an open, stirred solution. That the important variable is the time during which both components are present and able to exchange is shown by catalysts F-4 and F-5. In the former, the copper (and, unavoidably, some of the magnesium) was precipitated rapidly (one minute) and the magnesium at the rate for a two-hour catalyst (ninety-three minutes). Thus there was approximately the same opportunity for exchange of the components as in the standard two-hour catalyst, and the activity ($k = 7.2$) was nearly the same as that of the two-hour catalyst ($k = 6.7$). The difference between these is probably within the experimental error for this series. In marked contrast to this activity is that for catalyst F-5 ($k = 4.2$). Here the copper was precipitated at the two-hour rate (twenty-six minutes) and the magnesium in one minute, allowing only one minute for the bulk of the magnesium to exchange with the copper–magnesium mixture precipitated at first.

The results for variation of activity with washing may be explained as follows. The initial rises in both curves probably result either from removal of adsorbed material, giving access to more active portions of the surfaces, or to decrease in particle size from incipient peptization. The further slow increase in activity of the catalysts prepared by reverse coprecipitation is perhaps caused by continuation of either of these effects, or by an actual change in surface composition through differential solubility. The rather rapid fall in activity with further washing of the catalysts prepared by ordinary coprecipitation may have one of two explanations. Either it results from actual change in composition of the surface through differential solubility, or, as seems more likely when the results of the analyses are considered, some of the more active material is lost in the wash water through peptization (which began to be marked from the second washing on). The composition change with washing is erratic for this series, as would be expected for peptization, while that for the reverse series is uniform and in the direction demanded by the solubilities.

Summary

1. The activities for hydrogen peroxide decomposition of copper hydroxide–magnesium hydroxide catalysts prepared by ordinary coprecipitation are affected by changes in the rate of precipitation and the extent of washing. These changes in activity are comparable to those caused by wide variations in composition.

2. Similar catalysts prepared by reverse coprecipitation (addition of metal nitrates to base) are affected only slightly by these variables.

3. The results can be interpreted in terms of the inhomogeneity previously shown to exist in catalysts prepared by ordinary coprecipitation.

SALT LAKE CITY, UTAH RECEIVED AUGUST 6, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Anhydrous Sodium Soaps. Heats of Transition and Classification of the Phases*

BY ROBERT D. VOLD†

It has already been established[1] that instead of melting directly from crystal to liquid, sodium salts of long-chain fatty acids pass through a remarkable series of forms, each constituting a definite stable phase existing over a definite range of temperature. A calorimetric investigation has now been made of sodium laurate, myristate, palmitate, stearate and oleate to aid in interpretation of the phenomena occurring at transitions between these phases. This study has given values for the heats of transition and provides an independent determination of the transition temperatures. Further confirmation has been obtained of the reality of some of the transitions which had previously been found only with the microscope or with the dilatometer, but not with both.

An important initial problem in connection with the multiplicity of soap phases is that of classification. To what extent can phases occupying the same numerical position in the sequence, beginning with isotropic liquid, be regarded as similar? A beginning[1,2] had already been made

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[1] M. J. Vold, M. Macomber and R. D. Vold, THIS JOURNAL, 63, 168 (1941).

[2] M. J. Vold, *ibid.*, 63, 160 (1941).

with this question by comparison of the optical and mechanical properties of the various phases of different soaps, study of the phase relations in binary mixtures and investigation of the regularities of the curves of transition temperature *vs.* number of carbon atoms in the chain (hereafter referred to simply as chain length). The present work assists in the identification of corresponding transitions since it can be presumed that the heat of transition will be similar or vary regularly with the chain length in the case of transformations involving changes between corresponding phases of different soaps.

Comparison of the magnitude of the heat effect and volume effect at different transitions and consideration of the way in which these quantities vary with the chain length of the soap can be made the basis for speculation concerning the actual mechanism of some of the steps in the process of melting.

Experimental Method and Results

Apparatus.—The experimental procedure consisted of measuring the difference in temperature between a sample of soap and a reference sample of similar size, shape and heat capacity as both were heated in the same environment. Whenever the soap underwent a transition with evolution or absorption of heat, the temperature difference between the two cells usually changed abruptly. The apparatus designed is shown in Fig. 1.

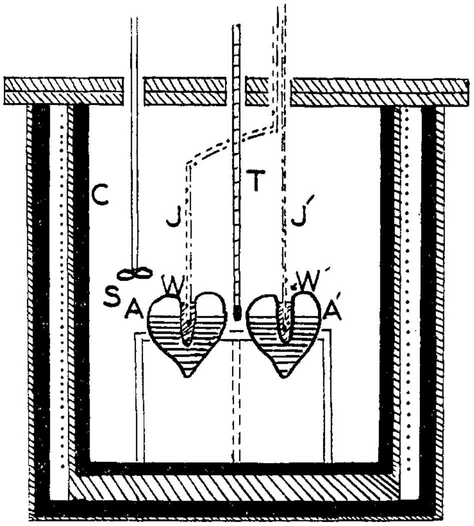

Fig. 1.—Diagram of differential calorimeter.

