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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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STUDY OF THE GEL-FORMING ABILITY OF ALUMINUM OLEATES IN BENZENE

Aluminum soaps of fatty acids of the general formula $Al(OH)_n(OOCR)_m$, where $n + m = 3$, are known to be thickeners of various hydrocarbon liquids. A large number of works have been devoted to the study of the structure and properties of such soaps, in which it has been shown that the presence of hydroxyl groups in the molecule of an aluminum soap with a given hydrocarbon radical R determines its thickening ability (1). The greatest thickening ability is possessed by disubstituted soaps $Al(OH)(OOCR)_2$ (where $n = 1.0$), which is apparently associated with the association of individual molecules into chains by means of hydroxyl groups, with the subsequent formation, through van der Waals forces and hydrogen bonds, of a disordered network—the structure of the gel. The insufficient thickening ability of monosubstituted soaps $Al(OH)_2(OOCR)$, where $n = 2.0$, may be explained by the occurrence of intramolecular hydroxyl bonds. The possibility of the existence of trisubstituted soaps $Al(OOCR)_3$ is considered unlikely (the ease of their hydrolysis—instability associated with the steric factor, which hinders the arrangement of three organic radicals around one aluminum atom, etc.) (1,2).

Fig. 1

The structure-forming properties of Al soaps depend to a large extent on the molecular weight and the nature of the radical (1,3). Thus, in the formation of Al soaps of naphthenic acids, whose hydrocarbon radicals have a complex cyclic structure, the soaps precipitated at an excess of free alkali of 75% (relative to the bound alkali), i.e., at $n = 1.17$ (4), possessed optimal thickening properties. This proved to be true for naphthenic acids of various average molecular weights from 214 to 250, although the thickening ability of the soaps increases sharply with decreasing molecular weight in this interval (5).

Aluminum soaps of unsaturated fatty acids have not received sufficient attention in the literature. It is of interest to determine the influence of the double bond in the fatty-acid radical on the structure-forming ability of Al soaps and

Fig. 2

Figure 2: Fig. 2

to establish which soap composition of oleic acid corresponds to the greatest viscosity and stability of oleogels.

Preparation of aluminum oleates and their gels in benzene

Al soaps of oleic acid were prepared by us by the usual method of double exchange decomposition (by adding a solution

$Al_2(SO_4)_3$ to an alkaline solution of the sodium soap of oleic acid containing a definite amount of free alkali). Precipitation was carried out at 70°; the pH of the medium at the end of precipitation was 5.0–4.5.

These soap gels were prepared by dissolving (with vigorous shaking) a weighed portion of the soap in cryoscopically pure benzene at room temperature. The process of dissolving the soap and of "maturation" of the gel proceeds much more slowly than in the case of aluminum naphthenates; therefore the first viscosity measurement was made 3-5 days after the gel had been prepared. It was found that aluminum oleates have a considerably lower thickening capacity than aluminum naphthenates prepared under analogous conditions and according to the same recipe. Aluminum oleate gels are elastic-brittle, in contrast to aluminum naphthenate gels of the same concentrations, which have high limiting high-elastic deformation values (^{6}).

Effect of the composition of aluminum oleates on the properties of their oleogels. Al soaps of oleic acid were precipitated with an excess of alkali from 25 to 200%, and from them 8% gels were prepared in cryoscopically pure benzene.

The viscosity of the gels was characterized, as in our earlier experiments, by their greatest (limiting) viscosity η of the practically undisturbed structure. The invariance of this viscosity—its independence of the flow regime under the measurement conditions (at low shear rates)—was specially checked by us.

Fig. 2

Figure 1 shows the dependence of the viscosity of 8% gels on the content of free alkali during precipitation of the soap for different gel storage times (curve 1—after 5 days, 2—after 7 days, 3—after 30-32 days). The viscosity reaches a maximum at a 50% excess of alkali ($n = 1.0$), then decreases and rises again, giving a second, smaller maximum at 150% ($n = 1.7$). This is apparently connected with an increase in the hydrophilicity (oleophobicity) of the soaps. Soap precipitated with a 200% excess of alkali, i.e., corresponding in composition to a monosubstituted soap ($n = 2.0$), already practically does not dissolve in benzene even on heating; on standing, individual soap particles swell and become enveloped

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

by gel, but no overall structure formation occurs in the volume. Consequently, in aluminum oleates, as in the case of saturated fatty acids, the disubstituted soaps ($n = 1.0$) possess the greatest thickening capacity.

