Physicochemical Studies on Cobalt Salts of Higher Fatty Acids. VIII. Some Rheological Properties of Solutions of Cobalt Soaps. Specific Viscosities and Non-Newtonian Flow

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It has been shown in the preceding part of this series[1] that cobalt is hard to dissolve in common solvents at room temperatures. It shows relatively higher solubilities in hot aromatic hydrocarbons, but these solutions gelatintize after cooling. The flow properties of these gelatinous solutions are investigated in the present paper. Intrinsic viscosities of red and blue cobalt stearates were obtained from specific viscosities of dilute benzene solutions. Jellies, formed by solutions in benzene, were peptized by adding a small amount of ethanol. It was observed in specific viscosities. The non-Newtonian flow of concentrated solutions of cobalt soaps in benzene, toluene, xylene and *n*-heptane were measured with capillary viscometers. These solutions, particularly with higher concentrations, were gelatinized, and the capillary was often blocked by a slump of jelly. The jelly was so thixotropic and syneretic that the reproducibility of measurement was poor.

Experimental

Materials.—Cobalt stearates were used as in previous papers. Benzene, toluene, xylene and *n*-heptane, used as solvents, were purified as usual. Soap was mixed with an appropriate amount of solvent and dissolved by shaking while hot. Jellies or viscoelastic solutions were obtained after cooling in the viscometer.

Viscometry. — Specific viscosities of the dilute solution, η_{sp}, at several concentrations, were measured with an Ubbelohde suspended-level viscometer[2]. Intrinsic viscosity, $[\eta]$, was obtained by an extrapolation of the linear plots of reciprocal reduced viscosity, c/η_{sp}, against concentration, c, as applied by Gray and Alexander[3] to solutions of aluminum soap in benzene, using the following formula:

$$\frac{c}{\eta_{sp}}=\frac{1}{[\eta]}-k'c \qquad (1)$$

The non-Newtonian flow of solutions was measured by using a Tsuda[4] or Philippoff[5] viscometer of horizontal capillary with a manostat. Shearing stress $P_R=R\Delta P/2L$ and nominal rate of shear $\dot{e}_R=4Q/\pi R^3t$ at wall were calculated and plotted as a flow curve; where R and L are radius and length of the capillary respectively, Δp is a pressure difference at both ends of the capillary, and Q is a volume of liquid flowing through the capillary during time t. Kinetic energy corrections are negligible. The dimensions of the capillaries are shown in Table I.

TABLE I. DIMENSIONS OF VISCOMETERS

Type	V cm³	L cm.	R cm.
Tsuda	1.295	8.0	0.0554
Philippoff A	1.000	11.6	0.025
Philippoff B	1.000	12.1	0.052

Results and Discussion

Specific Viscosity. — Specific viscosities of solutions of red cobalt stearate dihydrate and blue cobalt stearate anhydrate in benzene are

TABLE II. SPECIFIC VISCOSITIES OF COBALT STEARATES IN BENZENE, AT 30°C
$\eta_0=0.563$ cp.

Concn. c g./dl.	Viscosity η cp.	Specific viscosity η_{sp}	Reduced viscosity η_{sp}/c dl./g.	Reciprocal reduced viscosity c/η_{sp} g./dl.
(Red soap)				
0.0431	0.830	0.474	11.0	0.091
0.0294	0.702	0.247	8.40	0.119
0.0220	0.622	0.105	4.77	0.210
0.017	0.606	0.076	4.37	0.229
0.0147	0.599	0.064	4.35	0.230
(Blue soap)				
0.0237	0.629	0.117	4.94	0.202
0.0158	0.612	0.087	5.50	0.182
0.0118	0.606	0.076	6.45	0.155
0.0095	0.577	0.025	2.63	0.380
0.0075	0.575	0.021	2.80	0.357
0.0068	0.569	0.011	1.62	0.617

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1) H. Kambe, This Bulletin, 34, 1786, 1790, 1794 (1961); 35, 78, 265 (1962); H. Kambe and I. Mita, ibid., 34, 1797 (1661); H. Kambe, T. Ozawa, M. Onoue and S. Igarashi, ibid, 35, 81 (1962).
2) L. Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, 9, 35 (1937).
3) V. R. Gray and A. E. Alexander, *J. Phys. Coll. Chem.*, 53, 9 (1949).
4) S. Tsuda, *Kolloid-Z.*, 45, 325 (1928).
5) W. Philippoff, ibid., 75, 155 (1936).

