Thermal Analysis and Calorimetry of Some Fatty Acid Sodium Soaps[1]

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Abstract

Transition temperatures and enthalpies and some phase diagrams of pure odd and even sodium soaps have been determined by means of differential thermal analysis and scanning calorimetry. Branched sodium soaps have been added for comparison.

No essential difference has been found between the number, type, and enthalpy of the transitions of the neighboring odd and even soaps. The total enthalpy and entropy of transition are considerably lower than those of the corresponding paraffins and fatty acids. The entropy of the subneat-neat and perhaps of the neat isotropic transition has an alternating character, which suggests a different methyl end-group packing for even and odd soap. These two facts suggest that the melted soap is still in an organized state.

Introduction

THE EXISTENCE OF SEVERAL allotropic modifications of the sodium salts of straight-chain fatty acids has been known since 1910 (1). In the last 30 years extensive research has been carried out, by using several techniques, to investigate the number and structure of the different phases which occur on heating. The results show that, when the temperature is raised, the structure of the anhydrous soaps changes stepwise from a three-dimensional ordered crystalline state up to 120–140C through liquid crystalline phases of various degrees of order to the isotropic liquid condition (above 260–350C, depending on chain length).

There are still some points which should be elucidated by more or better experiments. For instance, nearly all papers deal with soaps of an even number of carbon atoms in the chain as occurs in biological fats and oils. But with the advent of synthetic fatty acids, which consist, apart from chains with an even or odd number of C-atoms, also of branched chains, we became interested in the behavior of the pure sodium soaps of the latter compounds.

In this paper is described an investigation into a) the transition temperatures of Na-salts of straight-chain fatty acids in the range C_{10}–C_{19} (two branched-chain soaps have been added for comparison); b) the phase diagrams of some binary systems, obtained with the soaps; and c) the enthalpies of transitions. This investigation was carried out by means of differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

Experimental Procedures

Materials

Even and odd soaps $CH_3(CH_2)_nCOONa$ (where n has a value from 8 to 17) were prepared in this laboratory. Gas-chromatographic analysis showed a purity higher than 99.5% except for $C_{11}Na$ (98.2%) and $C_{17}Na$ (98.6%). The two branched soaps (also prepared at URL, Vlaardingen) were 2-methyl myristate (purity 99.2%) and 2-methyl palmitate (97.2%).

DTA and DSC

Differential thermal analysis was carried out with two instruments, viz., a Dupont 900 DTA and a Perkin-Elmer DSC-1. Before measurement the samples were deaerated and dehydrated by evacuating and filling the cell with dry nitrogen several times and heating the samples up to the melting point. In no case could any chemical decomposition under these conditions be detected. Successive measurements, carried out on the same samples, immediately or after conditioning (up to 60 hr) gave identical results. With the Dupont instrument, variation of the heating rates from 1 to 16 degrees per minute showed no influence on the features of the thermogram and only a little on the transition temperatures. The accuracy of the transition temperature measurements was about 1 degree, provided the peak was sharp. With broad or double peaks an error as large as 5 degrees might occur.

The transition heats were determined by means of a Perkin-Elmer DSC. The samples (dehydrated) were weighed on an electrical balance (accuracy 0.02 mg); afterwards the measurements were carried out as with the Dupont. Peak surfaces were measured with a planimeter.

Every determination was carried out several times; the surface of the sharp peaks was reproducible and an accuracy as high as 5% might be obtained. Broad peaks might lead to large errors because it was difficult to draw the base line exactly. For both, determining transition temperatures and enthalpy cooling curves were also recorded.

Sample Preparation for Binary Systems

After weighing in the different amounts of each soap, ethanol analytical grade was added. The mixture was heated until the soap was entirely dissolved. The solution was evaporated and dried under vacuum at 105C to a constant weight.

Results

Transition Temperatures

Straight-Chain Soaps. The transition temperatures of the even straight-chain fatty acid soaps are in general agreement with the literature, for instance, the data of Vold et al. (2) (the most complete as of this date, obtained with dilatometry, microscopy, hot wire), those of Ravich and Neckitailo (3) (DTA), and Skoulios-Luzzati (4) (X-ray). Other DTA investigations in the range of C_{12}–C_{18} (5,6) give some lower transition temperatures, but the general agreement remains.

