the neighborhood of 0.4 to 0.5. This approximate constancy is interesting although no simple quantitative explanation is forthcoming.

The equivalent conductance (per fraction ionized) of the polymer, Λ_p, was found to fluctuate in the neighborhood of approximately 25 ohm^{-1} cm.^{2} equiv.$^{-1}$ for the experimental concentrations and neutralizations investigated. The product of "rational mobility," ω_p, and s, the degree of polymerization, for a 0.0250 N solution averages about 1.8×10^{-8} cm. per sec. per dyne.

URBANA, ILLINOIS RECEIVED DECEMBER 11, 1950

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Thermal Analysis of the System Sodium Stearate–Cetane

BY F. H. STROSS AND S. T. ABRAMS

The phase behavior of anhydrous sodium stearate in various hydrocarbons reported in the literature does not present a consistent picture, possibly because of the presence of traces of water. An attempt has been made to obtain a phase diagram of carefully prepared and rigorously dried sodium stearate and cetane by means of differential thermal analysis, supplemented by some visual observations under polarized light. This diagram indicates that there is no appreciable interaction between soap and medium below about 140°. At higher temperatures, however, the transition temperatures of the soap are depressed by the addition of solvent, but the depression is constant over most of the concentration range studied. No phase islands have been found by the techniques used. Approximate measurements of the latent heats were made and the summed molal latent heats for sodium stearate and the summed partial molal latent heats for the soap in the solvent were found to amount to about 10,700 g. calories.

In the study of grease-like systems it is most useful to have available the oil–soap phase diagram, so that the state of the system is known for any temperature and concentration desired. Such phase diagrams are difficult to construct because no single method known appears capable of a complete analysis of the behavior of the system. Some visual and microscopic observations of a typical system, namely, sodium stearate–cetane, have been referred to in a previous publication,[1] but these methods do not give complete and consistent diagrams which can be readily reproduced. The method of differential thermal analysis is attractive because it yields an objective record of any transition with a palpable latent heat, and because the latent heat itself can be determined with reasonable accuracy. This method has found widespread application in the study of clays, and has also recently been used in the study of soaps,[2] and soap–hydrocarbon mixtures.[3] The instability of many soaps in air at temperatures above about 150°, the large number of transitions below the melting point and other characteristics of soap–hydrocarbon systems make necessary more refined instruments for the thermal analysis than those used for clays, including high sensitivity and sealed calorimeters with good internal heat distribution. The object of this study, to contribute to the construction of the phase diagram mentioned, made necessary the design of appropriate equipment, which is briefly described in the following section.

Experimental

The demands of the problem were met by the construction of twin cylindrical calorimeters made of stainless steel, with a threaded closure fitted with a silicone rubber gasket; by means of this closure the atmosphere of the calorimeter could be replaced or evacuated, and the calorimeter then could be hermetically sealed. The favored calorimeter heat distributing system, of several tried, consisted of a flattened silver helix winding around the well and extending to the walls of the calorimeter. The maximum heat lag in a sample of grease was calculated to be about 0.5° at a heating rate of 2° per minute. The calorimeters were spaced symmetrically by means of glass and Mykroy spacers in a copper block, with a thermal barrier consisting of a 2 mm. air space around each calorimeter. The copper block which was used to provide uniform furnace temperature was heated at a constant rate in an air-bath at rates varying from 0.4 to 2.0° per minute. The dimensions of the calorimeters were 12 mm. dia. by 20 mm. height; with their closures they weighed between 9 and 10 g., and had a free capacity of about 2 ml.

The difference in temperature between the calorimeters was automatically recorded by means of a differential copper–constantan thermocouple connected to a Leeds and Northrup Type HS galvanometer operating a photopen deflection recorder. Periodically, the thermocouple-galvanometer circuit was manually disconnected and the temperature of either of the individual calorimeter thermojunctions was measured by means of a Leeds and Northrup Portable Precision Potentiometer. Figure 1 shows a typical thermogram of a mixture containing 34.9% sodium stearate. A thermogram of the pure soap is shown in Fig. 2. It was obtained by heating to 300° at a rate of 2°/min. immediately followed by cooling at a rate of 2°/min. in a new instrument that provided controlled cooling as well as heating.[4]

In a differential analysis run, soap sample and the inert sample are heated in the copper block; when the active sample undergoes a phase change, there arises between it and the inert sample a difference in temperature which is measured.