TABLE III. VISCOSITIES OF COBALT STEARATES IN MIXTURES OF BENZENE AND ETHANOL, AT 20°C

Mixed solvent			Soap solution		
Concn. of ethanol vol. %	Viscosity of solvent η_0 cp.	Concn. of soap c g./dl.	Viscosity of soln. η cp.	Specific viscosity η_{sp}	Reduced viscosity η_{sp}/c dl./g.
(Red soap)					
0	0.620	0.0456	0.969	0.563	11.095
2	0.616	0.0460	0.620	0.0063	0.137
4	0.613	0.0448	0.618	0.0068	0.151
6	0.611	0.0454	0.617	0.0093	0.204
8	0.610	0.0460	0.615	0.0110	0.217
10	0.609	0.0450	0.612	0.0064	0.140
(Blue soap)					
0	0.620	0.0266	0.762	0.229	8.57
2	0.616	0.0290	0.638	0.0369	1.260
4	0.613	0.0264	0.614	0.0024	0.091
6	0.611	0.0266	0.613	0.0016	0.060
8	0.610	0.0272	0.611	0.0027	0.099
10	0.609	0.0264	0.610	0.0023	0.087

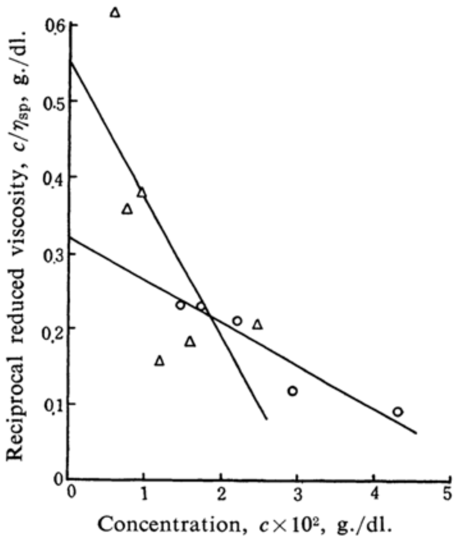

Fig. 1. Concentration dependency of reduced viscosities of solutions of cobalt soap.
○ Red soap △ Blue soap

shown in Table II and are plotted in Fig. 1. Intrinsic viscosity was obtained by applying Eq. 1 to Fig. 1. The coefficients of Eq. 1 were determined by the least-square method. The following formulas were obtained for each soap:

$$c/\eta_{sp}=(0.32\pm0.02)-(0.005\pm0.005)c$$

for red soap.

$$c/\eta_{sp}=(0.55\pm0.10)-(0.18\pm0.07)c$$

for blue soap.

The values of $[\eta]$ are 3.13 for red soap and 1.81 for blue soap. They were larger than the