About one gram of soap was weighed into the pear-shaped glass cell A, blown from Pyrex tubing of 7 mm. o. d., whose over-all dimensions were about 2.5 × 2.5 cm. This was then sealed at the neck. The soap was melted and allowed to solidify in a coherent cake around the thermocouple well W. Thermal contact between the iron–constantan single junction thermocouple J (insulated with glass fiber binding) and the glass cell was made by filling the well with a specimen of polyisobutylene which did not evaporate completely even when the temperature rose to 360°. A′ was a similar cell filled with Nujol, a medicinal paraffin oil which, in a sealed cell, has no discontinuities in thermal properties between room temperature and 360°. Heat was transferred to the cells by radiation and convection from the heated walls of the container C, which consisted of two concentric cans insulated with asbestos, the outer surface of the inner can being wound with resistance wire. The furnace was provided with a double cover of asbestos board, through which extended the shafts of small electrically driven stirrers, the thermocouple leads and a mercury-in-glass thermometer T, calibrated in place for emergent stem correction, whose bulb was located on a level with and midway between the sample cells. The temperature was controlled by manual adjustment of a variable transformer so as to maintain the rate of heating or cooling nearly constant. Rates of 1.5 and 1° per minute were generally used. The e. m. f. produced by the thermocouple was measured by a Leeds and Northrup Type K potentiometer and Type HS galvanometer, the sensitivity of the circuit being such that 1-mm. scale deflection equaled 0.15 microvolt, or about 0.003°. The maximum fluctuation in the temperature difference between the two cells due to uncontrolled factors was about ten microvolts.

Both the temperature of the system and the difference in temperature between the cells were recorded every two minutes. These values were then plotted against time, typical curves for each of the soaps being shown in Fig. 2.

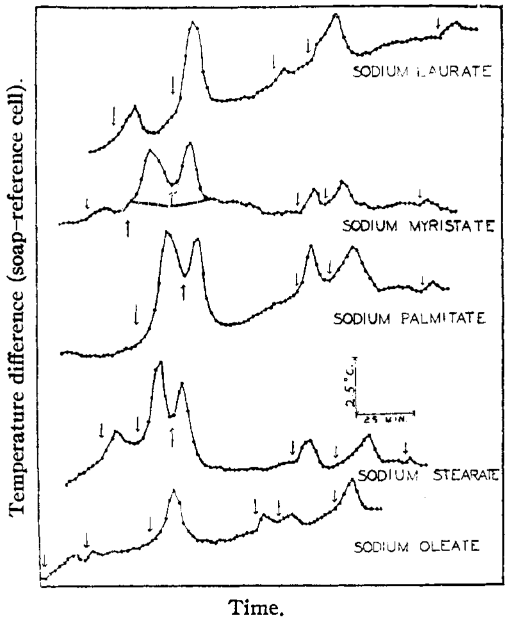

Fig. 2.—Typical time–differential temperature curves.

Transitions are indicated by the occurrence of peaks in the curves, the transition temperature being taken as that value of the all-over temperature at which the ΔT curve first deviates from a smooth course. These temperatures are marked by arrows in Fig. 2. In cases where ΔT is already increasing fairly rapidly, due to premelting or other factors, precise location of the exact time and thus the exact temperature of the transition was somewhat arbitrary. However, the margin for choice was not large, either in the temperature itself or in the quantities (ΔT and area) used to calculate the heats of transition.

Precautions.—The successful operation of this technique depends on the attainment of a steady state involving the balance of a large number of experimental variables. A temperature difference develops between the soap cell and the Nujol cell even at a steady rate of temperature change because of differences in packing of the samples, in their heat capacity, geometry of the cells, etc. Neither the absolute value of ΔT nor its sign is of any significance since these depend to a large extent on accidental factors, such as the exact position of the cells in the calorimeter, whether the temperature is rising or falling, etc.

In the absence of transitions, ΔT can be expected to remain nearly constant or change slowly and continuously as the temperature changes with time. The temperature where peaks in the ΔT curve *just begin* to form is the proper value for the transition temperature rather than the temperature at the maximum of the peak, since time is required after the transition has occurred before thermal equilibrium is reached. The "steady state" value of ΔT after the transition may differ markedly from that before the transition because of changes in the thermal contact between the sample and the glass of the cell, and in the specific heat of the sample.

Many factors other than transitions in the soap sample can cause fluctuations in the ΔT curve. These factors were evaluated experimentally by numerous preliminary experiments (23 on sodium palmitate with various alternative reference materials and liquids for use in the thermocouple wells) until a satisfactory technique was evolved.

One of the most important sources of difficulty is change in the rate of heating of the calorimeter. Other disturbing influences include poor or variable thermal contact between the thermocouple junction and the samples because of gradual volatilization of polyisobutylene at the higher temperatures, changes in the position of the sample in the cell due to softening as the temperature increases, formation or disappearance of vacuoles in the soap, and chance draughts affecting the calorimeter or the thermocouple leads. Further disturbing possibilities are traces of decomposition which may occur when samples remain too long at very high temperatures, or too rapid a rate of heating which would be expected to give rise to spuriously high transition temperatures. In some instances premelting was marked, the transition beginning to take place at somewhat lower temperatures than that at which the bulk of the change occurred.

If a given transition has only a very small heat effect (transitions with ΔH as low as 200 cal./mole were readily detected) it may not give rise to a sufficient difference in temperature to show on the curves. Similarly, if a transition occurs very slowly, or over a range of temperature, it may not be marked by a peak, or sharply defined change of slope of the ΔT curve, and so might not be detected. Consequently, although the presence of a peak in the ΔT curve denotes a transition, the converse is not necessarily true.

Despite its limitations, however, the present apparatus provides a powerful tool for the study of transitions even in cases where the very existence of a change is difficult to establish by other methods. Although this calorimeter is very much cruder and less precise than that of a similar type described by Stull,[3] it is much simpler to set up and use, very sensitive, can be used at elevated temperatures, and yields reasonably satisfactory results.

