

ardized soil, and perhaps to act as a guide in advancement of this field as a whole.

It is granted that the reflectance method for evaluation is comparative rather than absolute, but reflectance is the measure generally used for estimation of cleanliness. Soiled test fabrics are currently used in screening operations and as a quick guide to research and development. Successful evaluation of detergents is accomplished by preliminary evaluation in a laboratory washer with standardized soiled fabric, followed and supplemented by practical laundering tests in the equipment and with the soiled articles it is expected the detergent will be required to clean.

There doubtless are other variants in procedure which have been operated as successfully as the one described. It should be heartening to realize that moderate success in standardization of a soil and wash test method has been achieved, and simultane-

ously discouraging to confirm the tremendous amount of effort required to attain such standards.

Acknowledgment

Fully appreciated is the encouragement of management in permitting us free scope in our standardization and evaluation work and also the close cooperation of those many persons who have performed these tests.

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Physical Properties of Fatty Acids. I. Some Dilatometric and Thermal Properties of Stearic Acid in Two Polymorphic Forms

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DILATOMETRY as a means of determining the expansibility of fatty acids has heretofore been employed by only one investigator (1). Moreover the dilatometers used in this early work were of the volumetric type, and the fatty acid samples evidently contained impurities since their reported melting points are not consistent with the values now accepted for these compounds when of the highest purity.

The ability of stearic acid to exist in different polymorphic modifications and data with reference to the long diffraction spacings of these modifications have been reported by a number of workers (2, 3, 4, 5). It has been stated (6) that the volume changes accompanying the transformation of stearic acid from one polymorphic form to another were unobservable and therefore the conditions with respect to the polymorphic transition of stearic acid have not been completely established.

Garner and co-workers (7) have reported some of the thermal properties of the *n*-aliphatic fatty acids, but detailed data for the specific heat, heat of fusion, and molal entropy of stearic acid are not available.

The purpose of the present investigation has been to determine certain useful physical properties of stearic acid, including a) its expansibility in the solid and liquid states, b) the temperature and volume changes associated with the polymorphic transformation of this acid, c) the absolute density and specific volume, d) the specific heat and heat of fusion, and e) the entropy calculated from heat capacity data.

Preparation of Stearic Acid

A commercial product containing about 85% stearic acid was subjected to sulfonation followed by

water washing to remove unsaturated impurities. The saturated fatty acid fraction was esterified with methanol and fractionally distilled, the methyl stearate converted to stearic acid, repeatedly recrystallized from acetone, and dried over phosphorous pentoxide. Characteristics of the purified stearic acid were: setting point, 69.20°C.; melting point, 69.5°C.; and absolute density, 0.8474 g./ml. at 72.0°C. ($\pm 0.05^\circ$).

X-Ray Examination of the Samples

Slow crystallization of the purified stearic acid from benzene at room temperature and from hot glacial acetic acid yielded two distinct polymorphic forms. The crystals of stearic acid obtained from benzene were transparent, monoclinic, and variable in size, the largest being approximately 6 x 6 x 3 mm. A tendency toward crystal-twinning was noted. The X-ray diffraction pattern of these crystals exhibited a long spacing characteristic of the B-form while the crystals obtained from hot glacial acetic acid were opaque and flaky, and not characteristic with respect to size or system. These latter crystals exhibited a shorter diffraction spacing characteristic of the C-form of the acid. Although crystallization from benzene at room temperature yielded crystals corresponding to the B-form of the acid in every case, crystallization from this solvent above 53°C. resulted in the C-form. Likewise crystallization of stearic acid from glacial acetic acid at temperatures below 35°C. resulted in the B-form of stearic acid. These observations would indicate that the spacing exhibited by stearic acid is dependent upon the temperature at which crystallization occurs with either benzene or glacial acetic acid as the solvent. Crystallization at temperatures above the transition point results in the stable C-form of stearic acid and below

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the transition point in the unstable B-form, regardless of the solvent used.

Some of the original sample of stearic acid was melted and immediately dropped into liquid nitrogen for quick chilling. This material, after careful pulverizing to insure the absence of voids and examination by X-ray diffraction, gave a diffraction pattern corresponding to the C-form of the acid.

