Differential Thermal Analysis of the Systems Aluminum Soap-Hydrocarbon

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Studies on the metal soap-hydrocarbon systems have been carried out in order to obtain basic knowledge on the industrial applications of the metal soaps, especially for the manufacture of lubricating greases. Visual observation and optical methods have been used to establish the relation of the phase state on temperature and composition. Recently, differential thermal analysis offered a powerful means for obtaining such diagrams precisely.

Disagreements in the results have been observed due to the complex behaviors of the systems and the differences in the experimental techniques used: Doscher and Vold[1], and also, Stross and Abrams[2] reported quite different types of phase diagrams on the system sodium stearate-cetane; Vold[3] and Cox[4], on the system lithium stearate in cetane and in mineral oils.

Phase behaviors of the aluminum soaps were discussed in the preceding paper with the aid of differential thermal analysis[5]. In this paper, the thermal behaviors of aluminum soap-hydrocarbon systems are studied by the same method to obtain the phase behaviors of the systems and to have some information on the structure of the systems and the aluminum soaps themselves.

Experimental

The aluminum soaps used in this study were prepared by an aqueous metathetic process. Details of the preparation were described in the preceding paper[5]. Nujol, a liquid paraffin of commercial grade, was used as a model of the mineral oils. The purity of the Nujol was checked by infrared absorption measurement, which proved that it is a paraffin-rich hydrocarbon, and showed the absence of aromatic components or impurities. The physical properties were, $d_4^{25}=0.8429$, $n_D^{20}=1.467$, $\eta_{25}=0.217$ poise.

The apparatus and procedure were also described previously.

Results and Discussion

The System Aluminum Stearate-Nujol.—The transition temperatures and heats of transition, obtained from the heating and cooling thermograms on the aluminum stearate-Nujol, are summarized in Table I. The aluminum soaps have three transition points in general. They are named for convenience the transitions I, II and III, from low to high temperatures. Thermograms for repeated heating and cooling show that the phase changes are practically reversible. In the initial heating, however, slightly different transition temperatures and appearance of peaks, for instance, that of the soap itself, are obtained incidentally, and they are not found in the following runs. This may be due to the difference in heat transfer in the specimens and incomplete mixing of the soaps in oil.

An equilibrium phase diagram for the

1) T. M. Doscher and R. D. Vold, *J. Colloid Sci.*, **1**, 299 (1946).
2) F. H. Stross and S. T. Abrams, *J. Am. Chem. Soc.*, **73**, 2825 (1951).
3) M. J. Vold and R. D. Vold, *J. Colloid Sci.*, **5**, 1 (1950).
4) D. B. Cox, *J. Phys. Chem.*, **62**, 1254 (1958).
5) S. Shiba, This Bulletin, **34**, 2611 (1961).

TABLE I. TRANSITION TEMPERATURES AND HEATS OF TRANSITION OF THE SYSTEM ALUMINUM STEARATE-NUJOL

Soap conc.	Heating		Cooling	
wt. %	Tr. temp. °C	Heat of tr. cal./g.	Tr. temp. °C	Heat of tr. cal./g.
100	99 119 162	5.8 0.4 2.1	89 144	10.6 2.5
90	94 114 159	5.0 1.1 0.7	85 140	12.8 1.9
70	96 109	14.4	81 95	12.4
50	101	11.8	87	14.7
30	99	13.4	80	14.1
10	98	12.6	71	15.4
5	100	13.3	71	11.5

