is the climbing of non-Newtonian liquids along the wall of the inner cylinder or rod in the gap between two coaxial cylinders, in opposition to centrifugal and gravitational forces. This effect was also studied in ([2]).

Beginning with Weissenberg, who used a rheogoniometer, in many subsequent works of a theoretical and experimental nature ([3]-[7]) the effect of normal stresses in elastic liquids is considered for steady flow of the system, without taking into account the features of the stages of deformation preceding the attainment of steady state. It is assumed that the system obeys the law of a Hookean (neo-Hookean) body up to any deformations and deformation rates (experimentally no less than 100-300 sec^{-1}) attained in steady flow. Thus no assumptions are made about any special significance of the initial and transitional regions from rest to steady flow, characterized by destruction of the structure and by the influence of this factor on the values of the rheological constants. This may be attributed to the fact that, according to the view of Weissenberg and his followers ([5]-[8]), in elastic-viscous non-Newtonian liquids, i.e., in systems that flow at arbitrarily small shear stresses, the viscosity anomaly is associated not with destruction of the structure but is only a consequence of a purely orientational (geometrical) factor, connected with the divergence between the directions of the stress ellipsoid and the ellipsoid of deformation rates ([5]-[7]), which, in turn, is ascribed to the presence of elastic deformation in the liquid. The latter, however, as a rule, is only calculated indirectly from the ratio of normal and tangential stresses or from the angle of orientation, but is not measured by a direct method. However, in Reiner' s opinion ([9]), the existing explanations of the mechanism of the Weissenberg effect are far from definitive.

In the work of our laboratory, special attention was directed precisely to the

Fig. 1

Figure 1: Fig. 1

initial stage of development of deformation and to the transition from the state of rest to steady flow for flowing systems that were called viscoplastic ([10]). In studies carried out earlier only on shear deformations, it was shown that, at deformation rates greater than some critical rate ($\dot{\varepsilon} > \dot{\varepsilon}_k$), many systems begin to behave as a solid body possessing a structural strength limit P_r. It was especially noted that the decrease in viscosity (anomaly) is connected mainly with destruction of the structure. In this connection it is of interest to point out that the attempt recently undertaken by Jobling ([5], [6]) to correct the decrease in viscosity by a correction for the orientation factor, calculated from the normal stresses according to Weissenberg, led only to a partial—and in some cases to a very weak—increase of the recalculated viscosity.

In work ([11]) it was noted that, according to visual observations, the climbing of a gel or polymer solution subjected to shear along the rod of the inner cylinder in an elastoviscometer or elastorelaxometer practically begins and reaches its greatest value only after passing through the structural strength limit P_r, or after the deformation ε_m corresponding to the maximum elastic deformation $\varepsilon_{e\ \max}$, i.e., in a region where the structure of the system is already considerably destroyed. In this connection it was assumed that the maximum value of the normal stress P_{nr} develops only after passing through the shear-strength limit and after considerable destruction of the structure. For direct measurements of the elastic deformation of the system, which is a very important characteristic of it, special methods and instruments were developed ([11], [12]).

Fig. 1

The present work was undertaken for the purpose of quantitatively studying the development of normal stresses in time and as a function of the magnitude of deformation during the continuous transition from the state of rest to steady flow. The object studied was a 2% gel of aluminum naphthenate in vaseline oil, one of those investigated earlier ([13]), aged for 3 years.

For simultaneous measurement of the normal stress P_n and the shear stress P_τ, a rheogoniometric attachment was constructed for an elastoviscometer that had previously been used in the laboratory for studies of shear stresses. A diagram of the attachment is shown in Fig. 1. The attachment is based on a cone-disk combination (1 and 2), whose diameter was 75 mm. The angle of the conical gap was $\alpha = 3^\circ 20'$. The apparatus made it possible to measure simultaneously the vertical displacement of the disk under the action of the normal force F_n and the rotation of the disk under the action of the torque produced by the tangential force F_τ. The dynamometers were two mutually perpendicular, independently operating flat steel springs working in bending (4 and 5). The deflection of the springs was measured by means of two independent capacitive pickups (3 and

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

6) in a resonance circuit, with recording on an EPP-09 self-recording electronic potentiometer or on an MPO-2 loop oscillograph. The springs were calibrated beforehand. The accuracy of estimating the displacement of the disk was not less than 0.00025 mm. The total deflection of the springs did not exceed 0.02 mm. Constancy of the rate of deformation and its control were ensured by the drive of the elastoviscometer, switched on through an electromagnetic starting clutch.

