THE INFLUENCE OF THE CONCENTRATION OF ALUMINUM NAPHTHENATE OLEOGEL ON THE MAXIMUM LIMITING DEFORMATION AND THE CORRESPONDING STRUCTURAL STRENGTH

1958

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

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THE INFLUENCE OF THE CONCENTRATION OF ALUMINUM NAPHTHENATE OLEOGEL ON THE MAXIMUM LIMITING DEFORMATION AND THE CORRESPONDING STRUCTURAL STRENGTH

(Presented by Academician P. A. Rebinder, February 7, 1958)

For a general understanding of the complex of deformation-strength properties of a colloidal system, and especially for elucidating its highly elastic properties, it is of great importance to study the dependence of the magnitude of the limiting (rupture) deformation ε_r, determined from the maximum P_r of the curve $P(\varepsilon)$ (where P is stress and ε is deformation), on the corresponding shear stress P_r (^{1}). In aluminum naphthenate oleogels, limiting rupture shear deformations are especially clearly expressed, reaching several thousand percent, which makes it possible to regard such systems as similar to superelastic high polymers.

In order to study changes in the physicomechanical parameters that determine the highly elastic properties of the system with gel concentration, the dependence of ε_r on P_r was investigated for 2-20% aluminum naphthenate oleogels in decalin*.

Fig. 1

The curves** $\varepsilon_r(P_r)$ obtained on a complex elastoviscosimeter (some of them are shown in Fig. 1) make it possible to determine, for each oleogel concentration, the value of the maximum limiting deformation ε_{rm}, corresponding to the constancy of ε_r with continuing increase of P_r and indicating the maximum possible elastic deformation of the system as a whole***. From these same curves one can find the values $P_r = P_{r_2}$ corresponding to the onset of attainment of ε_{rm} (the values P_{r_2} in Fig. 1 are indicated by arrows).

* The oleogels were studied on the 20th day after preparation. As a decalin thickener, aluminum naphthenate was used, prepared according to the precipitation recipe at pH 5 with 36% free alkali, as described in work (^{2}).

** A detailed description of the method for determining ε_r and P_r on the complex elastoviscosimeter is given in (^{3}).

*** In some cases, the values of actually obtained elastic deformations ε_e (elastic recovery) may be smaller than ε_{rm} (^{4}).

The values of ε_{rm} and P_{r_2} for different C, determined from the curves $\varepsilon_r(P_r)$, are given in Table 1.

From the data of Table 1 (and Fig. 1) it follows that ε_{rm} decreases with increasing C. This indicates a decrease in elasticity, i.e., in the limiting deformability of the oleogel, as its concentration increases.

The decrease in the elasticity of the system with increasing content of the disperse phase (aluminum naphthenate) in the oleogel can be explained as follows.

Table 1

C, %	ε_{rm}, %	$P_{r_2} \cdot 10^{-3}$, dyne · cm^{-2}	$A_{r_2} \cdot 10^{-4}$, erg · cm^{-3}
2	7600	1.0	3.80
3	5000	3.0	7.50
4	4200	4.5	9.45
6	2660	7.0	9.31
8	2420	11.5	13.91
10	1960	15.0	14.70
15	1030	24.0	12.36
20	540	32.0	8.64

The presence of a small number (at low concentrations of thickener) of local (possibly very labile) bonds, which act as nodes (cross-links) joining the structural network together, does not strongly hinder the deformation of the intermediate portions of the chains enclosed between the nodes. In this case the local bonds are situated so sparsely that large flexible segments of chain molecules fit between them and are capable of giving large reversible deformations. This accounts for the high elasticity of the network at low aluminum naphthenate content in the oleogel (as, for example, in the case of a 4-2% gel concentration, when ε_{rm} reaches values on the order of 4000-7000%).

The longer such intermediate chain segments are, the higher the elasticity of the system should be. With increasing gel concentration, the formation of additional cross-links between chains leads, simultaneously with an increase in the total number of bonds per unit volume of the system, to a decrease in the length of the intermediate chain segment between nodes. This is what causes the decrease in the elasticity of the system, which may be judged from the greatest rupture deformation. An increase in the number of cross-links in such a colloidal network structure is equivalent to "spatial polymerization." The latter, of course, does not exclude the possibility of simultaneous "linear polymerization," i.e., an increase in particle length as the gel concentration rises. However, such elongation of particles in the region of high gel concentrations probably plays a subordinate role.

