Differential Thermal Analysis of Aluminum Soaps

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It has been known that the metal soaps show complex thermal behaviors due to their polymorphism when they are heated. Lawrence[1] pointed out the temperature at which the soaps become plastic, before they reach the melting points, and the soaps show swelling and gellation in hydrocarbon media. The application of the differential thermal analysis, which has been used in metallography and in the study of clay minerals, to these phenomena, was attempted first by Vold[2], and the phase state of the metal soaps and soap-hydrocarbon systems were investigated successfully. Later, many authors reported the differential thermal analysis of metal soaps and the experimental apparatus applicable to such substances[3-5].

The thermal behaviors of aluminum soaps have not yet been fully clarified, and conflicting data were reported due to their relatively low heat of transition and the difficulty of obtaining pure soaps[6]. It is generally believed from various experiments, that the aluminum soaps, prepared by the usual metathetic process from aqueous solution of alkali soaps and aluminum salt, consist mainly of aluminum hydroxydisoaps, $\mathrm{Al(OH)A_2}$, and they are the only definite compounds as aluminum soaps[7-9]. Recently, it was found that the aluminum trisoaps can be obtaind through interaction of aluminum trialkoxide or trialkyl aluminum with fatty acids in anhydrous organic media, and they are decomposed to disoaps in the presence of water[10-12].

The present investigation was carried out to examine the thermal behaviors of aluminum soaps by differential thermal analysis, and to obtain some information on the structure of aluminum soaps from thermal data.

Experimental

Preparation of Soaps. — The aluminum soaps used in this work were prepared from purified fatty acids by an aqueous metathetic process. The fatty acids which were solid at room temperatures (stearic-lauric) were purified by repeated recrystallization from 80 vol. % ethanol. Capric and caprylic acids were purified by distillation under reduced pressure. The purity of the acids was examined by melting points and neutralization equivalent through titration, as is shown in Table I.

TABLE I. PHYSICAL CONSTANTS OF FATTY ACIDS

Fatty acid	M. p., °C		Neut. equiv.	
	Found	Lit.[13]	Found	Calcd.
Stearic	69.5	69.6	282	284.5
Palmitic	62.2	62.9	258	256.4
Myristic	54.5	54.4	229	228.4
Lauric	43.3	44.0	201	200.3
Capric	30.1	31.3	173	172.3
Caprylic	14.3	16.3	144	144.2

Fatty acid was treated with an excess of 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, 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 the precipitation was complete. The precipitated aluminum soap was filtered off and washed with distilled water, until the filtrate was free from sulfate when tested with barium chloride solution under slightly acidic medium. The soap was then dried to constant weight at 110°C, and stored in a desiccator over phosphorus pentoxide. Dried soaps were analyzed for aluminum by ignition to oxide.

The reaction between sodium soap and aluminum salt solution in the presence of excess of sodium hydroxide is expressed generally by,

$$2n\mathrm{NaA}+\mathrm{Al_2(SO_4)_3}+2(3-n)\mathrm{NaOH} \rightarrow 2\mathrm{Al(OH)}_{3-n}\mathrm{A}_n+3\mathrm{Na_2SO_4} \tag{1}$$

$$n=0\sim3 \tag{2}$$

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[1] A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660 (1938).

[2] R. D. Vold, *J. Phys. Chem.*, **49**, 315 (1945).

[3] C. J. Penter, S. T. Abrams and F. H. Stross, *Anal. Chem.*, **23**, 1459 (1951).

[4] D. Evans, J. F. Hutton and J. B. Matthews, *J. Applied Chem.*, **2**, 252 (1952).

[5] D. B. Cox and J. F. McGlynn, *Anal. Chem.*, **29**, 960 (1957).

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[8] W. W. Harple, S. E. Wiberley and W. H. Bauer, *Anal. Chem.*, **24**, 635 (1952).

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[13] A. W. Ralston, "Fatty Acids and their Derivatives", John Wiley and Sons Inc., New York (1948), p. 23.

where, A is the acid radical, and it is assumed that the soaps containing continuously 0~3 mol. of fatty acids per 1 mol. of aluminum are obtainable. It is possible by this relation to control the composition of the aluminum soap changing the excess of the sodium hydroxide in the aqueous medium. The composition of the soaps is shown in Table II.