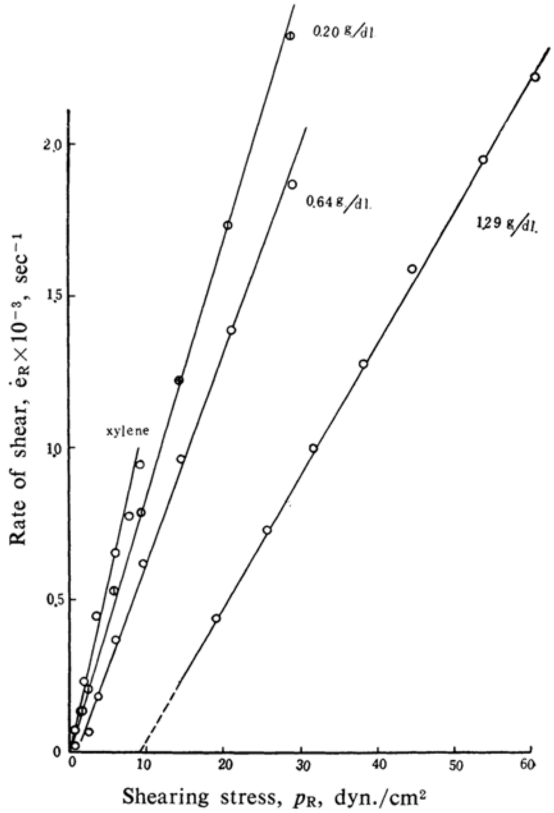

Fig. 2. Flow curves of solutions of red cobalt stearate in xylene, at 20°C.

value obtained for aluminum stearate in benzene by Gray and Alexander[3]. This discrepancy is because of the gelatinous character of cobalt soap in benzene.

Specific viscosities of cobalt stearates in mixtures of benzene and ethanol are shown in Table III. At a concentration of 0.045 g./dl. for red soap and 0.036 g./dl. for blue soap, the viscosity of the solution is markedly lowered by the addition of a little ethanol. The viscosity of a solution in a mixed solvent containing ethanol above 2% by volume is essentially the same as that of the mixed solvent itself. Additions of ethanol prevent the gelatinization of the system, and the solubility of soap is so much suppressed that the cobalt soap is almost removed from the solution by being deposited on the wall of the vessel.

Non-Newtonian Flow. — Solutions of cobalt stearate in xylene are dark violet at boiling, but solidify to jellies after cooling. Below concentrations of 2.0 g./dl., the solution is slightly fluid, and below 1.0 g./dl., it is so thixotropic that it increases its fluidity when it was shaken.

The viscosities of these solutions at concentrations of 1.29, 0.62 and 0.20 g./dl. were measured with a Tsuda viscometer at a range of rate of shear, as shown in Fig. 2, and the apparent viscosities, calculated from $\eta_{app}=p_R/\dot{e}_R$, are plotted in Fig. 3 against rate of shear. In Fig. 2, a flow curve of the solution at 1.29

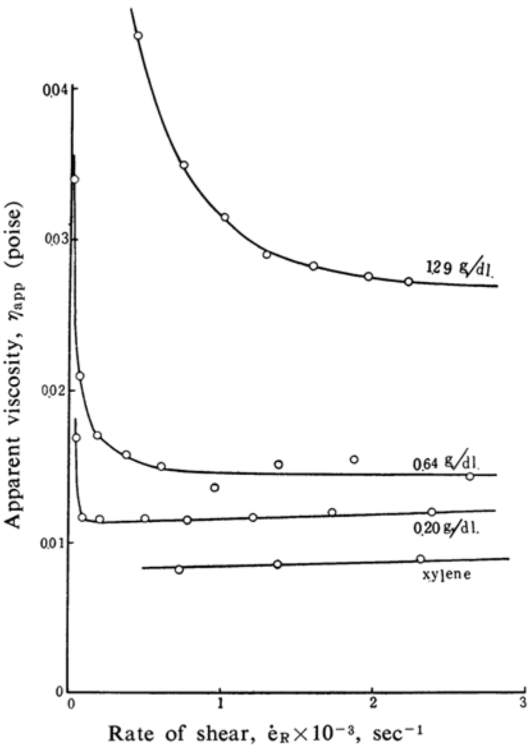

Fig. 3. Shear-rate dependency of apparent viscosity of solutions of red cobalt stearate in xylene, at 20°C.

