Flow Properties of Aluminum Soaps-Hydrocarbon Systems

By Sukekuni SHIBA

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It has been known that the aluminum soaps dispersed in hydrocarbon oils make stable gels and exhibit a wide variety of flow behaviors. The polymeric natures of the aluminum soaps have been pointed out by many authors[1-3] from the osmotic pressure and viscosity data on aluminum soaps in benzene. These properties indicate that the soap molecules aggregate to form fibrous micelles and are dispersed polymerically with a network structure in hydrocarbon.

Garner, Nissan and Wood[4], studying thermodynamics and rheological behaviors of the aluminum stearate gels in petrol, found that the apparent viscosity at different rates of shear was at first constant, but at higher rates of shear, the apparent viscosity decreased, reaching approximately constant value at very high rates of shear. Weber and Bauer[5], and also Bauer, Weber and Wiberley[6,7], studying the flow properties of aluminum laurate-toluene gels, the effect of peptizers and entrance effects in capillary, by a pressure capillary viscometer over a wide range of mean rates of shear, ranging from 10^{-3} to 10^{+6} sec^{-1}, obtained the shear stress-rate of shear curves, which showed three types of flow: Newtonian flow at low rates of shear, rapid increase in shear rate with shear stress in the region of shear rate above 10^{-2} sec^{-1}, and constant slope in log-log plot at shear rate above 10^{-2} sec^{-1}.

Some of the manifold flow properties were clarified by these investigations; however, many aspects of flow behaviors are not fully explained, due to the variability of flow properties with the nature of soaps, solvents, soap concentrations and physical conditions of measurements especially the rate of shear. Measurements with the capillary type viscometers are liable to be affected by the capillary end effects and the changes in properties during the flow. Therefore, it is desirable to take measures under a uniform rate of shear with specimens not subjected to shear. In this investigation, the flow properties of aluminum soaps of various parent fatty acids in hydrocarbon were measured with a concentric cylinder type rotational viscometer of small clearance; the flow properties and especially the time effects under shear were examined.

Experimental

Materials.—The alminum soaps used in this investigation were prepared from purified fatty acids by an aqueous metathetic process. Stearic and palmitic acids were purified from pure acids (Nihon Yushi Co.) by repeated recrystallization from 80 vol.% ethanol. Myristic and lauric acids were purified from commercial reagents by the same method. Capric and caprylic acids were purified from the commercial reagents by distillation under reduced pressure. The purity of the acids was examined by melting points and neutralization equivalents by titration. The physical constants of fatty acids are shown in Table I.

TABLE I. PHYSICAL CONSTANTS OF FATTY ACIDS

Fatty acid	M. p., °C		Neut. equiv.	
	Found	Lit.[8]	Found	Calcd.
Stearic	69.5	69.6	281.9	284.5
Palmitic	62.2	62.9	258.0	256.4
Myristic	54.5	54.4	229.1	228.4
Lauric	43.3	44.0	201.3	200.3
Capric	30.1	31.3	173.1	172.3
Caprylic	14.3	16.3	143.8	144.2

Fatty acid was treated with a 40~50% excess sodium hydroxide solution and distilled water to yield an approximately 5% solution of sodium soap. The mixture was heated to dissolve the soap, and the solution was kept completely transparent at 70~80°C for soaps from stearate to laurate and at 50°C for caprate and caprylate. A hot solution of aluminum sulfate was added slowly while being stirred vigorously, until a slight excess was present and precipitation was complete. The precipitated aluminum soap was filtered and washed with distilled water, until free from sulfate. The test for sulfate ion was made by adding barium chloride solution to the filtrate, which was made slightly acidic with hydrochloric acid. The soaps

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

[2] H. Sheffer, *Canad. J. Research*, **B-26**, 481 (1948).

[3] V. R. Gray and A. E. Alexander, *J. Phys. Colloid Chem.*, **53**, 9 (1949).

[4] F. H. Garner, A. H. Nissan and G. F. Wood, *Phil. Trans. Roy. Soc.*, **A-243**, 37 (1950).