Heats of Transition.—In order to obtain values for the heats of transition from the curves of differential temperature against time, the calorimeter was calibrated with a series of solids of known melting point and heat of fusion, these being palmitic acid, benzoic acid, silver nitrate and sodium nitrate. Results were calculated using the equation

$$\Delta H = \frac{k\,(c_{p,g}\,m_g + c_{p,s}m_s)\int \Delta T\mathrm{d}t}{m_s\,\Delta t} \qquad (1)$$

where ΔH is the heat of fusion per gram, k is a proportionality constant, $c_{p,g}$ the specific heat of the glass in the calorimeter cell, m_g the weight of the glass, $c_{p,s}$ the average value of the specific heat of the calibration substance in the solid and liquid state, m_s the weight of the sample, $\int \Delta T\,dt$ the area under the peak in the differential temperature–time curve, and Δt the total time during which there is a peak in the ΔT–time curve. The area taken was that included between the peak and the curve of ΔT *vs.* time which would have resulted in the absence of transition, obtained by extrapolation of the fore and after curves through the region of transition. The values used and results obtained are assembled in Table I, where it is clear that k is reasonably constant over the whole range of temperature.

This equation differs from the method of calculation used by previous authors[4] who have taken only the area under the curve as being a measure of the heat effect. In order that the equation may be dimensionally correct it is necessary to divide by Δt, the time during which the thermal disturbance occurs. The situation is complicated by the fact that differential thermal analysis measures no real physical constant of the system, at least three time lags being important to the observed phenomena: (1) the rate of transfer of heat from the hot walls of the oven to the sample, (2) the rate at which temperature equality is reestablished between sample and reference material after a transition, and (3) the intrinsic rate at which a given transition occurs. Unless nearly equal increases in temperature occur at each of the transitions, and unless all the transitions occur at substantially the same rate, a condition not realized in the case of the soaps,[5] the second and third factors may be sufficiently important to introduce serious errors into the results as calculated from the area under the peak. Dividing these areas by the respective times over which change occurs in the differential temperature amounts essentially to calculating the magnitude of the heat effect from an average value over the time interval of the rise in temperature caused by the transition.

In a few instances peaks corresponding to two adjacent transitions were not completely resolved. For purposes of calculation these partially superposed peaks were separated and the area of each taken as what it would have been

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(3) D. R. Stull, THIS JOURNAL, **59**, 2726 (1937).

(4) S. B. Hendricks, R. A. Nelson and L. T. Alexander, *ibid.*, **62**, 1459 (1940).

(5) R. D. Vold and M. J. Vold, *ibid.*, **61**, 808 (1939).

TABLE I

CALIBRATION DATA

Substance	M. p., °C.	Obs. m. p. in calorimeter	ΔH	c_p liquid	c_p crystal	$\bar{c}_p$	k of Eq. 1	Av. k
Palmitic acid	62.3[a]	61	13030[a]	0.542[a]	0.492[a]	0.52	88.4	92.0
		59					95.7	
Benzoic acid	121.8[b]	122	4140[c]	.514[b]	.346[b]	.43	77.2	81.9
		122					79.4	
		122					89.0	
Silver nitrate	208[b]	202	2760[d]	.195[b]	.156[b]	.18	88.9	89.1
		203					89.3	
Sodium nitrate	308[e]	304	3850[b]	.431[b]	.388[b]	.41	94.8	94.8
		303						
							Av.	89.5±4.2

[a] W. E. Garner, F. C. Madden and J. E. Rushbrooke, *J. Chem. Soc.*, 2491 (1926); also, Stratton and Partington, *Phil. Mag.*, **48**, 1085 (1924). [b] "International Critical Tables," Vol. V. [c] D. H. Andrews, G. Lynn and J. Johnston, THIS JOURNAL, **48**, 1274 (1926). [d] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Co., New York, N. Y., 1936, p. 78. [e] Landolt–Börnstein, "Tabellen," 5th ed., Vol. I, p. 349.

in the absence of the other. An example of this procedure is illustrated in Fig. 2 for sodium myristate. The intercept of the extrapolated portion of the second peak with the ground curve might constitute a more consistent choice for the temperature of this transition than is the bottom of the trough between the two peaks, but is not significantly different from it in practice and furthermore is unsatisfactory because of the necessity for two extrapolations in its determination.

Since the calorimeter was being used essentially as a transfer instrument, one might think that correct values would be obtained for the heats of transitions of the soaps provided the experimental conditions were similar, regardless of how the results were calculated, so long as the soaps and calibration substances are treated alike. This, however, is not the case. With a value of k calculated from the results with reference materials by using only the areas under the peaks, the heat of transition of sodium palmitate from curd fiber phase to subwaxy soap, calculated in a similar manner, was 3270 cal./mole (mean of four). The same data gave a value of 4800 cal./mole when calculated allowing for the time factor. To help decide between the two, the heat effect at this transition was determined independently by a "method of mixtures" in which a known amount of hot oil was run into a Dewar vessel containing the sample and a known amount of cold oil, the heat of transition being calculated from the differences in temperature on mixing. This experiment gave the value 4650 cal./mole (mean of two). Thus it seemed necessary to use an equation of the general form of (1) in order to obtain correct values for the heats of transition.

Materials.—For calibration substances Kahlbaum best (brown label) palmitic acid (m. p. 62.2° by M. E. L. McBain), Bureau of Standards certified benzoic acid, Baker and Adamson reagent quality silver nitrate, and Kahlbaum sodium nitrate (previously used to standardize our temperature scale) were used, all without further purification.