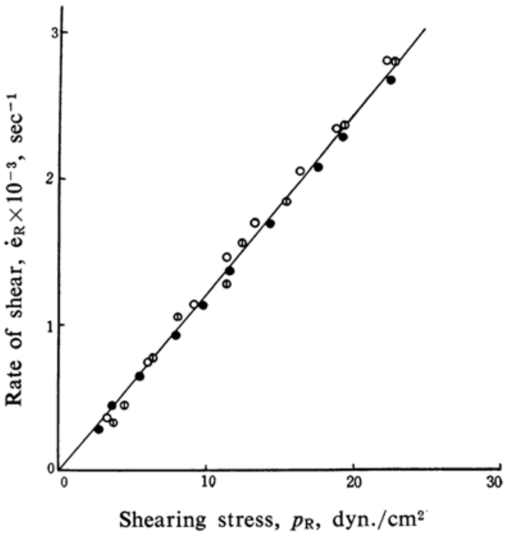

Fig. 4. Flow curve of solutions of cobalt stearate in benzene, at 30°C.
○ 0.020 g./dl. ⦶ 0.043 g./dl.
● 0.097 g./dl.

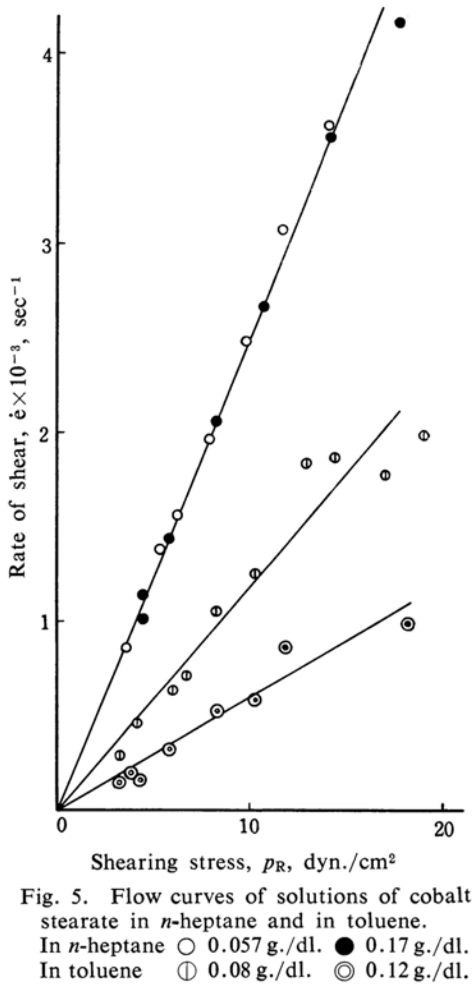

Fig. 5. Flow curves of solutions of cobalt stearate in *n*-heptane and in toluene.
In *n*-heptane ○ 0.057 g./dl. ● 0.17 g./dl.
In toluene ⦶ 0.08 g./dl. ◎ 0.12 g./dl.

g./dl. shows a typical form of the Bingham plastic flow, with a yield value of about 8.5 dyn./cm². At other concentrations, there appears no yield value. But in Fig. 3, it is evident that they also show structural viscosity at a low rate of shear range, which does not appear clearly in Fig. 2.

Non-Newtonian behaviors of benzene solutions, with concentrations of 0.097, 0.043 and 0.02 g./dl. at 30°C, were measured with Philippoff viscometers and are shown in Fig. 4. These solutions are blue when hot, but solidify after cooling to pink jellies. These jellies are viscoelastic, thixotropic and highly syneretic. Owing to their insufficient strength, they are easily crushed to pieces and their flow properties are poorly reproducible.

The flow curves of these systems are consistent with each other in this range of concentrations. It is apparently a Newtonian flow. The value of its apparent viscosity is obtained from Fig. 4 as 0.82 cp., which is not markedly different from that of pure benzene. In this case it is the viscosity of a saturated solution of a small concentration that is being measured.