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

[6] W. H. Bauer, N. Weber and S. E. Wiberley, ibid, **62**, 106 (1958).

[7] W. H. Bauer, N. Weber and S. E. Wiberley, ibid, **62**, 1245 (1958).

[8] A. W. Ralston, "Fatty Acids and their Derivatives", John Wiley & Sons, Inc., New York (1948), pp. 23-40.

were then dried to constant weight at 110°C, and stored in a desiccator over phosphorus pentoxide. Dried soaps were analysed for aluminum by ignition to oxide. The composition of the soaps is shown in Table II.

TABLE II. COMPOSITION OF ALUMINUM SOAPS

Aluminum soaps	No. of C atoms in acid	Al wt. % (analysed)	Mole acid per mole Al
Stearate	18	5.04	1.72
Palmitate	16	5.80	1.62
Myristate	14	5.96	1.77
Laurate	12	6.38	1.88
Caprate	10	7.36	1.87
Caprylate	8	9.17	1.72

Nujol was used as a vehicle. It is a liquid paraffin of a commercial grade, a paraffin-rich saturated hydrocarbon. The physical properties are as follows; $d_4^{25}=0.8429$, $n_D^{20}=1.467$, $\eta_{25}=0.217$ poise.

Preparation of Specimen.—Nujol was added to a weighed quantity of aluminum soap, and the mixture was heated slowly while being stirred until it became a transparent solution at 110~120°C. After maintaining this temperature for 15min. the solution was cooled and stored in a desiccator over phosphorus pentoxide.

Apparatus.—A concentric cylinder type rotational viscometer essentially the same as the apparatus developed by Green[9], was used. The outer cylinder was rotated and the torque necessary to keep the inner cylinder stationary was measured by a torsion spring. When the sample is a Bingham body of plastic viscosity η_{pl} and yield value f, the relation of angular velocity ω, troque M, η_{pl} and f is given by the Buckingham-Reiner equation[10];

$$\eta_{pl}\omega=(M/4\pi h)(1/r_i^2-1/r_e^2)-f\ln\ (r_e/r_i) \qquad (1)$$

where r_i and r_e are the radii of inner and outer cylinders; h is the height of the immersed part of inner cylinder; η_{pl} and f are obtained by the measurement of M corresponding to ω. The shear stress τ and the rate of shear D at radius r from the center of the cylinder are given by

$$\tau=M/2\pi hr^2 \qquad (2)$$

$$D=2\omega/(1/r_i^2-1/r_e^2)r^2 \qquad (3)$$[11]

The dimensions of the apparatus are as follows: $2r_i=29$ mm., $2r_e=30$ mm., $h=50$ mm., rate of revolution 0~400 rpm, torsion constants of the springs $3\times10^3\sim3\times10^5$ dyn. cm./rad. The apparatus was calibrated with viscosity standard oils. The absolute accuracy of the values obtained from dimensions and force constant of the apparatus was within 2%. The end effect was checked, changing the depth of immersion of the inner cylinder. It was found that the end effect was negligible.

Procedure.—The speicmen was placed between the cylinders and kept for 15 min. at the measuring temperature. The rate of revolution was raised stepwise, and at each step the equilibrium points where the deflexion of the torsion spring became constant were determined[12]. The down curve was obtained by reducing the rate of revolution down to zero to obtain the rate of shear-shear stress relation corresponding to the state. Measurements were made for systems containing 0.5~4 wt. % soaps in nujol at temperatures 15~75°C.

Results and Discussion

The aluminum soap-nujol systems give various types of flow. At room temperature, the system containing soaps above 1% makes a gel, and it changes to paste or liquid state by shear. The more diluted system makes a sol with fluidity, which shows linear or non-linear flow properties. At high temperatures above 80°C, the system becomes a homogeneous transparent elastic solution. Thus, the systems show various flow properties and are unstable in regard to shear and time. Therefore, it is necessary to study the change in properties corresponding to the variables.