The soaps were from the same stocks used for previous investigations and have already been described (two preparations of sodium laurate,[6,7] two of sodium myristate,[1,8] sodium palmitate,[5] sodium stearate,[9] and sodium oleate[10]). All the soaps were neutral and free from unsaponifiable material. They were dried at 105° immediately before use.

Experimental Results.—Values for the heats of transition of the soaps were calculated from the areas and time intervals under the peaks in the curves of differential temperature against time by means of equation (1), taking k as 89.5, and multiplying the values obtained by the appropriate molecular weight. Somewhat arbitrarily 0.50 cal./deg./g. was taken as the value of the specific heat of all the soaps at transitions through the waxy–superwaxy, 0.525 at the superwaxy–subneat transition and 0.55 at the two topmost transitions. These figures are based on the experimental result[11] that for all the common soaps the specific heat of the "crystalline form" above the genotypic temperature is close to 0.500 cal./deg./g. and for palmitic acid (see Table I) the specific heat of the liquid is about 10% greater than that of the solid. The change from low temperature to high temperature value was made with the soaps at the superwaxy–subneat transition since it is accompanied by one of the greatest changes in mechanical properties.

Typical data are shown for sodium palmitate in Table II. It is evident that the transition temperatures are quite reproducible. The results for heats of transition fluctuated much

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(6) J. W. McBain, G. C. Brock, R. D. Vold and M. J. Vold, THIS JOURNAL, **60**, 1870 (1938).

(7) R. D. Vold and M. J. Vold, *ibid.*, **61**, 37 (1939).

(8) R. D. Vold, R. Reivere and J. W. McBain, *ibid.*, **63**, 1293 (1941).

(9) J. W. McBain, R. D. Vold and M. Frick, *J. Phys. Chem.*, **44**, 1013 (1940).

(10) J. W. McBain, M. J. Vold and S. A. Johnston, THIS JOURNAL, **63**, 1000 (1941).

(11) P. A. Thiessen, J. v. Klenck, H. Gockowiack and J. Stauff, *Z. physik. Chem.*, **A174**, 335 (1935).

TABLE II

DATA FOR SODIUM PALMITATE

Run	Soap, g.	Glass, g.	Thermal history[a]	Rate of heating. °/min.
A	1.5855	1.7689	5 days	2
B	1.5855	1.7689	24 hrs.[b]	1
C	1.5610	1.1270	18 hrs.	1
D	1.5610	1.1270	9 mo.	1.5

Run	Temp., °C.	Area under peak, in.^{2}	Max. ht. of peak, μv.	Time under peak, min.	ΔH cal./mole
Transition curd–subwaxy					
A	114	6.05	160	30	3630
B	115	8.07	210	23	6310
C	113	6.75	200	24.5	4410
D	114	6.47	240	21.5	4820
Av.	114 ± 1				4800 ± 740
Transition subwaxy–waxy					
A	131	..	..	..	..
B	135	5.36	170	24	4030
C	134	5.12	164	23	3560
D	138	5.45	210	21.5	4060
Av.	135 ± 2				3880 ± 220
Transition superwaxy–subneat					
B	211	2.00	84	20	1860
C	205	1.70	60	19	1490
D	212	1.98	100	15	2200
Av.	209 ± 3				1850 ± 240
Transition subneat–neat					
B	240	1.45	48	24	1154
C	235	2.16	62	31	1203
D	235	2.63	90	20	2270
Av.	237 ± 2				1540 ± 480
Transition neat–isotropic liquid					
B	289	..	..	..	..
C	292	0.35	26	12	504
D	294	0.17	20	6	489
Av.	292 ± 2				500 ± 10

[a] All samples were first melted, then cooled to room temperature over a period of two to three hours, and allowed to stand for the length of time shown in the table. No experiments were performed to determine possible changes which might be brought about by annealing. [b] In this instance, the sample was first melted, cooled to room temperature, reheated to 140°, cooled, and let stand twenty-four hours at room temperature prior to the run.

more widely than did those on the calibration substances, possibly because of differences in the initial crystalline form of the soap or of incomplete conversion of the sample from one phase to the other on the initial cooling from isotropic liquid. However, they are sufficiently precise to permit unambiguous comparison of the relative magnitudes of the heat effect at the different transitions and of the variation of these values from soap to soap. The effect of such factors as changes in the relative weights of soap and glass cell, rate of heating (within limits), source of the soap, and previous thermal history caused variations in the heats of transition which were scarcely larger than uncontrolled experimental fluctuations. None of these factors caused any systematic change in the values with the possible exception that abnormally small samples seemed to give low results.

In one run, not shown in Table II, the differential temperature of a sample of sodium palmitate was determined on cooling from the melt to room temperature. Transition temperatures between isotropic liquid and neat soap, neat and subneat soap, and subneat and superwaxy soap were substantially the same as those obtained on heating, thus showing that any difference between the calorimetric values and previous data (*cf.* particularly the transition temperature of subneat to neat soap, to be discussed below) cannot be ascribed to errors due to premelting phenomena.

Values obtained on cooling for the transition temperatures between waxy and subwaxy soap, and subwaxy soap and curd fiber phase were, respectively, 6 and 7° lower than those obtained on heating. In the case of the curd–subwaxy transition this effect is probably due to undercooling. At the subwaxy–waxy transition, however, it may be due to a slow rate of transition just below the thermodynamic transition temperature, followed by a much faster rate at somewhat lower temperatures, as was found dilatometrically.[5] On this view, however, a similar phenomenon might be expected at the subneat–superwaxy transition, whereas here the same value is obtained calorimetrically on either heating or cooling.