Observations of the aging of these oleogels (Fig. 2*) showed that their stability is low—the viscosity decreases strongly with time. This is naturally associated with chemical instability due to the presence of a double bond in the hydrocarbon radical, which, on the other hand, itself promotes dissolution and subsequent thickening. However, additions (1.5%) to such a soap of a typical antioxidant such as α-naphthol ([7]),

* The numbers by the curves indicate the excess of NaOH, in percent, during precipitation of the soap.

as we have shown, does not change the course of the spontaneous decrease in the viscosity of the gels, i.e., their aging. The dependences $\lg\eta$—τ are sufficiently close to straight lines and have practically the same slope, except in the case of a 100% excess of alkali. Consequently, the composition of the soap affects mainly the level of viscosity of the gels, without significantly changing their stability. In contrast to this, in aluminum naphthenate gels the composition of the soap has a strong influence not only on the level of viscosity of the gels, but also on the course of their aging (Fig. 2, 6% soap in benzene, dotted curves) ([4]).

Fig. 3

Fig. 4

Effect of the concentration of aluminum oleate on the properties of its oleogels. Gels with a soap content of 6-12% were prepared. Fig. 3a* shows the increase in the viscosity of the oleogels with increasing concentration of soap in them (the soap was precipitated with a 75% excess of alkali, $n = 1.17$). It was found that, over fairly wide intervals of soap concentration, a simple general dependence holds:

$$\lg\eta = K + a\lg C, \qquad (1)$$

where the constants $K(\tau) = \lg\eta_{c=1}(\tau)$ and $a(\tau)$ prove to depend on the aging time of the gel:

$$a = a_0 + b\tau, \qquad (2)$$

$$K = K_0 - \alpha\tau; \tag{3}$$

$K_0 = K_{\tau=0}$ and $a_0 = a_{\tau=0}$ are constants that no longer depend either on C or on τ. From (1), (2), and (3) it follows that

$$\lg\eta = A - B\tau, \tag{4}$$

where

$$A = \lg\eta_{\tau=0} = K_0 + a_0 \lg C, \tag{5}$$

$$B = \alpha - b\lg C, \tag{6}$$

* The numbers by the curves indicate the storage time of the gels in days.

$b = da/d\tau$ is not only constant in time (linearity of $a(\tau)$ (2)), but also does not depend on the excess of alkali in the preparation of the soap in the range 75–150% (Fig. 3b). These linear dependences are well justified over a wide interval: τ from 3 to 70 days, η from $4.5 \cdot 10^3$ to 10, and C from 6 and 8% to 12%. As η decreases with time, increasing the concentration of the structure-forming agent becomes increasingly important for maintaining a high level of viscosity.

Increasing the concentration of the soap (the numbers beside the corresponding curves in Fig. 4), precipitated with a 75% excess of alkali, reduces the rate of the gel-aging process; however, even a 12% gel is not stable on storage for more than two weeks, appreciably reducing its viscosity. In contrast, already 4% gels of aluminum naphthenates, prepared under analogous conditions, remain stable for a long time ([4,8]).

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REFERENCES

[1] T. S. McRoberts, J. H. Schulman, *Nature*, **162**, 101 (1948); *Proc. Roy. Soc.*, **200 A**, 135 (1950); A. E. Alexander, V. R. Gray, *J. Phys. Coll. Chem.*, **53**, No. 9, 23 (1949); *Proc. Roy. Soc.*, **200 A**, 162 (1950).
[2] C. G. McGee, *J. Am. Chem. Soc.*, **71**, 278 (1949).
[3] G. A. Parry et al., *Proc. Roy. Soc.*, **200 A**, 148 (1950); F. J. Licata, *J. Am. Oil Chemists' Soc.*, **31**, No. 5, 204 (1954).
[4] G. V. Belugina, A. A. Trapeznikov, *Koll. zhurn.*, **20**, No. 1, 4 (1958).
[5] A. A. Trapeznikov, G. V. Belugina, F. M. Rzhavskaya, *Koll. zhurn.*, **20**, No. 2,

254 (1958).
[6] V. A. Fedotova, A. A. Trapeznikov, *DAN*, **120**, No. 4, 841 (1958).
[7] W. H. C. Rueggeberg, *J. Phys. Coll. Chem.*, **52**, No. 9, 1444 (1948).
[8] G. V. Belugina, S. Kh. Zakieva, P. A. Rebinder, A. B. Taubman, *DAN*, **126**, No. 2, 318 (1959).

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