Generally the thermograms of both odd and even soaps show some common features which permit a comparison of the results. For instance, two large peaks are always found in a temperature range of 135–145C and 245–255C. They may be identified with the subwaxy-waxy and the subneat-neat transitions. The thermograms can be divided into groups of similar features; one thermogram for every group is shown in Fig. 1 (except C_{10} and C_{11}). The transition temperatures as a function of the chain length for the normal soaps are shown in Fig. 2.

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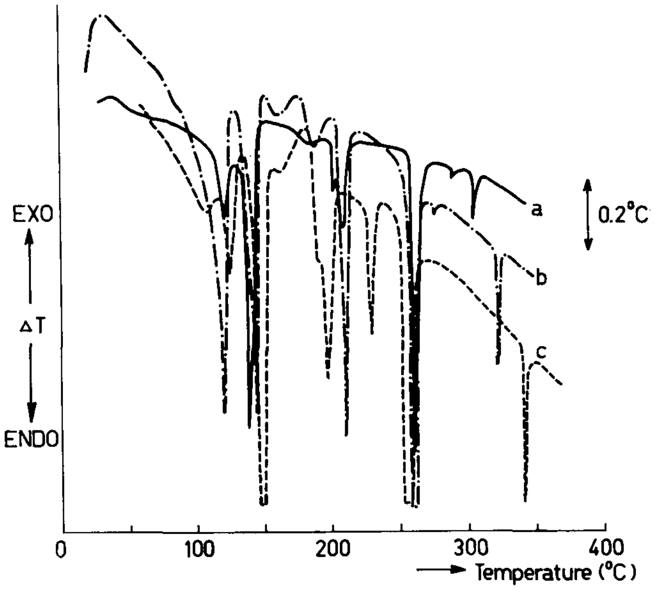

FIG. 1. DTA-curves of a) sodium palmitate (C_{16}), b) sodium myristate (C_{14}), and c) sodium laurate (C_{12}).

At 135–145C all the soaps show a large peak, which may be identified with the subwaxy-waxy transition. Below this temperature all the soaps show a generally smaller peak for the curd-subwaxy transition. Some of them also show a curd-curd transition, but often the results at low temperature are not convincing.

Above the subwaxy-waxy and below the waxy-superwaxy (which is also shown by all the soaps) is seen in the range C_{12}–C_{15}, the appearance of a transition which is not mentioned in the literature. To gain more information, the data obtained with the Dupont were compared with those obtained with the Perkin-Elmer. The latter seemed to give only a shift in the base-line (not a peak), corresponding to a change in the specific heat of the sample. This gave strong evidence for a second (or higher) order transition, not for a phase change.

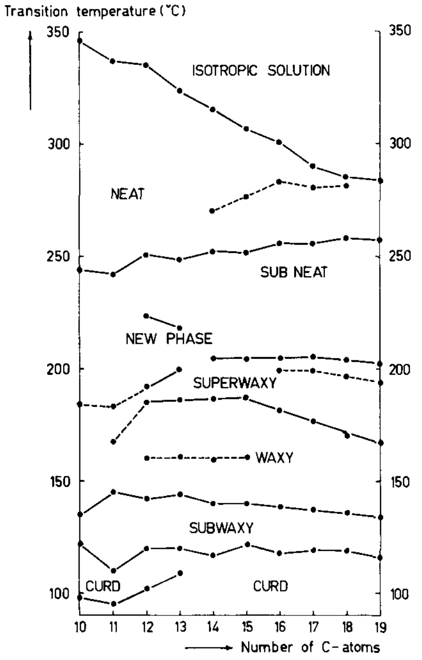

FIG. 2. Transition temperature of even and odd sodium soaps as a function of their chain-lengths.

The transition waxy-superwaxy occurred in these experiments at a somewhat higher temperature than mentioned in the literature, but this was a broad transition where an error in determining the temperature was possible.