Average values for the heats of transition of all the soaps studied are given in Table III. One typical ΔT–time curve for each soap is shown in Fig. 2.

It is noteworthy that no heat effects were detected corresponding to the genotypic temperature, a change believed to occur in the sodium soaps at a temperature near the melting point of the corresponding fatty acid.[11] This transition is probably either absent or has a heat effect considerably smaller than the reported value of 200.0 cal.,[11] since the curd–curd transition of sodium myristate (ΔH = 215 cal.) showed up clearly, although possibly the difficulties discussed earlier might be responsible for its failure to appear even though the transition actually did occur.

TABLE III

HEATS OF TRANSITION OF THE SODIUM SOAPS (CALORIES PER MOLE)[a]

Transition	Na laurate			Na myristate			Na palmitate[5]	Na stearate[9]	Na oleate[10]
	Kahlbaum[6]	Eastman[7]	Av.	Kahlbaum[1]	Lepkovsky[8]	Av.			
Curd–curd	abs.	abs.	abs.	200(1)	230(4)	215[b]	abs.	945(2)[b]	1610(5)
Curd–subwaxy	1220(1)	1080(2)	1150	2930(1)	4120(5)	3525	4800(4)	5180(2)	320(2)[e]
Subwaxy–waxy	3750(1)	2830(2)	3290	3210(1)	3600(4)	3405	3880(3)	4030(2)	2890(6)
Waxy–superwaxy	620(1)	580(2)	600	abs.	abs.	abs.	abs.	abs.	890(3)
Superwaxy–subneat	2220(1) abs.[c]	1180(2) 505(1)[e]	1950	1110(1) abs.[d]	1410(4) 1300(4)[d]	1910	1850(3)	1600(2)	860(1)[e]
Subneat–neat	abs.	abs.	abs.	1270(1)	1400(4)	1335	1540(3)	1560(2)	1920(3)[f]
Neat–isotropic	350(1)	1290(1)	820	260(1)	720(4)	490	500(2)	535(2)	
Total	8160	7465	7810	8980	12780	10880	12570	13850	8490

[a] Numbers in parentheses give the number of runs averaged to give the final result. [b] These transitions, occurring at 80 and 89°, respectively, for myristate and stearate, do not correspond to any of the transitions yet found for the other saturated soaps. [c] Extra transition occurring at 287°. [d] Double transition occurring at 204 and 220°. [e] These values were obtained with a preparation of sodium oelate made from a specially purified sample of oleic acid obtained from Professor Brown of Ohio State. The sodium oleate made from the British Drug Houses oleic acid failed to show either of these transitions calorimetrically. [f] In the case of sodium oleate, subneat soap melts directly to isotropic liquid, there being no phase corresponding to the neat soap of the saturated soaps.

TABLE IV

TRANSITION TEMPERATURES OF THE SODIUM SOAPS

Transition	Na laurate[a]		Na myristate[b]		Na palmitate		Na stearate		Na oleate	
	calor.	lit.[c]	calor.	lit.[c]	calor.	lit.[c]	calor.	lit.[c]	calor.	lit.[d]
Curd–curd	...	...	80	80	...	...	89	90	40	38[e]
Curd–subwaxy	98	100	106	107	114	117	114	117	66[e]	65
Subwaxy–waxy	130	141	133	141	135	135	134	132	115	118
Waxy–superwaxy	187	182	...	176	...	172	...	167	187	179
Superwaxy–subneat	220	220	215	217	209	208	208	205	202[e]	218[e]
Subneat–neat	...	244	233	245	237	253	238	257	237[f]	256[f]
Neat–isotropic	324	336	297	310	292	295	280	288		

[a] Soap made from Eastman Kodak Co. lauric acid. [b] Soap made from Kahlbaum myristic acid. [c] Values from reference 1. [d] Values determined dilatometrically and microscopically by Dr. M. J. Vold. [e] These values determined on a sodium oleate sample prepared from a specially purified oleic acid furnished through the courtesy of Professor J. B. Brown. [f] These temperatures refer to the melting of subneat sodium oleate to isotropic liquid, there being no neat soap phase with this soap.

The explanation is probably to be sought in the multiplicity of crystalline forms in which the soaps can exist.[12] In one experiment a sample of anhydrous sodium palmitate was prepared by drying an aqueous solution at 105°, and run directly in the calorimeter without prior heating to the melt. In this case also, however, there was no indication of a heat effect at the genotypic temperature. Possibly the genotypic transition occurs only with the monoclinic form of sodium palmitate obtained by heating the rhombic crystal.

The additional transitions found with the Eastman sodium laurate and the Lepkovsky sodium myristate, but not with the Kahlbaum products, are certainly real. They are quite confusing since there is no place for them in the regular series of transitions.

The transition temperatures obtained calorimetrically are compared in Table IV with values obtained by dilatometric and microscopic methods.[1]

Discussion

Classification of Phases.—The data of Table III can be used to help determine whether the same series of phases of the same structure appear on cooling the isotropic liquids of different soaps.