Fig. 2

In Fig. 2 are given the dependences of the tangential and mean normal

stresses on the magnitude of the relative shear deformation ε at different rates of deformation. The magnitude $\varepsilon = \theta / \operatorname{tg} \alpha$ was calculated from the angle $\theta = \Omega t$ traversed by the cone in time t at angular velocity Ω. The shear stress was calculated as $P_\tau = 3M/2\pi R^3$ (P_τ corresponds to P_{12} according to ([5–7])), where M is the torque and R is the radius of the part of the conical gap filled with gel. The average normal stress $P_n = 2F_n/\pi R^2$, which, in accordance with ([5–7]), is the difference of the components of the normal stresses $P_n = P_{11} - P_{22}$, was calculated from F_n, the total vertical force measured by the dynamometer.

Fig. 3

From the values of the steady tangential stress, the viscosity $\eta = P_{\tau s}/\dot{\varepsilon}$ was calculated; as usual, it decreases as $\dot{\varepsilon}$ increases (Fig. 3, 1). For the average normal stress one may formally introduce the equivalent ratio $P_{ns}/\dot{\varepsilon}$, the dependence of which (for two segments of the curves in Fig. 2) on $\dot{\varepsilon}$ is shown by curves 2 (at $\varepsilon = 450$) and 3 (at $\varepsilon = 10\,000$) (the symbol s means that P_n and P_τ are taken for steady flow). In calculating the quantity P_{ns}, a correction for the influence of the inertial force, which reduces the normal force, was introduced; in the data of the curves of Fig. 2 this correction was not introduced, and therefore the terminal portions of the curves after the second maximum at large $\dot{\varepsilon}$ lie lower than for smaller $\dot{\varepsilon}$.

Fig. 4

It is seen from Fig. 2 that the curves for both tangential and normal stresses

Fig. 4

Figure 4: Fig. 4

have two maxima. Earlier, in studies of shear stresses in aluminum naphthenate gels ([10–13]), one maximum of the strength of the structure, arising in the initial stage of deformation, i.e., before the establishment of steady flow, was described; however, in the work of A. A. Trapeznikov and T. G. Shalopalkina in 1955 (unpublished), a second maximum was also observed on the curves of shear stresses at large deformations. The second maximum, which now can be denoted as $P_{\tau 2r}$, was smaller than the first maximum $P_{\tau 1r}$. These data for a strongly aged 2% solution of another specimen than that studied here are presented in Fig. 4. It was assumed that the appearance of the second maximum could be connected with attainment of the rupture deformation ε_r for the cylindrical bottom part of the gel, in accordance with what was indicated in considering the maximum elastic deformation $\varepsilon_{e\,\max}$ ([11]). Measurement in a conical gap excludes the possibility of such an explanation; consequently, the appearance of the second maximum is connected with the presence of special structural changes in the gel.

Comparing the curves of Fig. 2, it should first be noted that the first maximum of the tangential stress $P_{\tau 1r}$ corresponds approximately to $\varepsilon_{\tau 1r} \approx 40$, while the first maximum of the normal stress P_{n1r} lies at $\varepsilon_{n1r} \approx 80$, i.e., the greatest normal stress P_{n1r} corresponds to the aver-

part of the descending branch of the tangential-stress curve. Thus, the greatest normal stress already corresponds to a fairly strong destruction of the structural network of the system.

