THE PREPARATION OF ANHYDROUS SODIUM STEARATE[1]

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Abstract

A method for preparing sodium stearate by the action of sodium amalgam with stearic acid under moisture free conditions is described. From the similar density-temperature behavior of these samples and those prepared by titration of stearic acid followed by melting *in vacuo*, it is concluded that melting under low pressure completely removes the water associated with the sodium ion in soaps.

Previous publications have described dilatometric studies on anhydrous sodium soaps from room temperature to the isotropic liquid state (1, 2, 4, 5). Since these soaps apparently do not melt suddenly but pass through several phases before liquefaction, the studies are of considerable interest. However, the published results have been justifiably criticized on the grounds that the soaps used were not unambiguously anhydrous (3). In most cases the samples were prepared by titration followed by melting *in vacuo* (about 300°C.) to remove the water. It has been considered by Ralston that this treatment is not sufficiently drastic to remove the last traces of water associated with the sodium ion and the same opinion is expressed by Lawrence (2). In view of this it is implied that the peculiar dilatometric behavior of these compounds may be partially due to incomplete dehydration of the samples. The present communication describes a method of preparation which appears to overcome this objection and dilatometric measurements have been made on samples prepared by both methods.

The soap was prepared by the action of sodium on stearic acid in a moisture free atmosphere. The apparatus is shown in Fig. 1 and the preparation was carried out as follows: Prior to assembly, a weighed quantity (5 gm.) of Eastman's white label stearic acid was placed in Flask C (capacity 10 cc.) and mercury in Flasks E and D (capacity 25 and 50 cc. respectively). Clean sodium in large excess of the amount required to neutralize the fatty acid was then placed in A. Tube A was immediately sealed off above the sodium and the pressure inside the apparatus reduced to 10^{-6} mm. The stearic acid was melted and boiled, the sodium melted, the mercury in Flasks E and D boiled, and the remainder of the apparatus strongly flamed.

The sodium was then freed from oxide. This was accomplished by filtering it through the 0.5 mm. capillaries in the column between A and B. Since the assembly could rotate freely about the ground glass joint at F, it was easy to control the flow of the molten sodium from bulb to bulb. Each bulb was sealed off as the sodium passed into the succeeding one. Bulb B was suffi-

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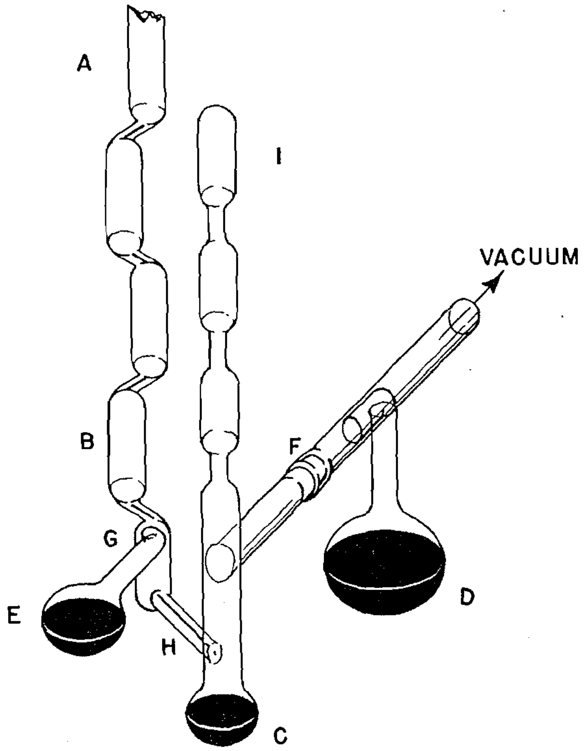

FIG. 1. *Apparatus.*

ciently large to hold about 50% more sodium than required for the neutralization of the acid and it was used as a meter, the excess being sealed off in the previous bulb. Early experiments demonstrated that pure sodium was not suitable for neutralizing the acid. The reaction tended to be too vigorous initially and sodium became trapped in the soap. Further, if the mix were heated too strongly the fatty acid decomposed with considerable blackening. This occurred at temperatures in the vicinity of 300°C.

In order to modify the rate of reaction the sodium was amalgamated in G by distillation in an appropriate volume of mercury from E. The amalgam was then transferred to C and the capillary sealed off at H. Preliminary experiments showed that a good deal of foaming occurred if the reaction were allowed to proceed under the low pressure and to prevent this, an inert gas, dried by passage through a liquid nitrogen trap, was added until the pressure was approximately atmospheric. It has been demonstrated frequently that sodium does not readily react with some acids when the system is completely anhydrous. The reaction between sodium and stearic acid proceeded smoothly under the conditions described above, however, and the temperature was gradually increased, by placing an air bath about Bulb C, until a temperature of about 300°C. was reached and no further hydrogen was evolved. The pressure in the system was then reduced to a hard vacuum and cooled until the soap solidified and pulled away from the walls. By rotating the apparatus through 180° and gently tapping it, virtually all of the residual amalgam flowed into I. This bulb was then sealed off and the assembly again rotated through 180° for further washing with fresh mercury.

In some cases if the amalgam were allowed to cool for an extended period either in G or C it formed a solid that was quite difficult to remelt. No difficulty was encountered when the procedure was carried out continuously. Any residue of the amalgam was removed by washing the soap twice with mercury. The mercury was distilled in from D, the inert gas added, and the soap melted as before, followed by the cooling and decanting of the mercury washings into the bulbs below I.