Since the heat of formation of neat soap from isotropic liquid is similar for all four saturated soaps studied, it is reasonable to assume that a similar structural rearrangement has taken place in all cases and that the neat soap phase has the same internal structure for all. This hypothesis is supported by the fact that these soaps are completely miscible either as the isotropic liquids or as neat soap phases.[2] However, it leaves unex-

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[12] A. de Bretteville and J. W. McBain, communicated to THIS JOURNAL.

plained the apparent existence of breaks in the curve of melting point *vs.* chain length.[1]

The heat effect at each of the lower transitions neat → subneat → superwaxy → waxy → subwaxy → curd fiber phase—is about the same for the myristate, palmitate and stearate, or varies regularly with the chain length. However, the succession of phases for sodium laurate does not appear to be entirely the same as for the other saturated soaps. No heat effect was found with the laurate at the neat–subneat transition, although the other saturated soaps all have appreciable heat effects at this change. The laurate behaves the same as the other soaps at the subneat–superwaxy and waxy–subwaxy transitions, but has an appreciable heat effect at the superwaxy–waxy transition where none was detected for the other saturated soaps and has a very much smaller heat of transition from subwaxy to curd fiber phase than do the others.

In view of these facts it is not surprising that the phase behavior of sodium laurate with other soaps is very complicated, with limited miscibility of the phases,[2] whereas mixtures of palmitate and stearate follow a much simpler pattern. Despite the limited miscibility of the lower temperature forms of the different soaps[2] it seems reasonable to call the succession of phases of the saturated soaps by the same names (with a presumption of a definite and identical type of mesomorphic structure, except possibly with the laurate), since the heat and volume effects are similar at the successive transitions with the exceptions noted above for the laurate.

It is difficult to imagine two completely different sets of discrete changes in the transformation from the monoclinic crystal[12,13] to a smectic liquid crystal in which the molecular axes are parallel with the heads still in parallel planes, since the net change in structure is relatively small. Consequently it seems likely that sodium laurate undergoes the same set of changes as the other saturated soaps but perhaps in a somewhat different sequence. Progressive shortening of the hydrocarbon chain alters the balance between polar and non-polar portions of the molecule and may be the reason for the difference in behavior noted first with the laurate.

The succession of phases of sodium oleate, counting down from the melting point, is different from that with the saturated soaps. The heat of fusion of subneat sodium oleate to isotropic liquid is of the same order of magnitude as the sum of the heat effects at the subneat–neat and neat–isotropic liquid transitions of the saturated soaps, in accord with the concept that this change is really a "double" transition.[1] Moreover, the heat effects at the successive transitions of sodium oleate are in general quite different from those of the saturated soaps, as is clearly evident in Fig. 3. Possibly these differences arise from the improbability of saturated and unsaturated chains packing together in the same manner. Thus, the total heat of fusion of sodium oleate (Table III) appears to be substantially smaller than that of sodium stearate where closer packing of the chains is possible.

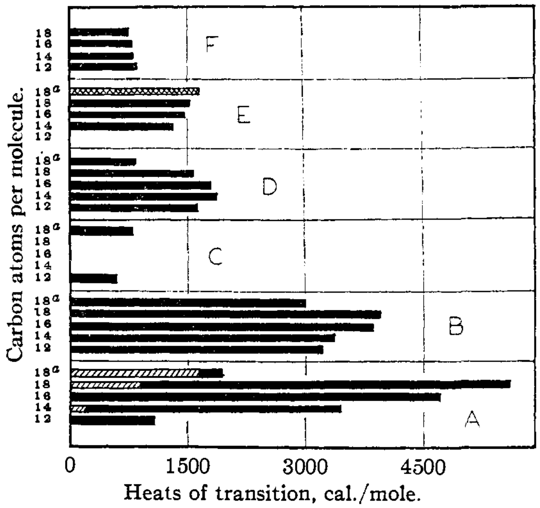

Fig. 3.—Dependence of the heat of transition on chain length and nature of the transition. 12 = laurate, 14 = myristate, 16 = palmitate, 18 = stearate, and 18^a = oleate. A is the transition from curd fiber phase to subwaxy soap except that the barred band is the contribution of a "curd–curd" transition; B is the subwaxy ⟷ waxy transition; C, the waxy ⟷ superwaxy transition; D, the superwaxy ⟷ subneat transition; E, the subneat ⟷ neat transition except the double-barred band for sodium oleate which melts directly from subneat soap to isotropic liquid; and F, the neat ⟷ isotropic liquid transition.

Despite these differences in relative heats of transition, the subneat phase of sodium oleate is completely miscible with subneat sodium stearate.[2] Similarly, although the changes in heat content and volume are much smaller for sodium oleate than for the saturated soaps at the transition corresponding to the subneat–superwaxy change of the latter, microscopic appearance

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(13) P. A. Thiessen and J. Stauff, *Z. physik. Chem.*, **A176**, 397 (1936).

shows definitely that the sodium oleate phase above this temperature is of the "neat soap type" (neat and subneat), while that below is unmistakably a member of the "waxy" group. In the interest of simplicity it seems necessary to call the successive sodium oleate phases, counting downward from subneat soap, by the same names as those used for the saturated soaps, even though there is no necessary presumption of identity of internal structure between the phases of sodium oleate and those of the saturated soaps.

Division of the Total Heat of Fusion among the Several Transitions.—Most of the energy of melting is absorbed in the transitions from curd fiber phase to subwaxy soap and from subwaxy to waxy soap. These two transitions are also accompanied by large changes in the specific volume. Consequently, it is plausible to assume that subwaxy soap and all phases occurring at higher temperatures are mesomorphic rather than fully crystalline, even though the flow properties of liquid crystals and such characteristic optical effects as batonnets, focal conic structures, etc., have not been observed below subneat soap.