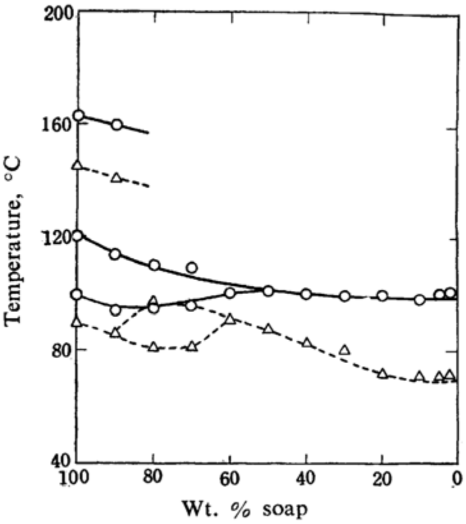

Fig. 1. Phase diagram of the system aluminum stearate-Nujal.

system, obtained from the transition temperatures, is shown in Fig. 1. The full lines represent the phase transitions on heating, and the dotted lines, on cooling. The transition temperatures when they are heated, undergo changes by the addition of Nujol. The heat of transition at high temperatures decreases conspicuously, and the transition III disappears when more than 10 wt.% of Nujol is contained. The transition II coincides with the transition I, when more than 30 wt.% is contained. In the system containing more than 30 wt.% of Nujol, the soap dissolves in Nujol at the transition I, and shows no transition above this temperature. Concerning the transition I, when a small amount of Nujol is added, the peak is broadened, showing sometimes 2 or 3 apexes. In this diagram, the most intense apexes are adopted as the transition temperatures. By further addition of Nujol, the peak of the transition I becomes sharp again, and the temperature reaches a constant value.

The phase diagram obtained by cooling shows only two transition temperatures which are lower than the temperatures obtained by heating, and in this case, both a change in transition temperatures and disappearance of the transition points are observed.

The disappearance of the transition points, which was also found in the case of the contaminant free fatty acids in the soaps[5], shows an entirely different behavior of aluminum soaps compared with other metal soaps. Most of the systems, metal soaps-hydrocarbon, undergo phase transitions on heating, which are either related to the transitions on heating, which are either related to the transitions of the oil-free soaps or are more complicated; and the transition temperatures are reduced in general by the addition of hydrocarbon[6].

The phase diagram is obtained concerning one vehicle, Nujol; however, essentially the same or at least similar results are expected for other hydrocarbons, e. g., petroleum oils, as were found for lithium soaps in various petroleum oils[4].

Systems of Aluminum Palmitate and Laurate-Nujol.—The phase diagrams for the systems of aluminum palmitate-Nujol and aluminum laurate-Nujol are shown in Figs. 2 and 3. Aluminum palmitate shows similar results to stearate: although slightly different transition temperatures are obtained. Aluminum laurate shows different behaviors. The transition

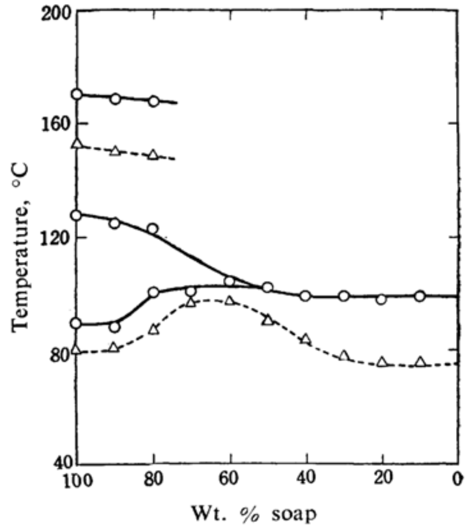

Fig. 2. Phase diagram of the system aluminum palmitate-Nujol.

6) M. J. Vold, G. S. Hattiangdi and R. D. Vold, *Ind. Eng. Chem.*, **41**, 2539 (1949).