Rate of Shear-Shear Stress Curves.—Examples of the curves exhibiting the rate of shear-shear stress relations are shown in Fig. 1. The lower curves are the equilibrium curves, which are obtained with the elevated rate of shear, and the upper curves are the $D-\tau$ curves (or down curves) for the states of the specimens equilibrated under the highest rates of shear. Two curves coincide for the dilute systems which behave as Newtonian liquids or Bingham plastic bodies. When the concentration is increased, the two curves make a loop. Plastic viscosity

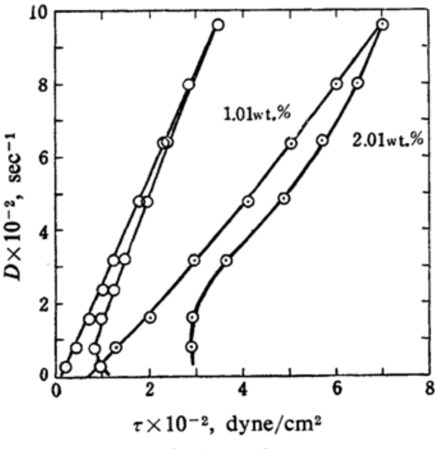

Fig. 1. Rate of shear-shear stress curves for aluminum stearate in nujol at 25°C.

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[9] H. Green, "Industrial Rheology and Rheological Structures", John Wiley & Sons, Inc., New York (1949), p. 99.

[10] M. Reiner, "Deformation and Flow", H. K. Lewis, London (1949), p. 44.

[11] For substances which show non-linear flow properties, Eq. 3 can not be used rigorously. In this apparatus, (r_e-r_i) is small enough compared with r, so that approximation with Eq. 3 is possible.

[12] The specimen was assumed to reach equilibrium when the change in deflexion angle became less than 1/2 deg./min.

and yield value are obtained from the down curve for the state.

Concerning the equilibrium curves, a rapid decrease in viscosity is observed in the range of rate of shear up to 200 $\sec^{-1}$. This is in agreement with the results of Weber and Bauer⁵⁾, who found a sudden viscosity decrease in the range of rate of shear up to 10^2 $\sec^{-1}$ for aluminum laurate-toluene gels. The curves which they obtained are likely to correspond to the equilibrium curves in this investigation, because the results by these authors will be subject to the effects of shear softening in capillary.

Ageing.—The flow properties of the system change with time while standing after preparation. The changes in viscosity and yield value at room temperature (20°C) are shown in Fig. 2. Where the viscosity is obtained from the inclination of the down curve at the rate of shear 5×10^2 $\sec^{-1}$, for the specimen equilibrated at 10^{-3} $\sec^{-1}$; the yield values are obtained from the intercepts of the extension of the down curves. Viscosity and yield value increase rapidly with time, exhibiting maximum values at about 4 hr. after preparation, and approach approximately constant values. Therefore, the measurements were carried out between 24∼96 hr. after preparation of the specimen. This effect is in agreement with the results of Gray and Alexander²⁾, and of McBain and Working¹⁾, who obtained the effect of ageing for the benzene solution of aluminum laurate, from flow birefringence and viscosity study. The mechanism of this phenomenon is explained as follows: The system cooled from a hot solution is a metastable jelly containing soap micelles; three dimensional networks of the soap crystallites grow rapidly, and are arranged slowly to the stable state.

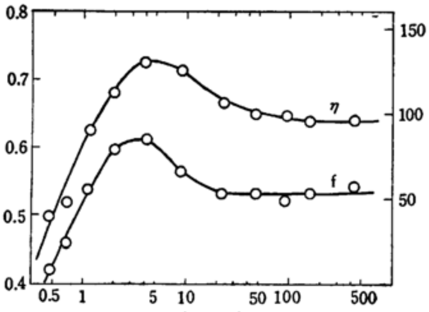

Fig. 2. Ageing of the aluminum stearate in nujol 2.01 wt.%, 25°C.