TABLE II. COMPOSITION OF ALUMINUM SOAPS

Al soap	No. of C atoms in acid	Excess of NaOH %	Al wt.% analyzed	Mol. acid per mol. Al
Stearate-3.22	18	−25	2.91	3.22
〃-2.29	〃	0	3.92	2.29
〃-2.12	〃	10	4.25	2.12
〃-1.89	〃	25	4.68	1.89
〃-1.71	〃	40	5.10	1.71
〃-0.95	〃	100	8.23	0.95
Palmitate	16	45	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

Apparatus. — An apparatus adequate to analyze the soaps or soap-oil systems, which are liable to be oxidized below their melting points, was constructed. The apparatus is able to control and record the temperatures automatically, in the temperature range up to 300°C, with a small amount of sample.

The apparatus consists of four basic parts; the sample and reference cells, electric furnace, temperature control mechanism, and recorder. The sample cells used are similar to those of Vold[14]. They are made of 18-8 stainless steel, machined to a wall thickness less than 0.4 mm., and have a sample capacity of 2 cc. The cells are closed by screw caps; a protection tube for the thermocouple is fitted in the center of the cap. The furnace is heated by a two-element heater, and the cells are set through a teflon collar and sleeve in a hole of a copper block which is placed in the center of the furnace.

The temperature of the block is detected by a chromel-alumel thermocouple, and is regulated by a potentiometer type controller. The controller detects the difference in the electromotive force of the couple and the settled potential which varies linearly with time, and regulates the temperature. The rate of heating or cooling is adjusted by changing the gear ratio of the controller. For the detection of the differential temperature of the sample and the reference cells, a chromel-alumel thermocouple was used, because of its sensitivity, stability, and linearity of the emf against temperature. The thermoelements were insulated with glass fiber tubing and impregnated with silicone varnish. The potential difference obtained from two cells is amplified by a chopper type DC amplifier, and recorded on a strip chart multipoint electronic recorder with the temperature of the reference cell. By a proper selection of the rang of amplifier and recorder, it is possible to record the temperature difference of ±0.3~±25°C on the full scale of the recorder.

Analysis of Thermogram. — The thermogram is analyzed for temperature and latent heat of transition. When the thermal transition does not occur, the temperature difference between the sample and the reference cells, y, is expressed by a curve which approaches y_∞ at time infinity; i. e.,

$$y=y_\infty+(y_0-y_\infty)\exp(-a(t-t_0)) \tag{3}$$

$$y_\infty=(C_s/\alpha_s-C_r/\alpha_r)\frac{\mathrm{d}T_r}{\mathrm{d}t} \tag{4}$$

$$a=\alpha_s/C_s \tag{5}$$

where, T is the temperature; C, the heat capacity, α, a constant including the coefficient of the overall heat transfer to the cell and dimensions of the thermal path as a whole: the subscripts s and r mean that the quantities refer to sample cell and to the reference cell. The interaction of the two cells are neglected. The temperature difference between the center (T_s) and wall (T_f) of the cell is expressed approximately by,

$$T_f-T_s=\frac{C_s}{\alpha_s}\cdot\frac{\mathrm{d}T_s}{\mathrm{d}t} \tag{6}$$

The actual temperature, at which the sample near the wall of the cell begins to undergo transition, is determined by the breaking point of the thermogram corrected by this relation.

When a transition of the sample is observed, enthalpy change of the sample cell, $\varDelta H$, is expressed as follows;

$$\varDelta H=\alpha_s\int_{t_1}^{t_2}(y-y')\,\mathrm{d}t=\alpha_s A \tag{7}$$

where t_1 and t_2 are the optional time before and after the transition, y' is the temperature difference when the transition does not occur, and A is the area of the peak of the thermogram.

The apparatus was calibrated with stearic acid (m.p. 69.3°C, heat of melting, 47.6 cal./g.) and benzoic acid (m. p. 122°C, heat of melting, 33.9 cal./g.). It was shown that the determination of the transition temperature could be made accurately by adopting the temperature at the apex of the peak in the thermogram, after being corrected to the temperature difference between the sample and reference cells. A conversion factor, 0.370 cal. per unit area of the peak (in deg. min.), was obtained from both acids, when 0.5~1.0 g. of the sample was used.

Procedure.—The soap was weighed in the sample cell, and alumina or Nujol as a reference material was also filled in the reference cell. The cells were placed in the furnace, and heating and cooling at a constant rate were repeated. Experimental conditions were;

Temperature,	up to 300°C
Rate of heating,	0.5~1.2 deg./min.
Weight of the specimen,	0.5~1.0 g.

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[14] M. J. Vold, *Anal. Chem.*, 21, 683 (1949).

[15] S. Shiba, *Railway Technical Research Report*, No. 162 (1960).