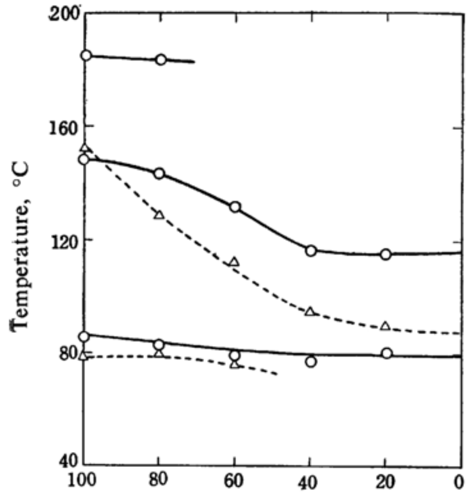

Fig. 3. Phase diagram of the system aluminum laurate-Nujol.

temperature varies definitely with the concentration of the soap, in both heating and cooling thermograms. The transition II shows marked absorption of heat, as the Nujol is added; on the contrary, the heat of the transition III decreases and disappears at the concentration of Nujol above 20 wt. %; and the heat of transition I remains unchanged. For instance, the heats of transitions I, II and III, of the system containing 40% of Nujol are 1.2, 6.3 and 0 cal./g., whereas the soap itself shows 1.4, 1.2 and 3.2 cal./g., respectively. In the system containing more than 20% of Nujol, the soap dissolves in hydrocarbon at temperatures above the transition II.

The phase transition of the system aluminum laurate-Nujol on cooling, shows tendencies similar to the transition on heating. In this case, the lower transition disappears and only the higher transition remains in dilute systems.

Colloidal Structures of the Aluminum Soaps in Hydrocarbon.—The aluminum soaps, which are composed mainly of aluminum hydroxy disoaps, and a small amount of contaminant aluminum hydroxide, free fatty acid, and a trace of water, make the stable skeletons of Al–O–Al with adjacent soap molecules through the hydroxyl group, which shows the polymeric nature of the soaps. These skeletons form fibrous soap polymer, and are maintained even when the soaps are dispersed in hydrocarbon media, and result in the extraordinarily strong gelling or thickening properties.

The dispersed systems, aluminum soap gels in hydrocarbon, are essentially a dispersion of aluminum soap particles combined weakly with secondary bonding, as found from X-ray diffraction, electron microscope techniques, and rheological measurements[7-9]. The results of differential thermal analysis, which show that the systems are thermally reversible, suggest that the structure of the soap particles at room temperatures, dispersed by heating in hydrocarbon media, are almost identical with the original solid phase of the soaps; i. e., the isotropic solution becomes a jelly by cooling, and the soap micelles in the jelly convert rapidly to soap crystallites.

At higher temperatures above their transition points, the soap crystallites are dissolved in the hydrocarbon media, and the system becomes a transparent viscous solution. It is supposed that the soaps retain their polymeric nature even in the solutions, because of their typical visco-elastic properties.

In the practical applications of the aluminum soaps, the soaps are used generally at concentrations of a few per cent. In such cases, the phase behavior is very simple as is expected from the phase diagrams as shown in Figs. 1—3, and the transition points correspond to the temperatures at which the systems become transparent viscous solution on heating, and turbid gel on cooling. The phase changes of the dilute systems obtained in this experiment are consistent with the results from the sudden change in dynamic rheological properties with temperature[10].

Summary

The phase behaviors of the system aluminum stearate, palmitate, and laurate-Nujol are studied by differential thermal analysis. Phase diagrams are obtained, and it is found for stearate and palmitate that soaps dissolve in hydrocarbon at the lower transition points of the soaps, and that the higher transition points disappear by addition of hydrocarbon. Differences in phase behaviors are found between laurate and other soaps. Some discussions are made on the colloidal structures of the dispersed systems aluminum soaps-hydrocarbon.

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7) S. S. Marsden, Jr., K. J. Mysels and G. H. Smith, *J. Colloid Sci.*, **2**, 265 (1947).
8) D. Evans and J. B. Matthews, ibid., **9**, 60 (1954).
9) W. H. Bauer, N. Weber and S. E. Wiberley, *J. Phys. Chem.*, **62**, 106 (1958).
10) S. Shiba, This Bulletin, **34**, 194 (1961).