The original stearic acid, after recrystallization from acetone, on examination with X-rays gave a diffraction pattern corresponding to the B-form although the orders of reflection were not sharp.

The diffraction patterns of all samples of stearic acid were compared with those obtained and classified with respect to B- or C-spacings by Francis and Piper (5) and illustrated by Markley (8).

Experimental

The dilatometric and calorimetric methods and calculations have been described in previous publications (9, 10). The samples of stearic acid were placed in calibrated dilatometers and subjected in duplicate to initial temperatures of -38.59°C . and -20.88°C . Dilation of the samples was continued from these temperatures to a temperature approximately 8 degrees above their final melting points. Another set of identical samples of stearic acid was subjected to the same temperature conditions and periodically withdrawn for observations of their X-ray diffraction patterns.

The specific heat of stearic acid was measured as previously described (10), with the exception that a calorimeter constructed of silver instead of copper was employed because of the corrosive action of fatty acids on the latter metal. Measurements were made over a temperature range of 154°K . to 352°K .

The X-ray diffraction patterns illustrating the marked differences between the spacings of the B- and C-forms of stearic acid are shown in Figure 1.

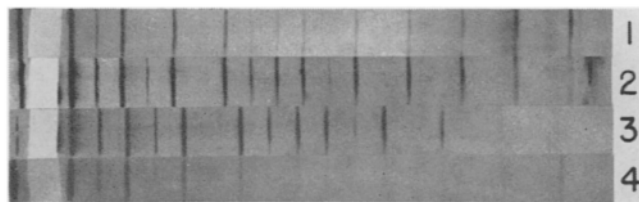


Fig. 1. X-ray diffraction patterns of stearic acid. (1) and (2) are the B-form as crystallized from acetic acid and benzene, respectively. (3) and (4) are the C-form as crystallized from the same solvents respectively.

The upper half of Figure 1 illustrates the characteristic diffraction pattern obtained with stearic acid crystallized from glacial acetic acid and from benzene at room temperature; the lower half illustrates the pattern obtained with the same acid after crystallization from hot glacial acetic acid and from benzene at 54°C . These patterns were made with a General Electric Diffraction Unit, Model XRD using Cu K α radiation with a nickel filter (0.0007 inches thick) and a plate distance of 5 centimeters.

Expansion and Transition

The specific volumes of stearic acid at different temperatures were calculated (11) from the expansion data and from the determined density of the

liquid. The average values for the B- and C-forms are shown in Table I and Figure 2.

Previous to the dilatometric observation of the polymorphic transition, transparent crystals representative of the B-form of stearic acid contained in capillary tubes were immersed in a water bath at various temperatures for visual observation of the oc-

TABLE I
Specific Volumes in Milliliters Per Gram of Stearic Acid
at Different Temperatures

Temperature $^{\circ}\text{C}$.	B-Spacing	C-Spacing
-20.88	0.9473	1.0446
-18.29	0.9477	1.0448
-16.92	0.9483	1.0455
-14.75	0.9488	1.0461
-10.19	0.9500	1.0468
- 5.45	0.9510	1.0486
- 1.70	0.9523	1.0500
+11.78	0.9558	1.0534
15.70	0.9570	1.0547
21.10	0.9586	1.0560
27.00	0.9603	1.0522
30.41	0.9614	1.0504
34.68	0.9633	1.0436
37.56	0.9835	1.0411
39.96	0.9847	1.0418
44.79	0.9873	1.0278
51.12	0.9911	1.0299
60.05	0.9978	1.0111
64.08	1.0026	1.0122
67.84	1.0150	1.0191
68.59	1.0275	1.0263
70.00	1.1780	1.1780
72.00	1.1801	1.1801
76.18	1.1842	1.1840

currence of any transition. The B-form of crystalline stearic acid rapidly became opaque, with apparent retention of original shape, at a minimum temperature of 52.9°C . The X-ray diffraction pattern of these opaque crystals exhibited both B- and C-spacings. Transition to the form exhibiting a C-spacing was completed by holding the crystals at 52.9°C . for a short time. This temperature of transition is essentially the same (53.0°C .) as that reported by Thibaud and La Tour (3).