Change of Flow Properties under Shear.—Decrease of shear stress with time under constant rate of shear is shown in Fig. 3. The curve for each rate is obtained for the specimen equilibrated under lower rates of shear. If it is assumed that the contribution of the rheological structures to the shear stress is proportional to the concentration of the structures, C, and that the rate of breakdown of the structure is also proportional to C, the decrease in shear stress under constant rate of shear is expressed by,

$$\tau-\tau_{eq}=aC \tag{4}$$

$$-\frac{\mathrm{d}(\tau-\tau_{eq})}{\mathrm{d}t}=-a\frac{\mathrm{d}C}{\mathrm{d}t}=kC \tag{5}$$

integrating (5)

$$\ln(\tau-\tau_{eq})=\ln(\tau_0-\tau_{eq})-(k/a)t \tag{6}$$

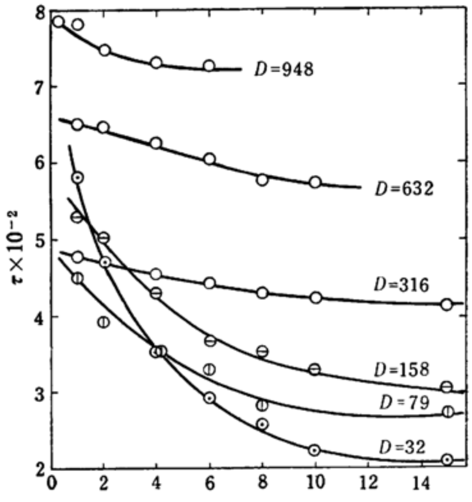

Fig. 3. Decrease of shear stress with time under constant rate of shear.
Aluminum stearate, 2.01 wt.%, 25°C

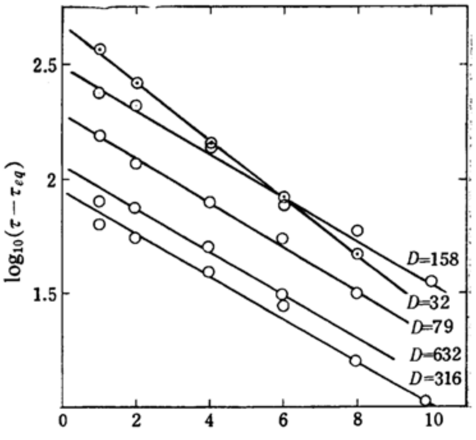

Fig. 4. Rate of degradation of the rheological structure.
Aluminum stearate, 2.01wt.%, 25°C

where τ_{eq} is the shear stress in quilibrium, τ_0 is the value of τ at time $t=0$. The decrease in $\log(\tau-\tau_{eq})$ with t is shown in Fig. 4. These results support the assumptions mentioned above. Rates of breakdown under various rates of shear are not constant in general; the rapid breakdown of weak structures under low rate of shear is recognized.

Examination on Thixotropy[13].—Flow measurements were repeated to examine the thixotropic recovery, after the specimen was kept standing for some time. The results are shown in Fig. 5. If complete recovery is present, the curves should coincide. However, the curves in subsequent measurements resemble the down curve in the first run, and the breakdown of the structures proceeds by repeated shear. Therefore, in these experimental conditions, thixotropy does not exist even after considerable time.

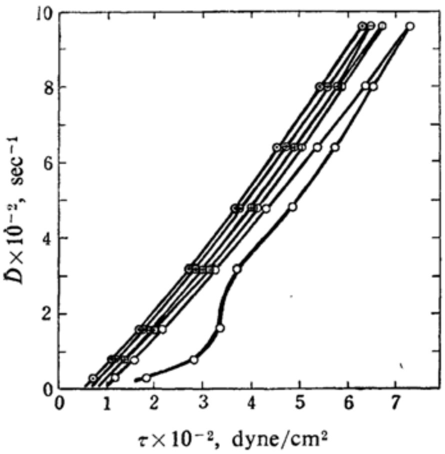

Fig. 5. D-τ curves for repeated shear. Alumium stearate in nujol, 2.01 wt.%, 25°C. ○ 0 hr., ⦶ 3 hr., ⊖ 20 hr., ⊙ 72 hr.