Details of the apparatus, analysis, and procedure were described in the previous paper[15].

Results and Discussion

Thermogram of Aluminum Stearate. — For most of the aluminum soaps, transition points are observed between room temperature and their melting points. Typical examples of the heating and cooling thermograms of an aluminum stearate are shown in Figs. 1 and 2.

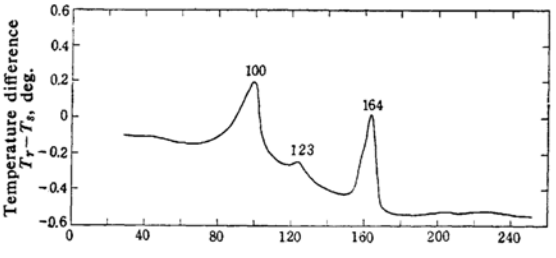

Fig. 1. Heating thermogram of aluminum stearate. (Ste−1.71).

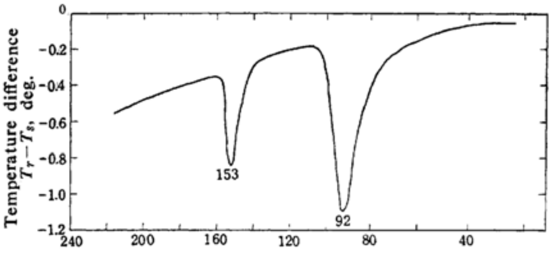

Fig. 2. Cooling thermogram of aluminum stearate. (Ste−1.71).

Three distinct peaks of transition are found in the heating thermogram, and two peaks are found in the cooling thermogram. Numbers in the thermograms show the temperature of the sample cell at the apex of the peaks. The cooling thermograms show a lower transition temperature and less repeatability due to the super-cooling of the soaps.

When heating and cooling are repeated for one specimen, the thermal behaviors are repeatable in general. However, the initial heating sometimes gives a little different thermogram from that obtained by the following runs; e. g., two indistinct peaks are observed in the initial run instead of one peak near 100°C in the following runs. These facts were reported by Vold[16], and they may be ascribed partly to the condition of the specimen packed in the cell before it is melted. In fact, the aluminum soap powders, when once melted, give a transparent glue-like mass, and show different bulk physical properties. No appreciable chemical changes of the specimen during the thermal analysis, oxidation, dehydration etc., were ascertained by the infrared absorptions before and after the analysis. In this report, discussions are held on the definite transitions which are obtained repeatably, and the small peaks which are obscure as found occasionally near 82°C are neglected.

Aluminum Stearates of Different Compositions. —The transition temperatures and heats of transition of aluminum stearates are summarized

TABLE III. TRANSITION TEMPERATURES AND HEATS OF TRANSITION OF ALUMINUM STEARATES

Sample	Heating		Cooling	
	Tr. temp. °C	Heat of tr. cal./g.	Tr. temp. °C	Heat of tr. cal./g.
Ste-3.22	69	16.0	58	14.2
	104	7.0	79	7.0
Ste-2.29	65	8.0	59	2.4
	104	8.1	87	6.8
Ste-2.12	66	3.0	85	7.4
	99	5.8	134	0.9
	150	0.9		
Ste-1.89	101	7.8	88	9.2
	157	3.2	137	2.1
Ste-1.71	99	5.8	89	10.6
	119	0.4	144	2.5
	162	2.1		
Ste-0.95	97	2.8	95	7.8
	124	0.8	145	1.1
	162	1.3		

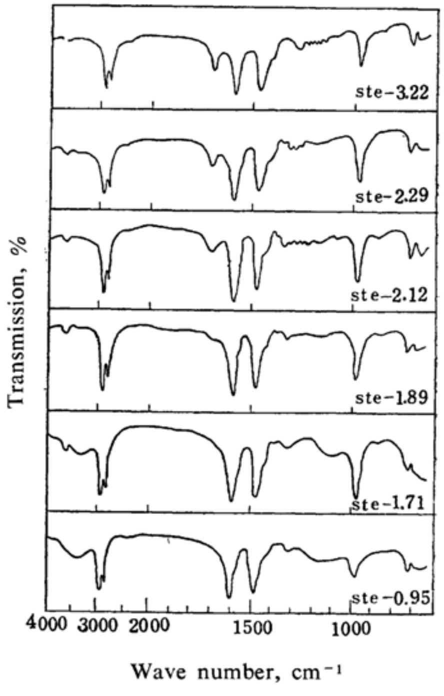

Fig. 3. Infrared spectra of aluminum stearates.

