Visco-elastic Behaviors of Aluminum Soap-Hydrocarbon Systems.
I. Aluminum Stearate in Nujol

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Aluminum soaps dispersed in hydrocarbon oils exhibit many interesting flow properties. Gelling characteristics of aluminum soaps and flow properties of aluminum soap-hydrocarbon systems have been studied by many authors1-3).

Flow properties have been studied usually for viscous or plastic properties under static conditions. The conception of "elastic fluid" for these systems was adopted first by Goldberg and Sandvik4), who studied visco-elastic properties (dynamic viscosity and shear modulus) of aluminum soaps gelled in varsol, and found breakdown under steady shear at audio frequency. Garner, Nissan and Wood5), studying elasto-viscous properties of aluminum stearate in petrol, found the correlation of free energy with the mechanical shearing of the system. Weber and Bauer6), studying flow properties of aluminum dilaurate-toluene gels, found from the initial elastic axial extension in a capillary that pronounced elastic properties appear abruptly in the gels as the concentration of soap increases, and a concentration of 1% by weight of aluminum dilaurate in toluene is reached.

In the preceding paper7), flow properties of aluminum soaps in nujol and time effects of flow under shear were studied in static conditions. In the present paper, dynamic visco-elastic behaviors of aluminum stearate dispersed in nujol were studied in a region of low frequency, rangining from 10^0 to 10^{-3} cycles/sec. to examine the correlation of the rheological properties and dispersed states of the soaps.

Experimental

Materials. — Aluminum stearate was prepared from purified stearic acid by a metathetic process as described in the previous paper7). Stearic acid, found: m. p., 69.5°C; neutralization equivalent, 281.9. Analysis of the soap showed that the ratio of moles of acid per mole of aluminum was 1.72. Nujol, which was a paraffin-rich saturated hydrocarbon, was used as a vehicle. Physical constants were: $d_4^{25}=0.8429$; $\eta_{25}=0.217$ poise; $n_D^{20}=1.4672$. The purity of the materials was checked by infrared absorption measurements.

Apparatus. — A top-drive concentric cylinder rheometer, essentially the same as the apparatus designed by Nakagawa8), was used. The outer cylinder was fixed in a thermostat; the inner cylinder was suspended coaxially on a torsion wire. The specimen was placed in the annular space between the two cylinders, and a sinusoidal torsional oscillation was applied at the top of the torsion wire. The oscillation of the inner cylinder was detected by a small mirror attached to the inner cylinder, and the oscillation was combined rectangularly with the driving oscillation optically. The resulting Lissajous' figure, which indicates the phase angle and amplitude ratio of the oscillations, was recorded on an oscillographic paper and analysed for visco-elasticity by an approximate method neglecting the inertia of the specimen. Details of the apparatus and analysis were reported elsewhere9).

Procedure.—Aluminum stearate was added to the weighed portions of nujol and the mixture was heated at 110∼120°C with stirring for 15 min. The resulting isotropic solution was cooled and kept in a desiccator over phosphorus pentoxide. The specimen thus prepared was aged more than 24 hr. at room temperature. Measurements were carried out under the following conditions:

Temperature; 15∼100°C.
Period of oscillation; 2∼1,000 sec.
Maximum shear strain; 0.01∼0.3.
Soap concentration; up to 1 wt. %.

Experiments were performed avoiding effects of humidity as far as possible.

Results and Discussion

The systems both in gel and sol states behave always as visco-elastic bodies. A relatively dilute system (sol) shows linear visco-elastic behaviors, whereas a more concentrated system (gel) shows non-linear behaviors as seen in the case of static measurements7). In this experiment, the systems were treated as linear visco-elastic bodies, because the shear strain was

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1) V. R. Gray and A. E. Alexander, *J. Phys. & Colloid Chem.*, **53**, 9 (1949).

2) H. Sheffer, *Can. J. Research*, **B-26**, 481 (1948).

3) E. K. Rideal et al., *Proc. Roy. Soc.*, **A200**, 135 (1950).

4) H. Goldberg and O. Sandvik, *Anal. Chem.*, **19**, 123 (1947).