Above the waxy-superwaxy transition, Luzzati's "new phase (4)" was observed for C_{12} and C_{13} and perhaps for C_{11}. This phase was originally observed by Vold (7) in a two-components system, but she failed to recognize it in pure C_{12}. Inspection of the data of Ravich (3) gave further evidence for this "new phase." In this temperature range another transition (again not mentioned in the literature) was observed for C_{16}–C_{19}. At present no explanation can be given for this phenomenon. Because there is a clear gap (C_{14}–C_{15}) between Luzzati's new phase and this transition, perhaps they should not be related.

Above that temperature all the soaps showed a peak for the superwaxy-subneat and a major peak for the subneat-neat transition. A small peak (at a temperature strongly depending on the chain length) showed the complete melting of the soap. Below this temperature, within the neat phase, some samples (C_{14}–C_{18}) showed a small but definite and reversible peak, which may be observed with both instruments; it suggested the presence of a third transition not yet mentioned in the literature for Na-soaps. A peak in this region may be found in the work of Stross and Abrams (8), who did not discuss it; similar transitions were observed for K-stearate (9) and Cs-palmitate (10). It should be noted that the transition temperatures of the subneat-neat and of the neat-isotropic showed an alternation as a function of the chain length; they were high for the even and low for the odd soaps.

Branched Soaps. Branched soaps give fewer transitions than the corresponding straight soaps (9). This may be easily explained by taking into account the structure of the molecule: obviously its more complicated form gives fewer possibilities for mesomorphic transitions. It is interesting that the behavior of branched soap is similar to that of normal soaps with a chain-length exceeding C_{22} (2). The two thermograms are shown in Fig. 3.

Phase Diagrams

$C_{12}Na$–$C_{13}Na$ (Fig. 4). These two soaps are completely miscible: one may pass from one phase of $C_{12}Na$ to one of $C_{13}Na$ without crossing a phase boundary. This is proof that any phase in NaC_{12} has its equivalent in NaC_{13}.

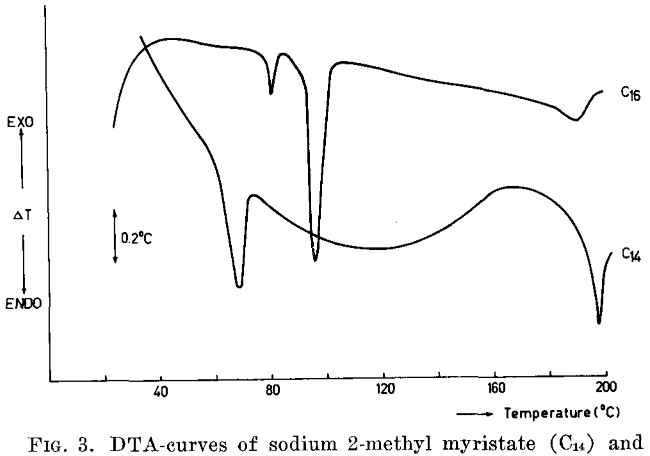

FIG. 3. DTA-curves of sodium 2-methyl myristate (C_{14}) and sodium 2-methyl palmitate (C_{16}).

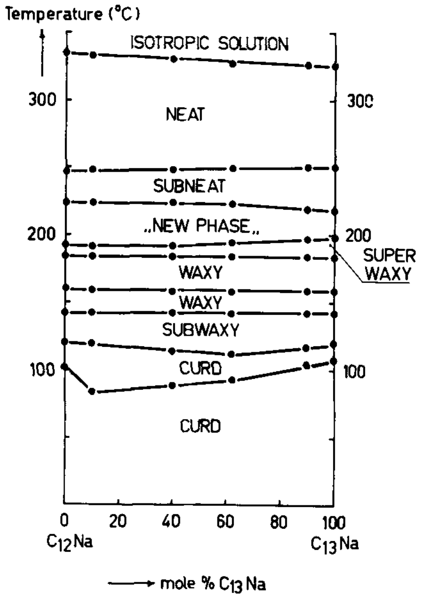

FIG. 4. Binary system sodium laurate (C_{12})—sodium tridecanoate (C_{13}).

