Visco-elastic Behaviors of Aluminum Soap-Hydrocarbon Systems. II. Aluminum Soaps in Nujol

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In the previous paper[1], dynamic behaviors of the aluminum stearate-nujol system were studied, and typical visco-elastic properties of the system were found. In this paper, visco-elastic behaviors of aluminum soaps from various fatty acids and aluminum stearates of different compositions dispersed in nujol were studied.

Experimental

Materials.—Aluminum soaps from various parent fatty acids were prepared from purified fatty acids. The purity of the fatty acids and method of preparation were described in the previous paper[2]. Results of aluminum analysis of the soaps are shown in Table I. Aluminum stearates of different compositions were prepared, varying the amount of excess of sodium hydroxide during the precipitation

1) S. Shiba, This Bulletin, 34, 194 (1961).
2) S. Shiba, ibid., 33, 1563 (1960).

TABLE I. COMPOSITIONS OF ALUMINUM SOAPS

Soap	No. of C atoms in acid	Al wt. % (analysed)	Mol. acid per mol. Al
Palmitate	16	5.80	1.62
Myristate	14	5.96	1.77
Laurate	12	6.38	1.87
Caprate	10	7.36	1.87
Caprylate	8	9.17	1.72

TABLE II. COMPOSITIONS OF ALUMINUM STEARATES

Excess NaOH %	Al wt. % (analysed)	Mol. acid per mol. Al
10	4.09	2.18
18	4.40	2.01
25	4.68	1.89
35	5.04	1.72
50	5.46	1.56
75	5.96	1.41

of the soaps. Compositions of the aluminum stearates are summarized in Table II.

The vehicle was the same nujol as in the previous work. Infrared absorption measurements showed no free fatty acid for the soaps from various fatty acids, whereas the spectra of aluminum stearates containing more than 2 acid molecules per aluminum showed the presence of free fatty acids.

Apparatus and Procedure. — Forced oscillation rheometer and the experimental procedure are the same as in the previous work[1].

Results and Discussion

Various aluminum soaps dispersed in nujol show thickening properties to some extent, and the system becomes an elastic gel at a high concentration or a viscous sol at lower concentrations. Gelling characteristics of the soaps were examined for varying fatty acids and soap compositions.

Frequency Dependence. — The frequency dependency of aluminum palmitate, caprate and caprylate in nujol is shown in Fig. 1. A gel

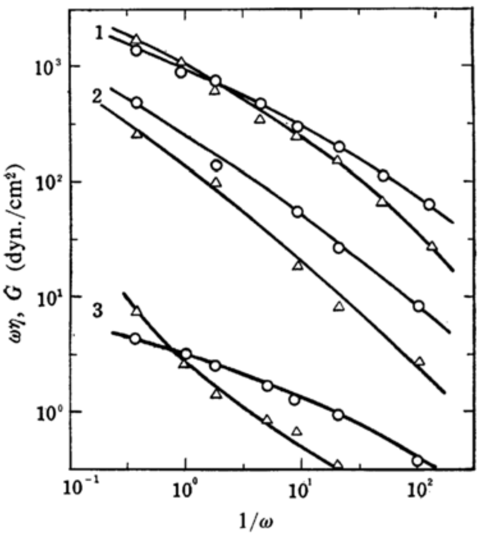

Fig. 1. Frequency dependence of dynamic loss (○) and shear modulus (△), aluminum soaps in nujol at 25°C.
1. Palmitate 1 wt. % 2. Caprate 2 wt. %
3. Caprylate 3 wt. %

containing 1 wt. % of palmitate shows frequency dispersion similar to stearate which indicates wedge type relaxation spectrum. A gel of aluminum caprate (2 wt. %) shows a dispersion which resembles that of palmitate as shown in Fig. 1, despite the higher concentration of the soap. Aluminum myristate and laurate show behaviors similar to palmitate; caprylate scarcely shows the elastic properties. That is to say, the visco-elastic properties of the systems decrease suddenly when the length of the fatty acid molecule decreases below ten carbon atoms.

Concentration Dependence. — The concentration dependences of visco-elastic properties for the systems are shown in Figs. 2 and 3.