In general the relative magnitude of the heat effect and the volume change is the same at different transitions, but at the transformation from superwaxy to subneat soap the change of volume is disproportionately larger than the heat of transition. In this instance a very large rearrangement of structure, judged by the change in volume, is accompanied by only a small change in the energy content. This might be interpreted to mean that only weak forces were operative to maintain the structure of the superwaxy phase. More likely, however, the "bonds" involved are strong, since the structure is not broken down until a high temperature, but their number is relatively small as would be the case if the terminal polar groups were chiefly responsible for the internal arrangement of the molecules in superwaxy soap.

This transition is also marked by the loss of mechanical solidity and a very great change in microscopic appearance. The subneat soap which is formed expels any residual traces of water which might be present. If the light scattering is dependent on the size of the scattering unit even in lyophilic colloidal systems,[14] then the oriented scattering regions in subneat soap are probably much larger than those in the other soap phases since the intensity of scattered light is much greater from this phase.[2]

The heat effect at the transition to isotropic liquid is very small, as has been observed before with other liquid crystalline materials.[15] Most of the "bonds" present in the original crystal must therefore have been broken already before neat soap is formed. By analogy with the findings of Smyth, Baker and Turkevich[16] that crystals which undergo a rotational transition before the melting point have abnormally low heats of fusion, one may conclude that the very smallness of the heat of transition of neat soap to isotropic liquid constitutes yet another argument that the preceding transitions have all been a part of the process of melting, which here takes place in a series of partial steps rather than all at once at a single temperature. Moreover, the sum of all the heats of transition of the soap (sodium salt of a fatty acid) is not very different from the simple heat of fusion of the corresponding acid which melts in a single step (12,570 cal./mole for sodium palmitate; 13,030 cal./mole for palmitic acid[17]).

Dependence of the Heats of Transition on Chain Length.—Theoretical consideration[18] of the variation in heat and entropy of fusion merely with the chain length in long-chain compounds leads to the equation $T = (A + Bn)/(1 + Cn)$, where T is the transition temperature, n the number of carbon atoms and A, B and C are constants. The equation is based on the fact that $T = \Delta H/\Delta S$, and the assumptions that the changes in heat content and entropy are both linear functions of the chain length. Hence the heat of transition should increase with chain length if the transition temperature does. However, the experimental values of the transition temperatures and heats of transition of the saturated sodium soaps do not behave as required by the simple theory. The disagreement suggests that changes in the balance between the polar and non-polar portions of the soap molecule (which is responsible for the multiplicity of liquid crystalline forms in the first place) are far more important than any simple homologous effect.

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(14) S. D. Gehman and J. E. Field, *Ind. Eng. Chem.*, **29**, 793 (1937).

(15) R. Schenck, "Kristalline Flüssigkeiten und Flüssige Kristalle," Wilhelm Engelmann, Leipzig, 1905. pp. 84, 117; M. Spaght, S. B. Thomas and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).

(16) W. O. Baker and C. P. Smyth, THIS JOURNAL, **61**, 2798 (1939); A. Turkevich and C. P. Smyth, *ibid.*, **62**, 2468 (1940).

(17) W. E. Garner, F. C. Madden and J. E. Rushbrooke, *J. Chem. Soc.*, 2491 (1926).

(18) W. E. Garner, K. van Bibber and A. M. King, *J. Chem. Soc.*, 1533 (1931); M. L. Huggins, *J. Phys. Chem.*, **43**, 1083 (1939).

The transformation of curd fiber phase stable above the genotypic point, called curd fiber II by Chesley,[19] to subwaxy soap involves two transitions for sodium myristate and stearate, proving the existence of yet another stable allotropic form. For the present this phase will be referred to as simply another modification of curd fiber phase, leaving a more definite designation until it has been shown whether it is more closely related to the crystalline curd or the probably mesomorphic subwaxy soap. No calorimetric, dilatometric or microscopic evidence has yet been obtained for the existence of a corresponding phase of the laurate and palmitate.

If the subwaxy phase is presumed to represent the same stage of disruption of the crystal in all cases, *i. e.*, to have the same internal structure, and if the initial crystalline state (curd fiber II) is considered to be the same in all cases, then the heats of the new curd–curd transition[20] of the myristate and stearate should be added to the observed values for the curd–subwaxy transition in considering the total increase in heat content accompanying the formation of subwaxy soap. On this basis the heat of transition increases with the chain length at the curd–subwaxy transition, as is also the case at the subwaxy–waxy transition. It therefore seems reasonable to attribute these transitions primarily to a change in the binding of the hydrocarbon chains. This hypothesis is also in accord with the low temperatures at which these transitions occur and the large magnitude of the heat effect. By analogy with the low melting points of the hydrocarbons and fatty acids, it might be expected that partial melting involving the hydrocarbon part of the soap molecule would occur at a low temperature, the large heat effect being due to the large area of contact of the chains.

At the superwaxy–subneat and subneat–neat transitions the heat effects are largely independent of chain length and are relatively small. This suggests that these transitions are caused by changes in the packing of the polar heads of the molecules without significant changes in the arrangement of the chains. Further, it leads to the deduction that in superwaxy and waxy soap the chains may already be essentially independent of one another, being held in position only indirectly through the constraints of their terminal polar groups.

The Transition between Subneat and Neat Soap.—This transition is remarkable in that the volume change occurs *reversibly* at a temperature about 15° higher than that of the likewise *reversible* heat effect occupying the same numerical position in the sequence of transitions.[21] Apparently a large fraction of the molecules must have taken up their new motions with resultant absorption of heat before the original structure is sufficiently weakened to permit the discontinuous change in packing which gives the dilatometrically determined transition temperature. A possible explanation is that the molecules begin to oscillate or rotate in subneat soap at a lower temperature than is required for the formation of a sufficient number of defects in the orderly arrangement to constitute a coöperative system in the sense of Oldham and Ubbelohde,[22] the latter change resulting in the genuine transition as found dilatometrically and microscopically. Alternatively it is possible that there are here two separate transitions.