A decrease in the elasticity of a colloidal system with increasing concentration has also been noted in studies of the elastic-viscous properties of calcium stearate gels in oil (^{5}). In this case, as a characteristic of the elasticity of the system, a quantity was used expressing the ratio of the shear moduli

$$\lambda = \frac{E_1}{E_1 + E_2},$$

measured at certain small shear stresses. This quantity λ, however, does not reflect the greatest (rupture) highly elastic deformations of the structural network, which manifest themselves especially clearly in the liquid-like systems studied by us. Systems with calcium stearate are solid-plastic, similar to highly concentrated consistent greases, possessing comparatively very small limiting shear deformations (^{6}).

Figure 2 shows the dependence of P_{r_2} on C, which is expressed quite well by a straight line. This means that the strength $P_r = P_{r_2}$, at which the limiting rupture deformation ε_r reaches (with increasing deformation rate) its greatest value, equal to ε_{rm}, increases in proportion to the concentration of the system, being as it were a linear function of the number of local (cross-) links arising between individual chains. The intersection of the straight line $P_{r_2}(C)$ (Fig. 2) with the abscissa axis, in accordance with the equation

$$P_{r_2} = K(C - C_0) \tag{1}$$

gives the value $C = C_0$ (equal in the present case to $\approx 1.43\%$), at which P_{r_2} becomes equal to zero and below which, i.e., at $C < C_0$, the system loses the structural character determining P_{r_2}. This may be associated with two causes: either, at such low concentrations, the high-polymer, chain-like macromolecules of aluminum naphthenate are so far apart

Fig. 2
Fig. 2

Fig. 3
Fig. 3

from one another that they cannot be connected into a single structural network, or dissociation of the polymer particles takes place, leading to a decrease in their "molecular" weight.

Figure 3a shows the curve of the dependence of the value of the maximum limiting deformation ε_{rm} on the concentration of the oleogel. In Fig. 3b the same dependence is presented in logarithmic coordinates. From the slope angle of the straight line in Fig. 3b, equal to 45°, it follows that the dependence of ε_{rm} on C corresponds to a hyperbola of the first degree and to the equation:

$$\varepsilon_{rm} C = B, \tag{2}$$

where B is a constant having physical meaning at $C \geq 1.43\%$.

From the values P_{r_2} and ε_{rm} one can approximately calculate the work of deformation of the gel $A_{r_2} = \frac{1}{2} P_{r_2} \varepsilon_{rm}$, assuming conditionally that the increase of P along the deformation curve $P(\varepsilon)$ is linear up to $P = P_r = P_{r_2}$. In this case, from relations (1) and (2) we find

$$A_{r_2} = \tfrac{1}{2} P_{r_2} \varepsilon_{rm} = q \left(1 - \frac{C_0}{C}\right), \tag{3}$$

where $q = \frac{1}{2} BK = 14.35 \cdot 10^4\ \mathrm{erg} \cdot \mathrm{cm}^{-3}$ and $C_0 = 1.43\%$.

Fig. 4

Fig. 4

The curve corresponding to equation (3) is shown by the solid line in Fig. 4. The experimental values of A_{r_2} given in Table 1 are marked there by points. As is seen from the curve, the value of this limiting work of deformation A_{r_2}, corresponding to $P_r = P_{r_2}$, rises rapidly at low gel concentrations and tends practically to a constant value at higher $C \simeq$ 6–8%. The observed scatter of the experimental points is connected mainly with fluctuations in the values of ε_{rm}, which do not fit the hyperbola quite exactly (Fig. 3).

The relative constancy of the work of destruction of the structure of a unit volume of gel A_{r_2} when the gel concentration is varied in the region of higher C shows that the increase in the number of bonds (nodes, entanglements) in the gel network, which requires an increase in stress for their destruction, is compensated to a certain extent by a decrease in the limiting rupture deformation of the system.