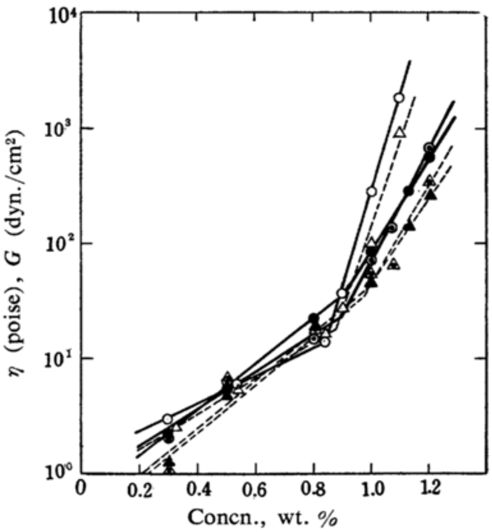

Fig. 2. Concentration dependence of dynamic viscosity (—○—) and shear modulus (--△--), 25°C period T=12 sec.
○ Palmitate ● Myristate ⊙ Laurate

Palmitate, myristate and laurate show curves similar to stearate, and each curve consists of two straight lines in the concentration range above and below the break point. The break points correspond to the critical concentrations necessary to form gels, and the two straight lines represent the concentration dependence of visco-elasticity of gels and sols respectively. These curves are expressed by empirical formulae;

$$\log \eta_s = a_s + b_s c, \qquad \log \eta_g = a_g + b_g c \qquad (1)$$

$$\log G_s = a_s' + b_s' c, \qquad \log G_g = a_g' + b_g' c \qquad (2)$$

where η and G are dynamic viscosity (poise) and shear modulus (dyn./cm^2), the subscripts s and g mean that the values are referred to the sol and gel states. Changes in critical concentration and constant b_g with soaps are summarized in Table III. The two values represent the gelling capacity of the soaps and the concentration dependence of the rheological properties of the resulting gel. The fatty acid of shorter hydrocarbon chain length gives an indistinct and higher critical concentration and a lower value of b_g. When the mole concentrations of the systems are considered, the difference will be larger. This tendency indicates the superiority of soaps from higher fatty acids as thickener. The results for laurate support those of Weber and Bauer[3], who found the appearance of pronounced elastic properties

TABLE III. CRITICAL CONCENTRATION AND CONSTANT b_g

Soap	Crit. conc. wt. %	b_g 1/wt. %
Stearate*	0.81	10.2
Palmitate	0.85	8.3
Myristate	0.92	4.1
Laurate	0.91	4.9
Caprate	2.0	1.4
Caprylate	—	—

* Obtained from Ref. 1.

in the gels as the concentration of soap increased over 1 wt. %.

Caprate and caprylate show a somewhat different type of concentration dependence, as shown in Fig. 3. Caprate has a critical concentration near 2 wt. % and visco-elasticity

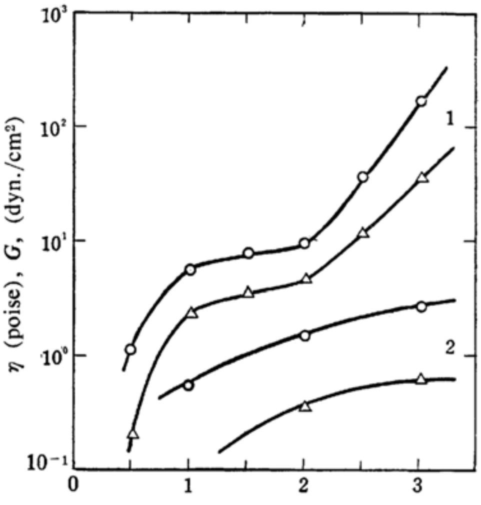

Fig. 3. Concentration dependence of dynamic viscosity (○) and shear modulus (△), 25°C period $T=12$ sec.

1. Caprate 2. Caprylate

decreases rapidly at a concentration below 1 wt. %. Caprylate shows neither conspicuous thickening effect nor gelling property. Thus, the aluminum soaps from fatty acid lower than capric acid, show remarkably different rheological behaviors.

A mixture of the stearate and palmitate shows intermediate concentration dependence of both soaps.

The experiments were carried out under definite conditions, however results similar to the case of stearate[1] are expected under various conditions, due to their relatively similar dependence on frequency and temperature.

3) N. Weber and W. H. Bauer, *J. Phys. Chem.*, **60**, 270 (1956).