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

in Table III. Infrared absorption spectra of the same soaps, obtained by the potassium bromide disk method using a double beam spectrometer (Perkin-Elmer IR-21), are also shown in Fig. 3.

The thermograms of these soaps are somewhat different from those of examples shown in Figs. 1 and 2. The soaps containing more than 2 mol. of fatty acid per mole of aluminum, exhibit transitions near 70°C which are not found in Fig. 1. This transition point corresponds to the melting point of stearic acid. The heat of transition of this peak increases with an excess of the fatty acid over 2 mol. per aluminum. The infrared absorption at 1720 cm^{-1}, which is due to the presence of the carbonyl group, shows the same tendency. These facts confirm the fact that these soaps contain free fatty acids, and that the peaks are due to the melting of the acids. The results also indicate that the preparation of aluminum trisoaps by metathetic processes is impossible. Even though trisoaps exist, they will be decomposed to hydroxydisoaps and fatty acids by the effect of water. The soaps containing more than 2 mol. of fatty acids per aluminum, show weak transition peaks or lack of them at higher temperatures. This is attributed to the co-existence of fatty acids which melt at lower temperatures. When the fatty acids in the soap are extracted off by heptane, the transition at 160°C is found for the residual soap.

The soaps containing less than 2 mol. of acid per aluminum show no additional peaks, and they show less heat of transition, probably due to the presence of aluminum hydroxide in the soap. Infrared absorptions at 3720 cm^{-1} which are assigned to free OH stretching, are found for most of the soaps; while in the soap Ste-0.95, a broad absorption is found near 3400 cm^{-1} corresponding to bonded OH, and both absorptions are found for Ste-1.71. The infrared data retain the possibility of the existence of dihydroxymonosoaps as a discrete compound; however, the thermal data offer no positive evidence for the existence of the monosoaps.

The heat of transition obtained, show rather disjoined results, presumably because of the difference in heat transfer between specimen and cell, and in the specimen. Total heat of transition per mole of Ste-1.89 is about 6.4 kcal./mol., considerably less than that of alkali soaps (e. g., NaSte, 14.6 kcal./mol.).

Aluminum Soaps from Various Fatty Acids.—Transition temperatures and heats of transition of various aluminum soaps are summarized in Table IV. The structure and composition of these soaps are essentially the same, and no free fatty acids are incorporated in the soaps, as are ascertained by the infrared spectra.

TABLE IV. TRANSITION TEMPERATURES AND HEATS OF TRANSITION OF ALUMINUM SOAPS FROM VARIOUS FATTY ACIDS

Sample	Heating		Cooling	
	Tr. temp. °C	Heat of tr. cal./g.	Tr. temp. °C	Heat of tr. cal./g.
Palmitate	90	4.0	80	4.5
	128	1.0	152	2.0
	170	2.1		
Myristate	92	3.0	84	2.1
	136	1.4	156	2.7
	179	2.5		
Laurate	86	1.4	78	1.2
	149	1.2	152	3.0
	185	3.2		
Caprate	196	4.8	160	4.2
Capylate	216	6.4	176	4.1

The thermograms of palmitate, myristate, and laurate show three distinct transition points similar to stearate; whereas, caprate and caprylate show only one transition point corresponding to the highest one of the soaps from higher fatty acids. The transition heat of the lowest transition decreases with the decrease in number of carbon atoms in the fatty acid, and disappears for caprate and caprylate. On the other hand, the heat of the highest transition increases with the decrease in number of carbon atoms, resulting in a similar total heat of transition per gram. The lack of these characteristic transitions of the aluminum soaps in the lower soaps, is consistent with the change of may other properties of the soaps with the change in the length of the constituent fatty acids; e. g., the thickening and gelling

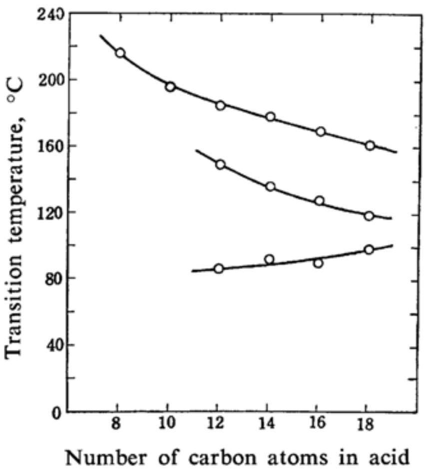

Fig. 4. Transition temperatures of aluminum soaps.

properties of aluminum soaps in organic media[17], etc.