It should be noted that, since with an increase in the rate of defor-

in the region $\dot{\varepsilon} > \dot{\varepsilon}_{r_2}$, the value P_r continues to increase while ε_{rm} remains constant; the work of rupture $A_r = \frac{1}{2} P_r \varepsilon_{rm}$ will also increase. Therefore, the quantities A_{r_2} calculated above are not the largest values of the work of rupture of the system, but only certain limiting values corresponding to the onset of attainment of the value ε_{rm}.

The value ε_{rm}, found by extrapolation from equation (2) to $C \approx 100\%$, i.e., for pure aluminum naphthenate, is $\sim 160\%$. This shows that under shear such a system (“dry”soap) can undergo a deformation not exceeding one-and-a-half-fold and, consequently, it almost completely loses its high elasticity in comparison with its dissolved (gel-like) state. (Aluminum naphthenate in its initial state outwardly resembles a rubbery powder, for which such a small deformability is quite probable.)

In the systems considered, the structure formed by the aluminum soap may arise through the formation of coordination-type bonds between oxygen atoms of one molecule and aluminum atoms of another molecule, through hydrogen bonds between hydroxyl groups or between the hydroxyl and carboxyl groups of different molecules, and between hydrating water molecules. Bonds of the types listed have been taken into account in gels of aluminum soaps by many investigators ([2,3,7–12]), and recently some of them have also been confirmed by more direct methods ([13]).

In these works, gels of aluminum soaps are regarded as high-polymeric compounds. Indeed, all the high-elastic properties we have studied indicate a very close similarity between gel-like solutions of aluminum naphthenate and typical high polymers in solution or in the initial state—without solvent. The difference, however, is probably the easier weakening of the interaction between naphthenate particles than in true polymers, under the influence of additions of polar substances, indicating the important role of weak associated bonds in naphthenates.

Received
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CITED LITERATURE

1. A. A. Trapeznikov, V. A. Fedotova, *DAN*, **81**, 1101 (1951); **82**, 97 (1952).
2. A. A. Trapeznikov, G. V. Belugina, *DAN*, **87**, 635, 825 (1952); **94**, 97 (1954).
3. A. A. Trapeznikov, V. A. Fedotova, *Proc. 3rd All-Union Conf. on Colloid Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1955.
4. A. A. Trapeznikov, *Koll. zhurn.*, **20**, No. 4 (1958).
5. E. E. Salova, P. A. Rebinder, *Koll. zhurn.*, **10**, 223 (1948); E. E. Salova, P. A. Rebinder, L. N. Sennorikina, *Koll. zhurn.*, **13**, 461 (1951).
6. A. A. Trapeznikov, S. Kh. Zakieva, *DAN*, **73**, 519 (1950); *Proc. 2nd All-Union Conf. on Colloid Chemistry*, Kiev, 1952; A. A. Trapeznikov, E. M. Shlosberg, *Collection: New Methods of Physicochemical Investigation of Surface Phenomena*, vol. 1, 1950, p. 39;
7. V. R. Gray, *Trans. Farad. Soc.*, **42B**, 196 (1946); V. R. Gray, A. E.

Alexander, *J. Phys. and Coll. Chem.*, **53**, 9, 23 (1949); A. E. Alexander, V. R. Gray, *Proc. Roy. Soc.*, A **200**, 162 (1950).

8. A. A. Trapeznikov, E. M. Shlosberg, *Koll. zhurn.*, **8**, 421 (1946).

9. E. P. Marion, A. W. Thomas, *J. Coll. Sci.*, **1**, 221 (1946).

10. T. S. McRoberts, J. H. Schulman, *Nature*, **162**, 101 (1948); *Proc. Roy. Soc.*, A **200**, 136 (1950).

11. H. Sheffer, *Canad. J. Res.*, **26**, 481 (1948).

12. C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949).

13. W. W. Harple, S. E. Wiberley, W. H. Bauer, *Anal. Chem.*, **24**, 635 (1952); F. A. Scott, J. Goldenson, S. E. Wiberley, W. H. Bauer, *J. Phys. Chem.*, **58**, 61 (1954).

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