Temperature Dependence.—Changes in visco-elastic properties of aluminum soap-nujol systems with temperature are shown in Fig. 4. The soaps examined do not show linear relation as described by the Andrade formula. In this temperature region, distinct transition was not

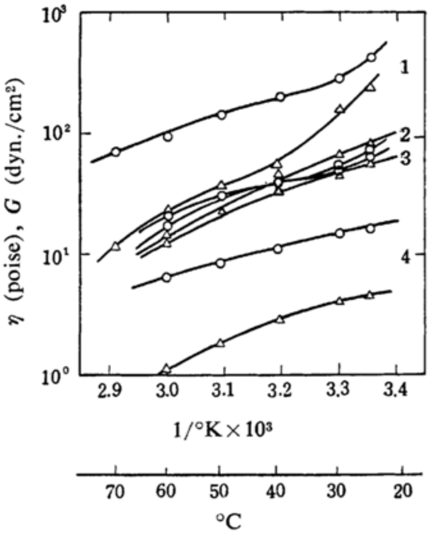

Fig. 4. Temperature dependence of dynamic viscosity (○) and shear modulus (△), aluminum soaps in nujol 1 wt. %, $T=12$ sec.

1. Palmitate 2. Myristate 3. Laurate
4. Caprate

observed; however, the transition from dispersion to solution found for stearate may exist in these cases. The curves show a convex type against temperature. This suggests that gradual transition or structural change occurs over a wide range of temperatures resulting in decrease in rheological properties. Therefore, the apparent activation energies of flow calculated from gradients of the curves are somewhat larger than that of the vehicle, nujol.

Effect of Soap Composition. — Aluminum stearate of different compositions that is, the soaps in which a different number of acids combined with the aluminum atom, in nujol were examined. Comparison of the results for 1 wt. % soaps in nujol is made in Fig. 5. An extraordinary difference was found; however, when the conspicuous concentration dependence of the systems as shown in Fig. 2 is considered, it is clear that the results expressed by single point observations on visco-elasticity do not reveal the full aspects of the properties of the soaps. The critical concentration was observed by a simple method: soap solutions of various concentrations were cooled in test tubes and kept still overnight; when the specimen did not flow in a minute after the

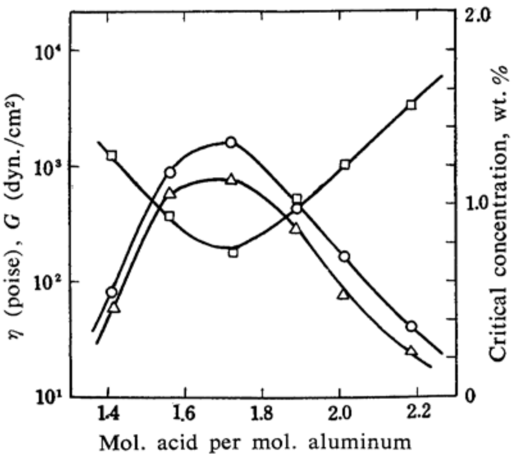

Fig. 5. Visco-elastic properties and critical concentrations of aluminum stearates in nujol at 25°C.
○ η, △ G for 1 wt. % soaps in nujol, T=12 sec., □ critical concentration.

tube was laid down, the specimen was judged to be a gel. The results are also shown in Fig. 5, which shows the maximum effects as thickener near 1.7 mol. acid per aluminum.

Rheological Structures in the Systems.—Visco-elastic behaviors of the systems show evidence of strong rheological structures in the systems. The system is essentially a colloidal dispersion of elongated aluminum soap crystallites in hydrocarbon media as ascertained by electron microscope observation[4]. The system containing soaps in more than the critical concentration exhibits typical visco-elastic properties of gels indicating the network structures of soap crystallites by secondary interactions. At lower concentrations the network is incomplete, resulting in a sol with fluidity. At elevated temperatures, e. g. above 80°C, the soaps disperse homogeneously to a transparent solution. Transition from dispersion to solution is expected from conspicuous change in rheological properties.

Static flow properties of the system under constant shear were discussed elsewhere[2]. Network structures suffer a breakdown by shear and result in relatively high fluidity in that case. In this experiment, extraordinarily high values of visco-elasticity were obtained, since the specimen was treated so as not to be affected by shear. The effects of weak secondary interactions which undergo breakdown are recognized as the difference between the two results.

4) D. Evans and J. B. Matthews, *J. Colloid Sci.*, **9**, 60 (1954).

Summary

Dynamic visco-elastic behaviors of aluminum soaps from various fatty acids and aluminum stearates of different compositions in nujol were studied, using a forced oscillation rheometer. The systems behave always as typical visco-elastic bodies in a wide range of concentrations and temperatures. Aluminum palmitate, myristate, and laurate show properties similar to stearate, whereas caprate and caprylate show less effects on rheological properties. Optimum composition of aluminum stearate as thickener was obtained. Rheological structures in the systems were discussed and comparison of the results by static and dynamic measurements was made.

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