The transition from the B- to the C-form of stearic acid was found to occur much below 52.9°C ., if sufficient time were allowed. In the course of the dilation of stearic acid, transition of the B- to the C-form occurred at 35.2°C . when the same was held for 380 hours in the range 30° to 35.2°C . The volumetric change accompanying the transition was considerable, and the occurrence of the transition was further confirmed by X-ray examination of the sample.

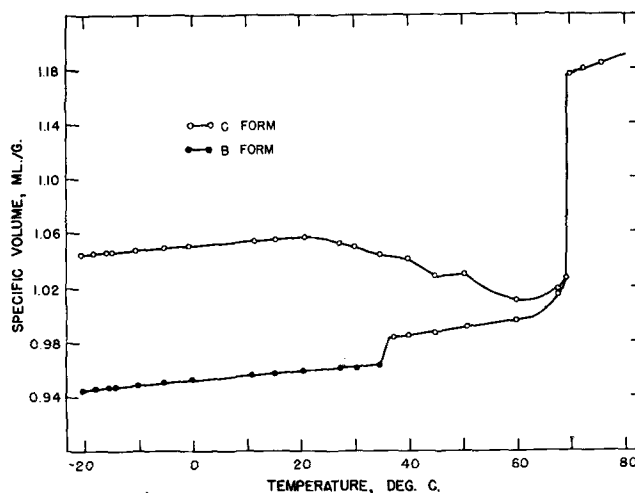


Fig. 2. Specific volume VS temperature of stearic acid in two polymorphic forms.

The slow transition at 35.2°C. is another example of reluctant transition and entirely analogous to the effect observed by Gibson and Markley (12) in an investigation of the dilation of a substituted thiazole in which a slow transition was noted approximately 36° below the rapid transition. The transition of B-form stearic acid at 52.9°C. in reality represents the temperature at which the rate of transition is rapid enough to be readily observed. These observations lead to the conclusion that the first break on the dilation curve of the B-form of stearic acid represents the temperature at which transition proceeds rapidly enough to be detected by dilatometric means and that the temperature above which the B-form ceases to be stable is certainly below 35.2°C. Actually, the volumetric increase of stearic acid with increasing temperature is greater after than before the completion of the transition.

Contraction of the C-forms of stearic acid began at approximately 25-30°C. and continued at different rates until the samples were within a few degrees of the melting point. There was no discernible change in the diffraction pattern of these samples and the X-ray diffraction patterns of the samples after removal from the bath at 38°C. and again at 64°C. exhibited the original C-spacing. Furthermore the heat content curve on this material indicated no abnormality.

The possibility that the contraction of the C-form resulted from the presence of voids in the sample is considered to be rather remote as two different samples of stearic acid crystallized in the C-form and the quick-chilled sample contracted equally. Also the C-form of stearic acid as crystallized from benzene at 54°C. exhibited contraction. The contraction probably resulted from the increased density of the C-form of the acid and therefore did not affect the (long spacing) diffraction pattern. A decrease in the size of the crystalline particles present is possible without a change in the sharpness or number of orders of reflection of the diffraction pattern, according to Hattiangdi (13).

The irreversibility of the polymorphic transition of stearic acid (3) from the B- to the C-form was substantiated by reversing the temperature, *i.e.*, lowering the temperature of the dilatometer bath from approximately 45°C. to 30°C. or below the initial transition point. The volume changes of the respective samples failed to coincide with the former abrupt changes at 35.2°C., which had denoted transition on heating.

Final melting of all the samples of stearic acid occurred at 69.5°C. The expansion of this acid in both the solid and the liquid states and the melting dilation of the B- and C-forms were calculated with the results shown in Table II.

Specific Heat, Heat of Fusion, and Entropy

Specific Heat. The specific heat of stearic acid in both the solid and liquid states was determined, and equations developed from the calorimetric data for expressing the specific heat (International calories per gram) of stearic acid in terms of temperature (degrees C.), which are as follows:

$$\text{Solid state } (-120^{\circ} \text{ to } 65^{\circ} \text{C.}) C_p = 0.4272 + 0.0018 t$$

$$\text{Liquid state } (70^{\circ} \text{ to } 78^{\circ} \text{C.}) C_p = 0.4266 + 0.0018 t$$

A comparison of the calculated and experimentally determined specific heat of stearic acid is shown in Table III.