Flow curves in *n*-heptane, shown in Fig. 5 at concentrations of 0.057 and 0.17 g./dl., are almost consistent with each other, as are benzene solutions. However, the flow curves of solutions in toluene, shown in the same figure at 0.08 and 0.12 g./dl., are considerably separated from each other. The apparent viscosity of the toluene solution at 0.12 g./dl. is considerably htgher than the other. Since this solution is most easily gelatinized, the capillary tube of viscometer was often blocked by a piece of gel in the solution. The low fluidity of xylene solution at a high concentration may be caused by such blockage.

The flow curves of benzene solutions at 0.152 g./dl. were measured with different capillaries in which R is 0.25 and 0.52 mm., as shown in Fig. 6. The flow curve must be principally unique to a material. The inconsistency of flow curves obtained with different bores might be caused by the slippage of the solution. In this case, the curve obtained with a large bore would be expected to show a large viscosity[6], and this holds true in Fig. 6.

Thixotropic effects often appeared in these systems. However, sometimes an antithixotropic hysteresis also appeared, as shown in Fig. 7. In this system, the viscosily becomes larger in the down-curve than in the up-curve. The origin of this behavior was not clarified, but blockage by gel is a conceivable cause.

6) M. Reiner, "Deformation and Flow", H. K. Lewis, London (1949), Chap. VIII.

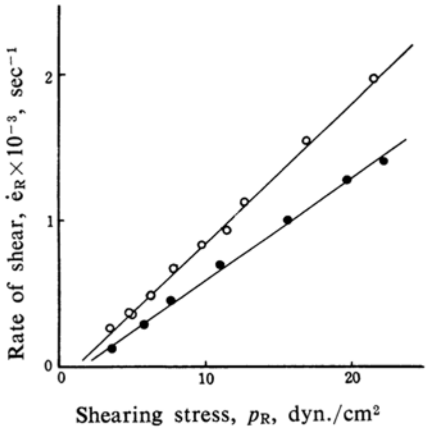

Fig. 6. Slip effect observed in the solution of cobalt stearate in benzene (0.152 g./dl.), at 20°C.

	Capillary	R, mm.
○	A	0.25
●	B	0.52

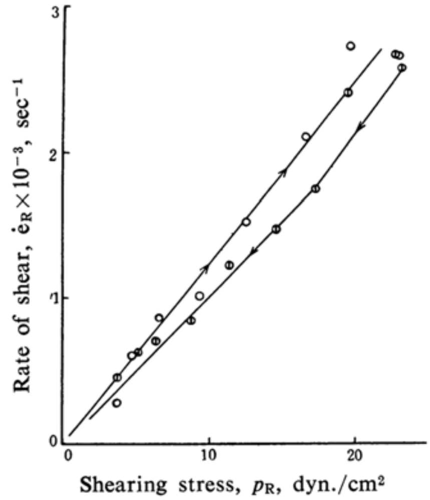

Fig. 7. Antithixotropic hysteresis in flow curve of a solution of cobalt stearate in benzene (0.17 g./dl.), at 20°C.
○ Up-curve ⦶ Down-curve

Summary

The specific viscosity of dilute solution of cobalt stearate in benzene has been measured. Intrinsic viscosities are 3.13 for red soap and 1.81 for blue soap. The specific viscosity of benzene solution is decreased markedly by the addition of a small amount of ethanol, owing to the subsequent decrease of solubility.

The non-Newtonian flow behavior of solutions in xylene, benzene, *n*-heptane and toluene are shown. At higher concentrations, in particular in xylene, these solutions are Bingham plastic. In benzene and *n*-heptane,

flow curves with different concentrations are consistent with a flow curve of Newtonian behavior, which corresponds to that of a saturated solution in benzene. In toluene, flow curves are scattered, possibly due to the blockage of the capillary by a piece of gel.

Different flow curves are sometimes obtained with capillaries of different bores, owing to slippage at the wall. An antithixotropic flow curve was obtained in some solutions.

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