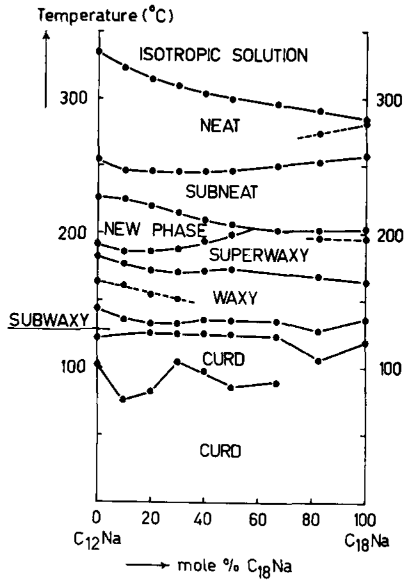

FIG. 5. Binary system sodium laurate (C_{12})—sodium stearate (C_{18}).

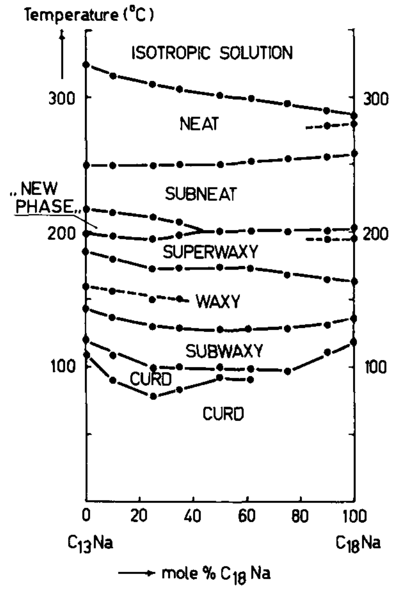

FIG. 6. Binary system sodium tridecanoate (C_{13})—sodium stearate (C_{18}).

$C_{12}Na$–$C_{18}Na$ (Fig. 5). Several regions of the diagram show complete miscibility, as in the previous case. There are some complications because not all the phases of $C_{12}Na$ are present in $C_{18}Na$ and vice versa. For instance, the "new phase" disappears at a NaC_{18} content larger than 40%. As in the previous case, the curd-curd line is a tentative one because the measurements are not reliable below 100C.

$C_{13}Na$–$C_{18}Na$ (Fig. 6). As may be expected, the behavior is the same as $C_{12}Na$–$C_{18}Na$. The region of the "new phase" is smaller.

$C_{13}Na$–$C_{16}Na$ (Fig. 7). The second-order transition at 160C shows a discontinuity at 40% $C_{16}Na$. No explanation can be given at present. As in the preceding diagrams, the transition in the superwaxy and in the neat phase, typical for the soap with the longer chain, disappears when its concentration is lowered.

NaC_{16}–Na-2-Methyl Palmitate (Fig. 8). A tentative phase diagram is given in the figure. As branched soap is introduced into the normal soap, the number of the phases decreases. At 66% a new compound, $C_{16}Na$–$2C_{16}Na$ branched, may be stable between 100C and 200C. An alternative explanation may be the presence of a miscibility gap.

Transition Enthalpies

Most of the transition enthalpies are given in Fig. 9 and 10. Sometimes the peaks overlap so that the transitions cannot be independently measured; therefore the total heat effect has been given for the low temperature region, for the "waxy" region, and for the neat region (thick lines). It is somewhat arbitrary to take the beginning of the "waxy" region at 140C by the subwaxy-waxy transition: most authors agree that the soap network passes from a tri-dimensional order to a two-dimensional order by the curd-subwaxy transition, at about 120C. Yet a large heat effect in these experiments is found in the subwaxy-waxy transition, and it is difficult to relate it with a minor molecular arrangement, such as would happen in the waxy region. A possible explanation is that most authors have carried out their experiments in the presence of water (for instance, with hemihydrate

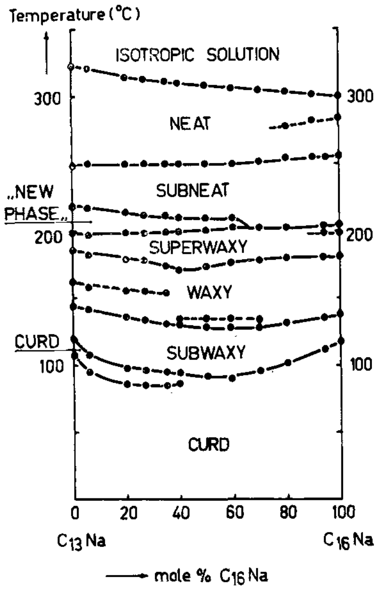

FIG. 7. Binary system sodium tridecanoate (C_{13})—sodium palmitate (C_{16}).