The author wishes to express his appreciation to Dr. J. W. McBain and Dr. M. J. Vold for their constant interest in this work.

Summary

A differential calorimeter has been devised suitable for determination of heats of transition and transition temperatures up to 340°. These were determined for the series of phases occurring between true crystal and true liquid for sodium laurate, myristate, palmitate, stearate and oleate.

Since the heat effects are similar at the successive transitions of sodium myristate, palmitate and stearate, it is inferred that similar changes in structure are involved. These structural changes may not occur in the same order at the numerically corresponding transitions of sodium laurate, and may also be different for sodium oleate.

At the transitions from curd fiber phase to sub-

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[19] F. G. Chesley, *J. Chem. Phys.*, **8**, 643 (1940).

[20] No corresponding transition was detected for laurate or palmitate. If present, these transitions probably have ΔH considerably less than 200 cal./mole.

[21] The calorimetric melting point to isotropic liquid is also lower than the values obtained by other methods. Here, however, the absolute value of the difference is considerably less and the lowering is not consistent, varying irregularly from practically zero for the palmitate to 12° for the myristate. The relatively greater importance of premelting phenomena due to the smaller value of the heat of transition, and the increased experimental difficulties at these higher temperatures may be contributing factors to the discrepancy. In any event, it does not seem reasonable to attach the same significance to these differences as to those at the subneat–neat transition.

[22] J. W. H. Oldham and A. R. Ubbelohde, *Proc. Roy. Soc.* (London), **A176**, 50 (1940).

waxy soap and from subwaxy to waxy soap the heat effect is large and varies with the chain length. At the higher temperature transitions the heat effect is small and relatively independent of the chain length. The conclusion is that the low temperature transitions are probably due to changes in the arrangement of the hydrocarbon chains while the high temperature transitions are due to rearrangement of the polar heads of the molecules.

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Analytical Procedures Employing Karl Fischer Reagent. VIII. The Determination of Water of Hydration in Salts

By W. M. D. Bryant, J. Mitchell, Jr., Donald Milton Smith and E. C. Ashby

The advantages of using Karl Fischer reagent for the quantitative determination of the water content of organic compounds have been discussed in earlier papers from this Laboratory[1] as well as by other investigators.[2,3,4] In the inorganic field the reagent affords a valuable means of determining the water present in hydrated salts or adsorbed on the surfaces of solids. Preliminary evidence to this effect was given by Karl Fischer in his original paper.[2] The writers have found the method to be precise and to have a wide range of application. Of course there are a number of inorganic materials that react abnormally with Fischer reagent to indicate a fictitious water content, but these compounds are readily classified and are in most cases subject to precise correction.

This titration method for water is more rapid and direct than the commonly used thermal drying procedures and is free from some objectionable features of the latter, namely, the difficulty of finding a safe drying temperature corresponding to a complete loss of moisture and the danger of losing other volatile constituents as a result of hydrolysis during drying. It is perhaps not immediately evident how Fischer reagent at room temperature can achieve results equivalent and often superior to those obtained by the older more tedious procedures based on weight loss. At least part of the explanation lies in the fact that the removal of water from hydrated salts and similar materials is greatly facilitated by the large excess of methanol normally present in the reagent. Where coördination affinity and adsorption are great, methanol is believed to readily replace water and so reduce the mass action or corresponding surface effects opposing the removal of water. For example, it was shown in an earlier paper[5] that methanol extraction combined with the Fischer titration would remove more water from native and processed cellulose than could be safely removed by thermal drying. Here the reagent was scarcely ever used in the direct presence of cellulose but instead was confined to analysis of the methanol extracts. A distribution equilibrium was evidently established between moisture in the solvent and in the pores of the solid.

In the present paper the writers have studied the behavior of twenty-five hydrated salts (see Table I) where there was no interference from side reactions. In many cases parallel analyses were made by titration, and by weight loss after oven-drying at specified temperatures. Although the hydrated salts available did not in all cases conform to the exact stoichiometric compositions, the effectiveness of the Fischer procedure was shown by the comparative analyses. The titration results were in most cases numerically greater and closer to theory.

The behavior of a large number of "reactive" inorganic compounds with Karl Fischer reagent was observed in an effort to obtain useful generalizations regarding interfering substances. The generalizations are as follows (a more detailed account of this work will appear in the next paper of the series). The ease with which hydrate water is titrated by Karl Fischer reagent depends

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(1) (a) Smith, Bryant and Mitchell, This Journal, **61**, 2407 (1939); (b) *ibid.*, **62**, 3504 (1940). The reagent (a solution of iodine with excess sulfur dioxide and pyridine in dry methanol) combines directly with water to form pyridine methyl sulfate and hydriodide, the color changing from brown to yellow. The reagent is added to the sample from a buret until the brown color is just restored. Except for examples to be discussed, the method is specific for water.

(2) Karl Fischer, *Angew. Chem.*, **48**, 394 (1935).

(3) Zimmermann, *Fette u. Seifen*, **46**, 446 (1939).

(4) Almy, Griffin and Wilcox, *Ind. Eng. Chem., Anal. Ed.*, **12**, 392 (1940)

(5) Mitchell, *ibid.*, **12**, 390 (1940).