5) F. H. Garner, A. H. Nissan and G. F. Wood, *Phil. Trans. Roy. Soc.*, **A243**, 37 (1950).

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

7) S. Shiba, This Bulletin, **33**, 1563 (1960).

8) T. Nakagawa and M. Senō, This Bulletin, **29**, 471 (1956).

9) S. Shiba, *Railway Technical Research Report*, **No. 112** (Feb. 1960).

small and approximation by linear behaviors was possible.

Aging.—It is necessary to examine the effect of aging in order to get reproducible results. Changes in dynamic viscosity η and shear modulus G with time are shown in Fig. 1.

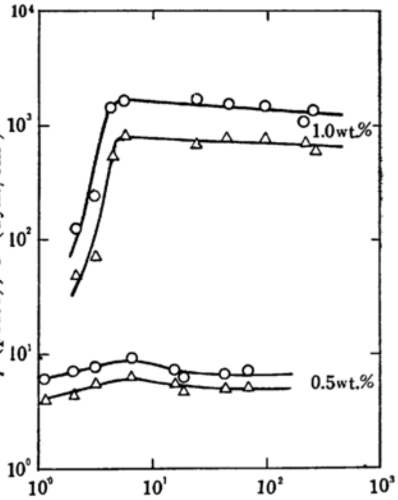

Fig. 1. Change in dynamic viscosity (○) and modulus (△) with time. 25°C, period T=12 sec.

Rapid increase in dynamic properties was found in the first stage of aging, then the properties approach constant values after they reach maximum values 4∼6 hr. after preparation of the specimen. This result supports the results obtained by viscosity and flow birefringence measurements for benzene and nujol solutions of aluminum soaps[7,10]. However, the change in the properties of a gel was extraordinarily great compared with other cases. This fact indicates that the properties of the system which has not been disturbed by shear were measured in this experiment; whereas in the former reports, a state in which the weak structures formed by aging in the system had been broken, was measured.

Amplitude Dependence.—Effects of amplitude of oscillation which are a measure of non-linear behavior, were examined changing the amplitude of the oscillation given at the top of the torsion wire. Results are shown in Fig. 2, where $\gamma_{\max}$ is the maximum shear strain at the wall of the internal cylinder expressed as follows;

$$\gamma_{\max}=\left[\frac{2Ar_e^2r_i^2}{(r_e^2-r_i^2)r^2}\right]_{r=r_i}=\frac{2Ar_e^2}{r_e^2-r_i^2} \qquad (1)$$

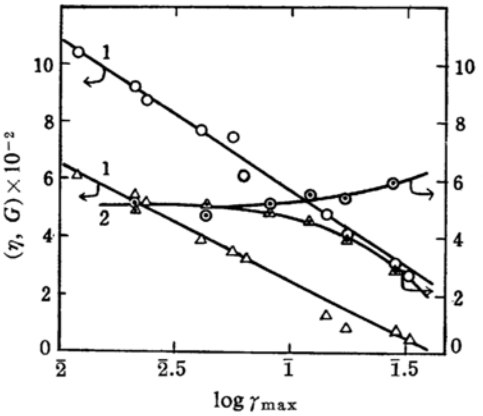

Fig. 2. Amplitude dependence of dynamic viscosity (○) and shear modulus (△), 25°C, period T=12 sec, 1. 1.0 wt. %, 2. 0.5 wt. %.

A is the amplitude of the oscillation of the internal cylinder; r_i and r_e are the radii of internal and external cylinders, respectively. The 1 wt. % gel shows marked amplitude dependence; for the 0.5 wt. % sol dependence is found for large values of γ, but is negligible for usual measurements carried out in the region of γ up to 0.1.

As was found from static measurements of viscosity[7], the aluminum soap-hydrocarbon gels undergo shear breakdown. Accordingly, amplitude dependence may be ascribed not only to the non-linearity but also to the shear breakdown of the rheological structures. In the first stage of flow, it requires a certain amount of work to begin deformation against the network structures in the gel, and this work results in the amplitude effect in this experiment. It is not clear, however, whether the effect is due completely to shear strain or to the rate of shear; because the maximum rate of shear changes proportionally to shear strain when other conditions are equal.