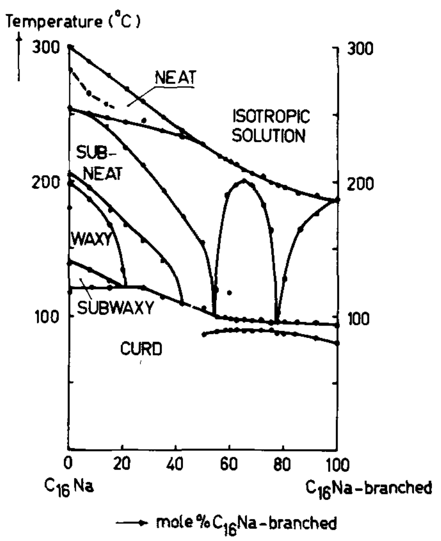

FIG. 8. Binary system sodium 2-methyl palmitate—sodium palmitate.

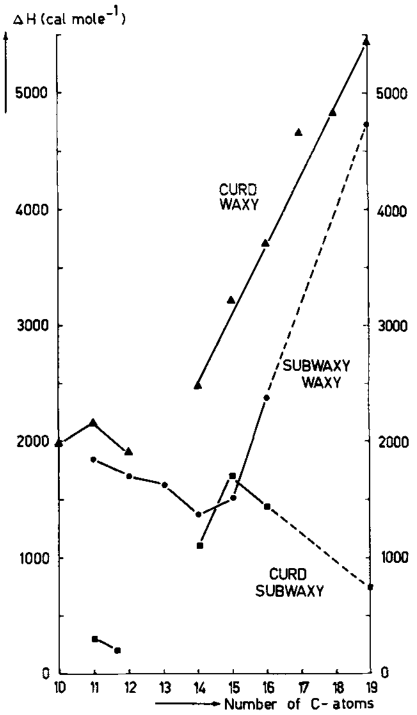

Fig. 9. Transition enthalpies of normal sodium soaps from 90 to 140C.

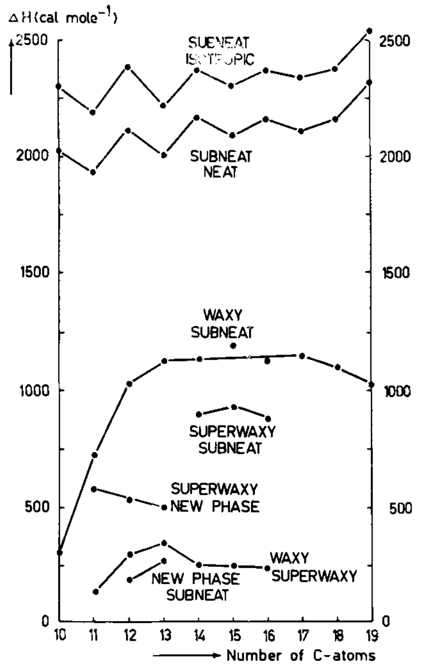

Fig. 10. Transition enthalpies of normal sodium soaps from 140 to 350C.

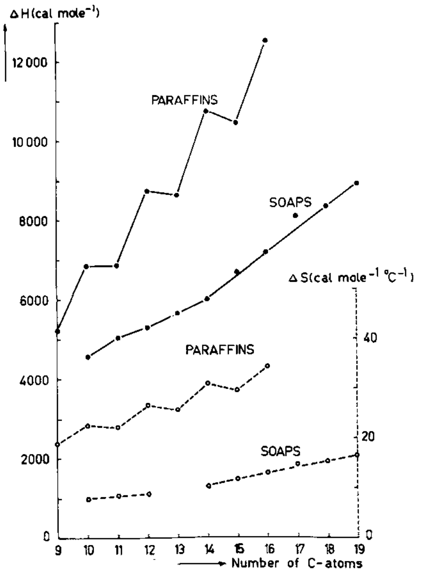

Fig. 11. Total enthalpy and entropy of transition for normal sodium soaps.

soaps); this might lower the temperature boundary of the waxy phase.