Changes in corresponding transition temperatures with the carbon number of the fatty acids are shown in Fig. 4. Each transition temperature changes regularly, and it seems that the temperatures approach constant values as the chain length increases.

Assignment of Transition Points. — It is an inherent characteristic of the differential thermal analysis that it enables some thermal change in the specimen to be caught, but gives no information on the nature of the transition. Some other data are necessary for this purpose.

The additional peaks which are obtained for the soaps containing more than 2 mol. of fatty acids in a soap molecule, are assigned to the fatty acid, and the disappearance of the higher transitions is also due to the presence of the fatty acid, as shown previously.

An observation was made on the visual change of the soaps under a hot stage microscope. The apparent melting points are summarized in Table V. It is apparent that these melting points correspond to the highest transition points, excluding some exceptions; i. e., the highest transition is due to melting.

TABLE V. APPARENT MELTING POINTS AND THE HIGHEST TRANSITION TEMPERATURES OF ALUMINUM SOAPS

Sample	M.p., °C	Tr. temp., °C
Ste-3.22	111	104
Ste-2.29	122	104
Ste-2.12	133	150
Ste-1.89	157	157
Ste-1.71	163	162
Ste-0.95	—	162
Palmitate	171	170
Myristate	183	178
Laurate	188	185
Caprate	196	196
Caprylate	209	216

Many disagreements have been reported on the melting points of aluminum soaps. Licata reported the melting point of aluminum monostearate as 158∼163°C; Lawrence, as 280°C for stearate[1,18]. The disagreement comes probably from the difference in the composition of the samples and in the experimental techniques used. Recently, Wagner reported the softening points of industrial aluminum soaps; 109∼118°C for tristearate, 121∼133°C for distearate, and 165∼170°C for monostearate[19]. It is interesting that these points correspond nearly to the three major transition points, or to the melting point of Ste-3.22, Ste-2.12 and Ste-1.71 in this experiment; however, in his report, one of the three transition points might be observed as melting points due to the impurities contained in the soaps.

The soap at room temperature is in crystalline phase, as found by X-ray diffraction measurement, although the crystallinity of the soap is not so good. The transition below their melting temperature, will be ascribed to some change in crystal structure of the soaps, and the soap passes into a plastic phase with less degree of crystallinity, presumably owing to the disordering of the lateral arrangement. It will be possible to consider that the degree of the loss in the crystallinity by a transition is proportional to the heat of the transition. In this consideration, the stearate shows the most plastic phase at temperatures between the lower and higher transition points. A less degree of crystallinity is found for the soap cooled from the liquid state, in X-ray diffraction measurement, which supports the fact that phase change in the initial heating is irreversible.

Mechanism of Formation of Aluminum Soaps. —The mechanism of soap formation in the aqueous metathetic process is examined. Alexander stated that the precipitate, formed by addition of aluminum salt solution into alkali soap solution, is fatty acid adsorbed on the precipitated aluminum hydroxide, and that the soaps are formed in the drying process. In fact, the fatty acids which are heated at 160°C with aluminum hydroxide give infrared absorption at 980 cm^{-1}, which shows the formation of the aluminum soap polymer skeleton, Al–O–Al. Similarly, the soaps containing more than 2 mol. of acid per aluminum and dried by heating to 110°C, show more intense absorption at 980 cm^{-1} and less absorption at 1720 cm^{-1} than the same soap dried in vacuum at room temperature; these facts suggest that the formation of the soap proceeds by heating, from the fatty acids and aluminum hydroxide in the precipitate. However, the soaps containing less than 2 mol. of acid per aluminum dried by the two methods, give quite identical spectra, which shows that in these conditions, the soaps are formed when precipitated from aqueous solutions.

Summary

Differential thermal analysis of two series of aluminum soaps—aluminum stearates of different compositions, and aluminum soaps from various parent fatty acids—are carried out, and

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[17] S. Shiba, This Bulletin, 34, 198 (1961).

[18] F. J. Licata, "Metallic Soaps", Metasap Chemical Co., Harrison, New Jersey (1940).

[19] E. S. Pattison (Editor), "Industrial Fatty Acids and their Applications", Reinhold Publishing Corp., New York (1959), p. 104.

transition temperatures and the heats of transition are obtained. Each transition point is assigned to a certain change in the structure of the soap or to the soap composition. The structure of the the soaps and the mechanism of soap formation are also discussed, based on the differential thermal analysis and infrared data.

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