Because of this dependence, a series of experiments should be carried out under constant shear strain and shear rate, but the apparatus is not suitable for this purpose. The amplitude was kept as small and constant as possible to avoid these effects.

Frequency Dependence.—Frequency dependence of the dynamic rheological properties of the system was examined under various conditions. Fig. 3 shows the shear modulus, dynamic loss, and relaxation spectra of a gel containing 1 wt. % of soap in nujol. The spectra were obtained from shear modulus (E') and dynamic loss (E'') by the approximation method[11],

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[10] J. W. McBain and E. B. Working, *J. Phys. & Colloid Chem.*, **51**, 974 (1947).

[11] F. Schwarzl, "Proceedings of the Second International Congress on Rheology" (Edited by V. G. W. Harrison), Butterworths Sci. Pub., London (1954), p. 197.

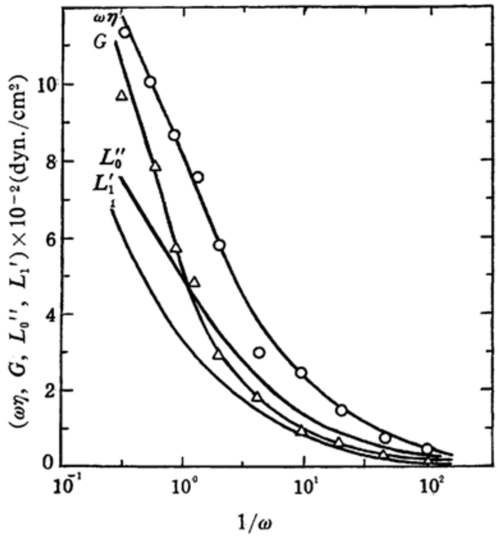

Fig. 3. Frequency dispersion of visco-elasticity and relaxation spectra, 25°C, 1.0 wt%.

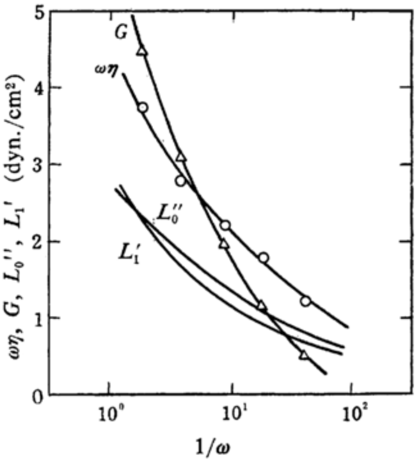

Fig. 4. Frequeny dispersion of visco-elasticity and relaxation spectra, 25°C, 0.5 wt. %.

$$L(t) \simeq L_1'(t) = [\mathrm{d}E'(\omega)/\mathrm{d}\log\omega]_{\omega=1/t} \qquad (2)$$

$$L(t) \simeq L_0''(t) = (2/\pi)\,[E''(\omega)]_{\omega=1/t} \qquad (3)$$

In these formulae L without index is the exact spectrum, whereas L with index indicates an approximation to the spectrum. The system shows typical visco-elastic properties. Curves of visco-elasticity show marked dispersion; the dynamic shear modulus and dynamic loss increase conspicuously with the increase of frequency. Relaxation spectra obtained from the two approximation methods show similar results. The spectra show a wedge type similar to the spectra found for polyisobutylene. This indicates that the gel resembles the polymer solution or gels in dynamic properties, accordingly the dispersed state of the soap crystallites as well. Fig. 4 shows the dispersion of a sol containing 0.5 wt. % of soap in nujol; similar results are observed in this case, although the visco-elasticity is far smaller than in the case of gel.