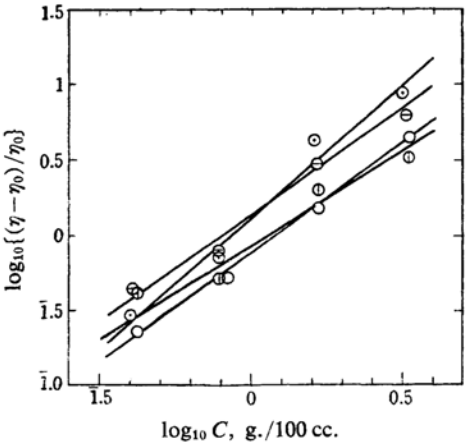

Fig. 6. Concentration dependence of specific viscosity.
○ 15°C, ⦶ 25°C ⊖ 50°C, ⊙ 75°C

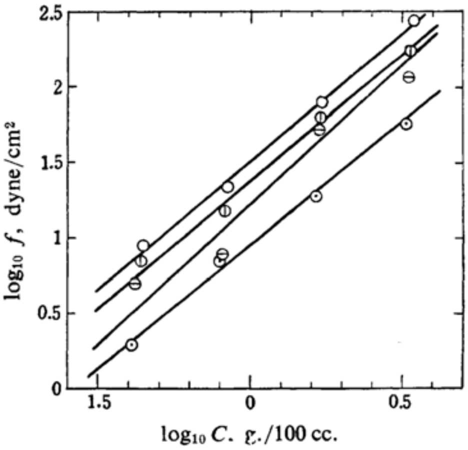

Fig. 7. Concentration dependence of yield values.
○ 15°C, ⦶ 25°C, ⊖ 50°C, ⊙ 75°C

Agreements in opinions concerning the time effects of flow behaviors on aluminum soap-hydrocarbon systems have not yet been obtained. Complete recovery was reported by Goldberg and Sandvik[14], and Carver and Van Wazer[15]; whereas, absence of thixotropy was pointed out by Evans and Matthews[16]. Evans states for aluminum greases that the change caused by the applied shearing stress is not thixotropic but appears to be a permanent change in the structure of the grease. Results of this experiment appear to support those of Evans and Matthews. However, the discrepancy of the results obtained by many authors will be ascribed mainly to the experimental conditions; for example, the rate of shear, temperature, concentration and properties of soaps which are not always pure substances. At high temperatures or under a very low rate of shear, it will be possible that the system is thixotropic.

Effect of Concentration.—The specific viscosity and yield values for various concentrations and temperatures are shown in Figs. 6 and 7, where the viscosity and yield values are obtained as previously described. These values show an approximately linear relation against $\log C$. That is, the dependence of the viscosity and yield values on concentration is expressed by empirical formulae,

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[13] It will be adequate to give a general definition of thixotropy in rheological terms as follows: "Thixotropy is the property of a body by virtue of which the ratio of shearing stress to rate of deformation is *temporarily* reduced by previous deformation.", E. K. Fischer, "Colloidal Dispersion", John Wiley and Sons, Inc., New York (1950), p. 183.

[14] H. Goldberg and O. Sandvik, *Anal. Chem.*, **19**, 123 (1947).

[15] E. K. Carver and J. R. Van Wazer, *J. Phys. Colloid Chem.*, **51**, 751 (1947).

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

$$\eta=\eta_0(1+aC^m) \tag{7}$$

$$f=bC^n \tag{8}$$

where values of m, a and n calculated from the data at 15, 25, 50 and 75°C are, $m=1.47$, 1.30, 1.39, 1.73; $a=0.73$, 0.78, 1.33, 1.33; $n=$ 1.72, 1.64, 1.72 and 1.61, respectively.