With further deformation of the system, after some decrease in both stresses under investigation, their increase is again observed. The increase in stresses continues up to $\varepsilon \simeq 1750$, exceeding the rupture deformations indicated above by factors of 40 and 20, respectively. At this deformation the maximum values on the curves of both stresses are observed simultaneously. It is interesting that the established value of the tangential stress $P_{\tau s}$ is approximately equal to its value in the interval between the two maxima $P_{\tau_1 r}$ and $P_{\tau_2 r}$, whereas the magnitude of the established truly stationary normal stress P_{ns} is very small in comparison with the magnitude of the same stress in the interval between the two maxima. Observation of the established flow of the system was continued up to $\varepsilon \simeq 40\,000$.

The experimental data show that at large ε (> 1700) the structure of the system undergoes changes that are reflected little in the tangential stress and strongly affect the normal stress.

It may be assumed that normal stresses are very strongly connected with the "irregularities" or "relief" (interweaving) of the particles, considered in the plane normal to the shear plane. In order to displace one chain relative to another along the shear plane, it is necessary, to some extent, to move apart the planes of the initial arrangement of the particles, i.e., to overcome normal forces. The more curved the particles are and the longer they are, i.e., the greater the elastic deformations of the system, the greater the normal forces that must arise during shear. The second maximum of both tangential and normal stresses may be associated with the destruction of the "remnants" of the structure that formed after the first destruction of the initial network (after the first maximum) and gradually became oriented in the flow. It is possible, of course, that particles with free cohesive forces (for polymers these may be radicals?), which arose during the first destruction of the initial structure, join in new places to create a new structure, the deformation and destruction of which leads to the second maximum. In this case, the constancy of the values $\varepsilon_{\tau_2 r}$ and $\varepsilon_{n_2 r}$ for the different $\dot{\varepsilon}$ used here should be attributed to similar dimensions and identical conditions of orientation of the structural elements. This explanation is preliminary and requires further investigation. It should be noted that the action of normal stresses during shear in elastic-viscous systems is of broad practical importance.

In conclusion, the authors express their deep gratitude to T. G. Shalopalkina for permission to use the data she obtained.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
18 III 1960

REFERENCES

1. K. Weissenberg, Proc. 1-st Intern. Congr. Rheologie, Amsterdam, 1, 1948, p. 29.
2. A. F. H. Ward, P. Lord, 2-nd Intern. Congr. Rheologie, Oxford, 1953, London, 1954, p. 214.
3. M. Mooney, J. Coll. Sci., 6, 96 (1951).
4. N. Pilpel, Trans. Farad. Soc., 50, 1369 (1954).
5. A. Jobling, J. Oil and Colour Chem. Assoc., 38, 739 (1955).
6. A. Jobling, I. E. Roberts, Rheologie, Theory and Applications, Ed. F. R. Eirich, 2, N. Y., 1958, p. 503; J. Polym. Sci., 36, 421, 433 (1959).
7. W. Philippoff, J. Appl. Phys., 27, 984 (1956); W. Philippoff, F. H. Gaskins, J. G. Brodnyan, J. Appl. Phys., 28, 1118 (1957); Trans. Soc. Rheol., 1, 95, 109 (1957).
8. B. Rabinowich, Zs. phys. Chem., A 145, 1 (1929); A 166, 257 (1933); R. Eisenschitz, Koll. Zs., 64, 184 (1933); Zs. phys. Chem., A 158, 78 (1931); W. Philippoff, Viscosität der Kolloide, Dresden, 1942.

9. M. Reiner, Handb. d. Phys., 6, Marburg, 1958, S. 516.

10. A. A. Trapeznikov, V. A. Fedotov, DAN, 81, 1101 (1951); 82, 97 (1952); 95, 595 (1954); A. A. Trapeznikov, T. G. Shalopalkina, Koll. zhurn., 17, 471 (1955).

11. A. A. Trapeznikov, Koll. zhurn., 21, 107 (1959).

12. A. A. Trapeznikov, T. G. Shalopalkina, DAN, 111, 380 (1956).

13. T. G. Shalopalkina, A. A. Trapeznikov, DAN, 118, 994 (1958).

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