The soap was finally melted and degassed under a hard vacuum. After cooling, mercury was distilled into Flask C until the neck was partially filled. The neck was constricted and cut off, after air was admitted to the system. The remainder of the dilatometer was then sealed on, evacuated, and completely filled with mercury.

Some experiments that were of considerable interest were carried out to obtain information on the thermal stability of the sodium stearate. Soap containing free fatty acid produced water and stearone when highly heated, until the excess acidity was removed. This reaction is easily detected when carried out at low pressure as the water and ketone deposit in separate bands on the cool part of the apparatus. The neutral soap appears to be very stable and, if oxygen is excluded, may be heated for at least 16 hr. at 350°C. with no apparent decomposition. The above decomposition was first noted when an attempt was made to prepare soap with insufficient sodium. No difficulty was encountered when an excess of sodium was used and the reaction kept at 200°–250°C. until substantially complete.

After completing the dilatometric measurements the soap samples were removed, weighed, and analyzed. The results are shown in Table I. The sample prepared using insufficient sodium to react with the stearic acid was neutral but was low in ash and also low in stearic acid when titrated with standard hydrochloric acid. The samples prepared using excess sodium, however, showed no significant departure from the theoretical. These samples were white solids and melted to give liquids with a faint yellow color.

TABLE I

Analysis of sodium stearate samples

Sample	Sodium used	% Ash	M.p. recovered stearic acid	Free acidity or alkalinity
1	Insufficient	15.4	—	Neutral
2	Excess	17.3	68.6	Neutral
4	Excess	17.2	—	Neutral
Theoretical	—	17.3	68.8	

The volume changes were determined using a weight dilatometer and an air thermostat that could be controlled to better than ± 0.05°C. over the range 25° to 350°C. Calibrated complete immersion thermometers were used to avoid stem corrections. Some difficulty was experienced in obtaining reproducibility in the weight of mercury expelled by the dilatometers at temperatures below 130°C. when the samples were taken to about 300° and then cooled. This seemed to be due to cavitation within the sample, on cooling. To reduce this effect the arms of the dilatometers were extended with 0.5 mm. capillary to give a pressure of about 4 atm. on the samples. Using this device, it was possible to go through the cycle of melting to isotropic liquid and cooling to room temperature several times with no substantial change in the low temperature volume.

For comparison, the density–temperature relations of a sample of sodium stearate prepared by neutralizing an alcoholic solution of stearic acid with alcoholic sodium hydroxide were determined concurrently. The behavior of the samples is shown in Fig. 2, where the weight of mercury (in grams) expelled from the dilatometers is plotted as a function of temperature. Samples 2 and 4 were prepared as described above. Sample 3 was obtained by neutralizing the stearic acid with alcoholic sodium hydroxide. As the same sample weights

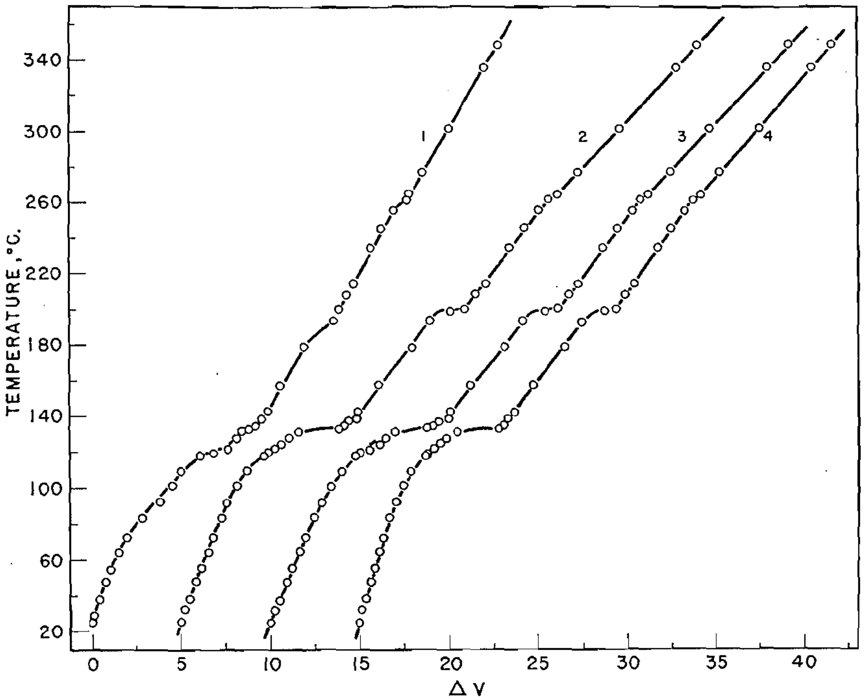

FIG. 2. *Dilatometric behavior of anhydrous sodium stearate. Graphs from left to right represent respectively the behavior of samples prepared (1) from sodium and stearic acid using an excess of stearic acid, (2) from sodium and stearic acid using an excess of sodium, (3) from sodium hydroxide and stearic acid by titration, and (4) from sodium and stearic acid using an excess of sodium.*

and similar dilatometers were used, the slopes should be comparable. Sample 1 indicates the behavior when insufficient sodium was used in the preparation. The sample weight here is also less than with the other preparations, which accounts for the difference in slope. It would seem probable that the extra points of discontinuity that occur in the graph representing the behavior of this sample are due to the presence of the decomposition products of the excess fatty acid that it contains.

Since the dilatometric behavior of the other three samples appears to be identical, it would seem that melting the soap under low pressure is sufficient to render it anhydrous.

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