TABLE II
Expansibility of Stearic Acid in the Solid and Liquid States, and Melting Dilation of the B- and C-Forms

State	Spacing	Temperature range °C.	Expansion ml./g./°C.	Average expansion ml./g./°C.	Melting dilation ml./g.
Solid	C	-20.88 to +18.42	0.000258	0.000262	0.1857 ^a
Solid	C	-20.88 to +18.42	0.000274		
Solid	C	-38.59 to +6.02	0.000255		
Solid	B	-20.88 to +30.41	0.000275	0.000269	0.2051
Solid	B	-38.59 to +28.87	0.000263		
Liquid	C	70.0 to 76.18	0.000953	0.000973	
Liquid	C	70.0 to 76.18	0.000990		
Liquid	C	71.85 to 76.05	0.000965		
Liquid	C	71.85 to 76.05	0.000957		
Liquid	C	70.0 to 76.18	0.000998		

^a Calculated from the specific volume of the B-form after transition to the C-form of stearic acid.

It was not possible to obtain an unstable modification of stearic acid in the calorimeter by quickly chilling the liquid sample, since the C-form of the acid was found to be unaffected by chilling.

Heat of Fusion. The heat of fusion of stearic acid was calculated from fusion data to be 57.5 cal./g. The melting point of the stearic acid sample calculated from the same data was 342.83°K. The melting point determined dilatometrically is considered to be more accurate.

There is some discrepancy between this heat of fusion and the data of Garner and associates (7). Stearic acid is omitted from the heat of fusion series of the latter workers but can be interpolated as 52.5 cal./g. Since their data are all consistent, it would follow that if their value for the heat of fusion of stearic acid is low, the results are correspondingly low for the other saturated acids. The value of 57.5 cal./g. appears more correct since this result places the molar heat of fusion of stearic acid quite close to one-third the molar heat of fusion of the triglyceride of this acid whereas 52.5 cal./g. indicates a value that is substantially lower. Moreover preliminary work on palmitic acid indicates a value for the heat of fusion of 51.8 cal./g., compared to 50.6 cal./g. as reported.

Entropy. The molal entropy of stearic acid was calculated from the heat capacity data and by the extrapolation method of Kelly, *et al.* (14), using the revised data for standard substances. These values, expressed as entropy units, are: 0°-90°K., 15.4; above 90°K., 88.7; 298.6°K., 104.1.

Discussion

The statement has been made by Francis, Collins, and Piper (15) that "during the course of this investigation we made the interesting and important observation that the crystals of fatty acids, with an even number of carbon atoms, which separate from glacial acetic acid on recrystallization, show the C-crystal spacings whereas the crystals from either ben-

TABLE III
Specific Heat of Stearic Acid as Determined Experimentally and by Calculation

Temperature °K.	Calculated C_p cal./g./°C.	Experimental C_p cal./g./°K.	Deviation
160	0.2236	0.2239	-0.0003
200	0.2956	0.2946	+0.0010
250	0.3856	0.3840	+0.0016
300	0.4756	0.4754	+0.0002
330	0.5296	0.5291	+0.0005
350	0.5650	0.5649	+0.0001

zene or acetone show the B-spacings only." In later studies these workers (5) found one fatty acid which gave B- and C-spacings when crystallized from glacial acetic acid. Also these workers found that impurities of from 1 to 3% were indicated when an aliphatic acid, crystallized from benzene, had both B- and C-spacings.

In view of the data of the present work it appears that the temperature at which crystallization of stearic acid from a solvent occurs is the dominant factor with respect to the polymorphic form obtained, and not the type of solvent; *i.e.*, crystallization below the beginning of transition at 35.2°C. for the B-form and above the final transition at 52.9°C. for the C-form. Either the B- or C-spacing can be obtained from the same solvent with proper temperature conditions. Furthermore to use the crystal spacing as a criterion of the purity of fatty acids, it must be known that the conditions of crystallization were such as to give the B-spacing only so that a mixture of B- and C-forms will be a valid indication of the degree of purity, and not due to polymorphism.