In more detail it is seen that the enthalpy for the curd-waxy transition increases markedly as a function of the chain length only for chains longer than 14 carbon atoms. Evidently at shorter chain-lengths the interaction between the polar heads is predominant. C_{11} and perhaps C_{13} have an enthalpy which is higher than C_{12} and C_{14} respectively. Because the transition temperatures are also higher, this would suggest an alternating transition entropy for the first terms (C_{10}–C_{14}); the odd terms would be higher than the even. But the evidence is not adequate.

The total amount of heat involved in the "waxy" region is divided into two or three steps, corresponding to different peaks, which may not always be accurately measured, owing to a superposition of the peaks. It is possible that the experimental conditions might influence the relative magnitude of the peaks, but this does effect that total heat value in the waxy region.

A large heat effect is connected with the subneat-neat transition (Fig. 10). This agrees with a major molecular rearrangement (from two-dimensional to one-dimensional order), as generally accepted. The neat-isotropic transition (not shown) is small, about 0.2 kcal/mole; this is consistent with the model of an organized liquid, similar to the neat phase (4).

For the subneat-neat (or the subneat-isotropic) transition there is evidence of an alternating value of the enthalpy as a function of the chain length. The magnitude of this effect, however, is not far from the experimental error; the chance of obtaining a strict alternation from experimental error only is very low indeed.

A comparison with the data of Vold (5) shows disagreement in most cases; for instance, lower heat effects, in general, were found in the curd-subwaxy region than the 1–5 kcal/mole values he mentioned. This might be explained by the fact that large peaks in this transition occur only when traces of water are present (3,6,8,9). For the other discrepancies we have no explanation. Comparison with the data of Stross and Abrams (8) for $C_{18}Na$ shows good agreement, at least at high temperature.

Discussion

The validity of a dynamic method (like DTA or DSC) in determining equilibrium quantities, such as enthalpies and transition temperatures, is generally accepted but remains a debatable point. An examination of the cooling curves may help; in some cases, either the transition temperatures or the transition enthalpies are almost equal to those obtained in the heating run. When this occurs (for instance always above 180C), one may be confident of working under or near equilibrium conditions. At lower temperatures not all the transitions may be detected (in cooling), only the largest. As far as the transition temperatures are concerned, those obtained by heating can be compared with those obtained by other methods; as far as the enthalpies are concerned, the data must be considered as open to further experiments.

Essentially no difference has been found between number, type, and enthalpy of the transitions (except for the enthalpy of the subneat-neat) of the neighboring odd and the even soaps. Similarity between their IR spectra has already been found by Chapman (11) at low temperature; the phase diagrams seem to give conclusive evidence at a temperature above 100C.

The enthalpy and the entropy of the subneat-neat and perhaps of the neat isotropic transition has an alternating character, similar to that of the melting of fatty acids (12) and paraffins (13) but, of course, much smaller. According to the current views (13–15), this would suggest a different methyl end-group packing for the odd and even chains because from the complete miscibility in this region there is no reason to expect differences in subcell packing between odd and even chains. If this is true, the chains are less "liquid-like" in character (4,11,16) than generally accepted; they would at least be fixed at the two ends. It is interesting now to compare the total amount of heat necessary to melt the soap with the melting heat of paraffins (13) and fatty acids (12) (Fig. 11). The values for the fatty acids are not reported; they approximate those of the paraffins. The value of the enthalpy and entropy for the soaps is much lower than that of the paraffin. The X-ray measurements at low temperature (14) show that packing densities of the hydrocarbon chains of anhydrous soap are similar to those of paraffins and fatty acids, therefore the lower enthalpy might be attributed to a more organized character of the melted soaps (4).

It is not surprising that the total enthalpy of all the soap transitions does not have an alternating character. The small effect in the subneat-neat transition is masked by the experimental error in the low temperature peaks and perhaps by the alternating enthalpies of the subwaxy-waxy transition for C_{10}–C_{14}.

A comparison with the branched soaps shows that the latter have a lower enthalpy than the straight chain (3.6 kcal/mole, for C_{16}) but a comparable value of the entropy (about 9 kcal/mole °C).

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