Frequency dependence at various temperatures is shown in Figs. 5 and 6. At each temperature, similar dispersion is found. It is possible to express these data by a single curve by the method of reduced variables[12]. The reduced curves for the dynamic shear modulus and dynamic loss are shown in Fig. 7. Good coincidence was found except for the data obtained at 80°C. The results suggest the

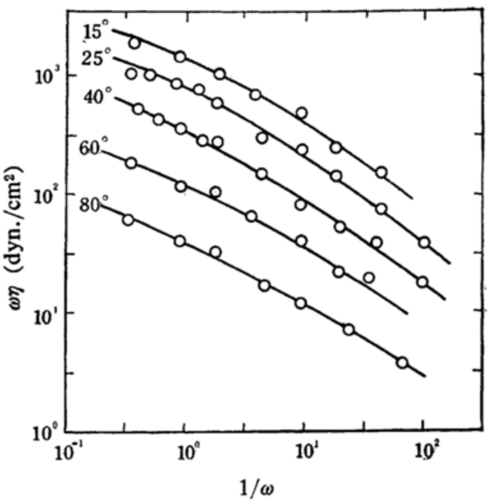

Fig. 5. Frequency dispersion of dynamic loss at various temperatures, aluminum stearate 1 wt. %.

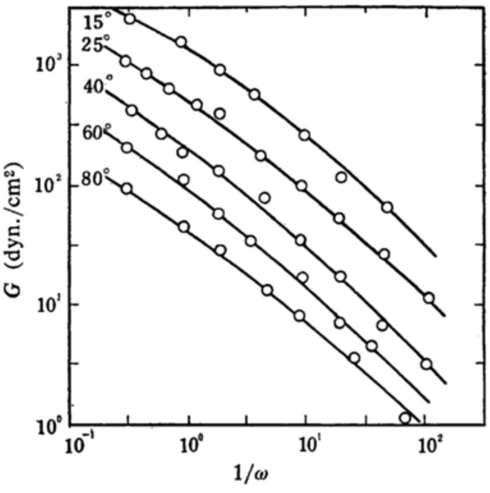

Fig. 6. Frequency dispersion of shear modulus at various temperatures, aluminum stearate 1 wt. %.

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[12] J. D. Ferry et al., *Ind. Eng. Chem.*, **44**, 703 (1952).

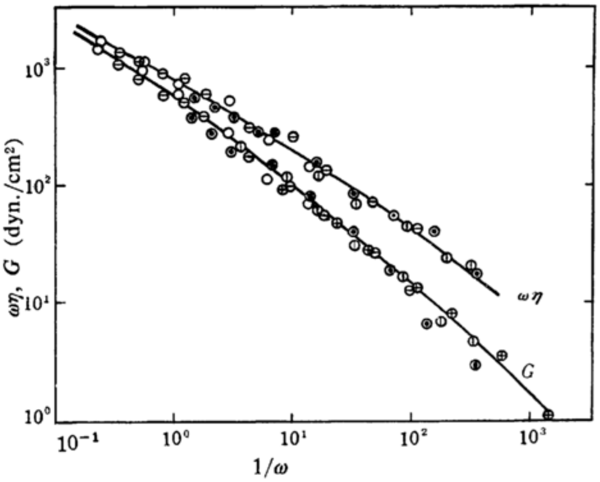

Fig. 7. Reduced curves.
○ 15°C ⊖ 25°C ⊙ 40°C ⦶ 60°C ⊕ 80°C

TABLE I. SHIFT FACTORS FOR ALUMINUM STEARATE-NUJOL GEL (1 wt. %)

Temperature (°C)	log a_T
15	0.52
25	0
40	−0.53
60	−0.97
80	−1.38

absence of serious changes in rheological structures up to 60°C, that is, the system is thermo-rheologically simple in that temperature region. The shift factors for this transformation to 25°C are summarized in Table I. Change in the reducing factor with temperature is somewhat small compared with the data of usual polymers.