In crystallographic observations of B-form stearic acid, temperatures in the range of the reluctant transition of this acid (35-53°C.) should be avoided since it is in this range that separation of a mixture of B- and C-forms from the crystallization solvent is possible.

Although results have been obtained only for stearic acid, the principles are probably applicable to other even numbered *n*-aliphatic acids, as indicated by preliminary results with palmitic acid.

Summary

1. Purified stearic acid (freezing point 69.20°C., melting point 69.5°C.) when slowly crystallized from benzene at room temperature, yielded transparent monoclinic crystals exhibiting an X-ray diffraction pattern (long spacing) corresponding to the B-form of the acid. Crystallization of stearic acid from hot glacial acetic acid resulted in a product exhibiting an X-ray diffraction pattern (shorter spacing) corresponding to the C-form of the acid.

2. Rapid chilling of a melted sample of stearic acid likewise yielded a product exhibiting the diffraction pattern characteristic of the C-forms of the acid.

3. The specific volume, expansion in both solid and liquid states, and melting dilation of stearic acid in both B- and C-forms were calculated from dilatometric data.

4. The irreversible transition of stearic acid from the B- to the C-form was rapid and visible at 52.9°C. but also occurred at 35.2°C. when sufficient time was allowed for the transition to occur.

5. The form of stearic acid which was obtained was found to be dependent upon the temperature at which crystallization occurred. When crystallization was carried out at temperatures below the transition point of the acid, the B-form was obtained, and above the transition point only C-form of the acid was obtained, irrespective of the solvent used for crystallization.

6. The specific heat of stearic acid was determined, and equations developed for expressing the specific heat of the acid in both solid and liquid states. From the calorimetric data, the heat of fusion, and the entropy of stearic acid were calculated.

Acknowledgment

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ABSTRACTS

Don Whyte, Editor

• Oils and Fats

A. R. Baldwin, Abstractor

THE MANUFACTURE OF SULFONATED OIL AND THE DETERMINATION OF THE WETTING POWER AND THE SURFACE TENSION OF ITS EMULSIONS. Liu-Chiao Fu and Chien-Hon Chen. *J. Chem. Eng. China* 15, 72-80 (1948). Good sulfonated oil can be prepared from any vegetable oil except those with high fatty acid content or high unsaturation. Sulfonated oils obtained by sulfonating castor, peanut, sesame, and cottonseed oils show little difference in surface tension; the wetting powers of these products decrease in the order named. These sulfonated oils are satisfactory for use in the textile industry. (*Chem. Abs.* 44, 353.)

THE CHEMIST AND THE COTTONSEED INDUSTRY. T. L. Rettger (Buckeye Cotton Oil Co.). *Oil Mill Gazetteer* 54 (7), 34-7 (1950). This paper reviews historically the development of the cottonseed processing industry.

HYDROPHOBIC MONOLAYERS ADSORBED FROM AQUEOUS SOLUTIONS. E. G. Shafrin and W. A. Zisman (Naval Research Laboratory). *J. Colloid Sci.* 4, 571-90 (1949). Experimental methods are described for the preparation and examination of hydrophobic monomolecular films adsorbed into platinum surfaces from aqueous solutions of primary normal alkyl amines. The critical limits to hydrophobic film formation and the degree of hydrophobicity are found to be functions of the amine concentration and the pH of the generating solution. A definite correlation is established for the relative effectiveness of these factors and the length of the hydrocarbon chain in the aliphatic portion of the amine molecule. The short chain amines (up through dodecyl) are found to be most adsorptive in the alkaline region, whereas film formation of the hexadecylamine is limited to the highly acid regions. The intermediate tetradecylamine evinces a transitional behavior, having two separate pH regions favorable to film formation.

OLEATE SYSTEMS CONTAINING POTASSIUM CHLORIDE. IV. FLOW PROPERTIES AS A FUNCTION OF SHEARING STRESS AT 15° AND CONSTANT KCl CONCENTRATION. V. VISCOUS AND ELASTIC BE-