The systems are considered essentially as colloidal suspensions of soap crystallites in oil. If the soap crystallites are non-attractive rod-like ellipsoidal particles of axial ratio over 20, specific viscosity is given by Simha[17], as a function of axial ratio and volume fraction of the particles. The formula gives very high values of axial ratio corresponding to the measured viscosity values. These facts indicate that it is more appropriate to consider the interaction between soap particles and the network structures in the system.

Effect of Temperature.—Viscosity-temperature relation is shown in Fig. 8. In this temperature region, approximately linear relations exist. This shows the absence of serious change in rheological structures in this region. Apparent activation energies of flow and constant A, calculated from Andrade equation,

$$\eta=A\exp(\varDelta E/RT)$$

are shown in Table III. Decrease in $\varDelta E$ with increase in concentration is apparent. This tendency, which is in agreement with the results of Carver et al.[15], will be understandable if it is considered that the flow mechanism, is divided into the usual friction and break down of secondary bonding, and the predominance of the latter mechanism in concentrated systems is considered.

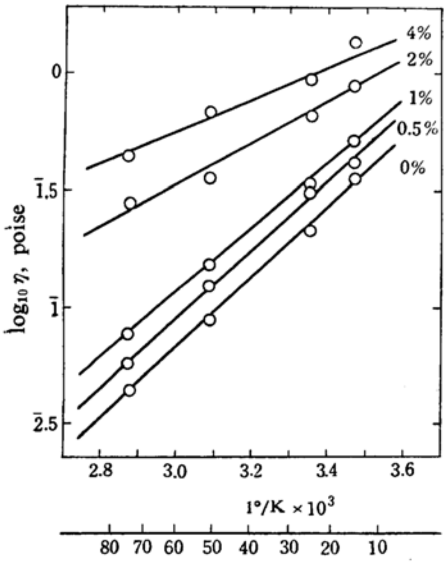

Fig. 8. Viscosity — temperature relations. Aluminum stearate in nujol.

TABLE III. CONSTANTS OF THE ANDRADE FORMULA
(Aluminum stearate in nujol)

Soap conc. wt. %	A	$\varDelta E$, kcal./mol.
0.00	2.5×10^{-6}	6.7
0.50	4.3×10^{-6}	6.6
0.99	9.4×10^{-6}	6.2
2.01	4.0×10^{-4}	4.4
3.99	4.7×10^{-3}	3.2

Effect of the Fatty Acids.—Results for soaps from various fatty acids are shown in Fig. 9. Soaps from stearate to laurate show similar flow properties, whereas caprate and caprylate show lower values, This fact correlates many other properties of soaps, which change abruptly for soaps below caprate.

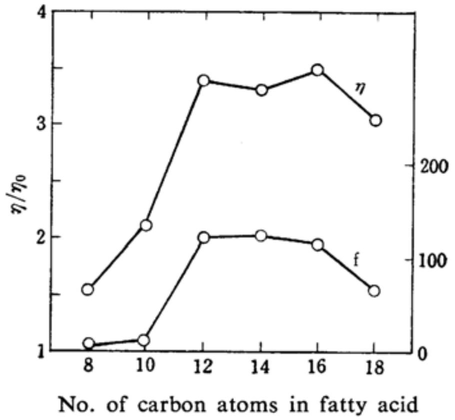

Fig. 9. Viscosity ratio and yield values of various Al soap-nujol gels, 2 wt. %, 25°C.

Summary

Flow properties of aluminum soap-hydrocarbon systems as viscous liquids or plastic bodies are studied with a concentric rotational viscometer. Results are obtained under the rate of shear up to 10^3 sec^{-1}.

(1) The systems behave as dispersions of soap crystallites with network structures combined by secondary interactions of the particles, and they exhibit marked viscosity increase.

(2) The rheological structures suffer shear breakdown under shear, resulting in decrease in viscosity.

(3) Recovery from the broken structures is impossible, that is, this change is not thixotropic but shear breakdown.

(4) Flow properties change with time while standing at rest.

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[17] R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

(5) The effects of concentration, temperature and fatty acids constituting soaps are clarified.

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Railway Technical Research Institute
Kunitachi, Tokyo