Concentration Dependence.—Change in shear modulus and dynamic viscosity with concentration at various temperatures is shown in Fig. 8. Modulus and viscosity show similar curves which are composed of two straight lines, and have a break point near concentration 1 wt. %. Above this point, modulus and viscosity increase abruptly. This point corresponds to the appearance of soft gel, therefore it is considered as the critical concentration for gel formation. Change in temperature has a minor effect both on the type of the curve and on the critical concentration. The critical concentrations of gel formation obtained from the curves at 15, 25 and 40°C are 0.86, 0.82, and 0.86 wt. % respectively. The curves were obtained from a single period of oscillation; however, these types of curves and critical concentrations are expected under various conditions, because the frequency dependence of the systems is similar,

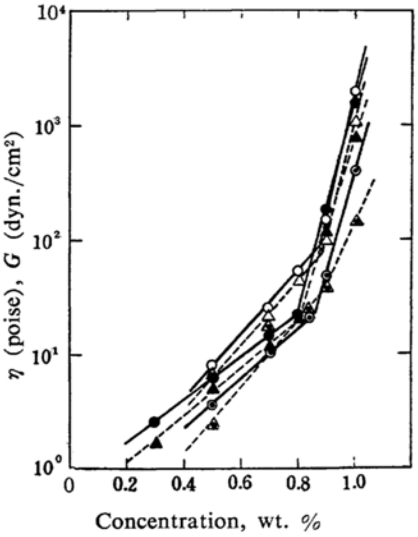

Fig. 8. Change in dynamic viscosity (—○—) and shear modulus (--△--) with concentration, period T=12 sec.
○ 15°C ● 25°C ⊙ 40°C

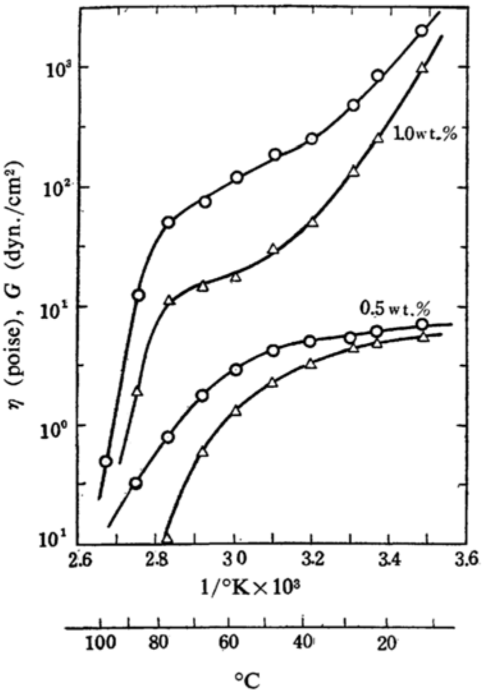

Fig. 9. Temperature dependence of dynamic viscosity (○) and shear modulus (△), period T=12 sec.

as shown in Figs. 5 and 6.

Below the critical concentration, the viscosity and elasticity change exponentially with concentration; this region corresponds to the sol in which the soap crystallites are dispersed with secondary interactions. Above the critical concentration, an extraordinarily sudden increase in visco-elasticity occurs due to the strong network structures in the system, which is stable under a very low rate of shear. This was not observed in a static viscosity measurement carried out under a high rate of shear, owing to the degradation of the structure under shear.

Effect of Temperature. — Changes in visco-elasticity with temperature are shown in Fig. 9. Viscosity change of the vehicle is expressed approximately by the Andrade formula; whereas the system shows complex thermal behaviors. The curves have deflection points near 80°C, which show some phase change in the structure of the systems, the transition from dispersion to isotropic solution. Below this transition temperature, the 1 wt. % gel shows greater temperature effect than the vehicle due to the effect of temperature on the strength of network structures; that is, the gel structures change continuously with temperature. On the other hand, a 0.5 wt. % sol undergoes less temperature effect than the vehicle, which shows that the rheological structures remain unchanged by temperature.

Summary

Dynamic visco-elastic behaviors of the aluminum stearate nujol system were studied, using a concentric cylinder type forced oscillation rheometer. The system behaves always as a typical visco-elastic body in a wide range of concentrations and temperatures, and manifests conspicuous amplitude and frequency dependence, which indicates non-linear visco-elastic properties. Wedge type relaxation spectra of the system were obtained, and it was found that the system is thermo-rheologically simple in a confined region of temperatures. The time effect of the specimen and temperature dependence of dynamic properties were examined, and the rheological structures in the system under various conditions were discussed.

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