In a given system with a well-defined thermal path, in which the conductivity within the sample is large compared to that of the thermal barrier, the latent heat ΔH of the transition is

$$\Delta H = K \int_a^b (t_r - t_a)dz \qquad (1)$$

t_r = temperature of the reference sample
t_a = temperature of the active sample
z = time
K = constant including conductivity and dimensions of the thermal path

provided that the quantity K is maintained adequately constant during the run. The integral is taken between two temperatures a and b at which the temperature difference $t_r - t_a$ is zero or negligible. The sensible heats of the two samples cancel if the heat capacities are equal. This condition is sufficiently well satisfied experimentally by adjusting the amount of samples used. Inadequate heat distribution within the calorimeter will cause distortion of the transition peaks with corresponding loss in characterization and accuracy in the latent heat values. It follows from equation

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(1) F. H. Stross and S. T. Abrams, THIS JOURNAL, **72**, 3309 (1950).

(2) R. D. Vold, *ibid.*, **63**, 2915 (1941).

(3) R. D. Vold and M. J. Vold, *J. Colloid Sci.*, **5**, 1 (1950).

(4) This instrument was constructed, and the curve was furnished by Mr. C. J. Penther of these Laboratories.

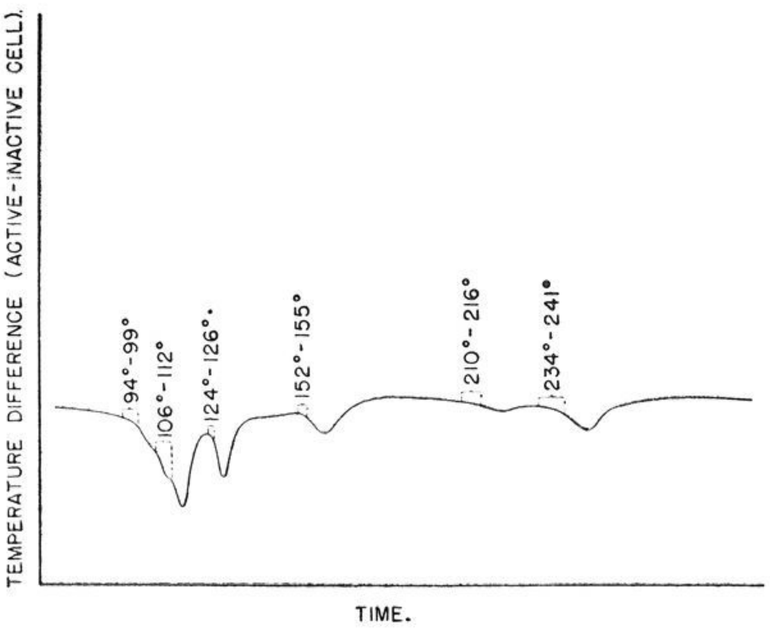

Fig. 1.—Thermogram of system sodium stearate-cetane, 34.9% sodium stearate.

(1) that the area of the transition peak is proportional to the concentration of an active sample dissolved or suspended in an inert solvent or matrix. After calibration with known samples the system can be used for measuring unknown latent heats. The measurements of latent heat are independent of the rate of heating as long as the requirements with regard to the constancy of K are complied with. With our best equipment the method is capable of reproducing the heat of fusion of the substance to about 1%. In the case of the composite system, however, the reproducibility of heats of transition was sometimes no better than 7 to 8%. Sharp breaks in the curves were usually reproducible within 1°, less sharp breaks within 3°.

It can be shown that in differential thermal analysis, with adequate thermal conductivity, the temperature at the beginning of a break (initial transition temperature) corresponds to the melting or transition point, or the beginning of the transition range of a sample. The initial transition point is found to be independent of the rate of heating, as expected, while the temperature at which the apex occurs may shift with a change of the rate (compare also Speil).[5]

In many cases runs were made at heating rates varying by a factor of four. In no cases did the initial transition temperatures change noticeably. This shows that in these cases thermal equilibrium was substantially reached for the transitions observed. At the slower heating rates the peaks have a smaller altitude and a correspondingly greater breadth. This elongation makes for less distinct break points, but for better separation of adjacent peaks which may overlap at higher heating rates. Therefore, a higher heating rate is desirable for good determination of the initial transition temperatures, while a slower rate is useful for resolving complex multiple peaks

The samples were prepared[6] as follows. Stearic acid of m.p. 68.9° was repeatedly recrystallized from methyl ethyl ketone, and washed with acetone. The product (m.p. 69.4°) was recrystallized from chloroform and treated with activated carbon, ground to a fine powder, and dried to give stearic acid of m.p. 69.6°. A boiling solution of the stearic acid in methanol was allowed to react with carbonate-free sodium hydroxide in methanol. After grinding the solidified mass and adding absolute ethanol, the soap was reheated and enough alcoholic sodium hydroxide added to maintain a pink color with phenolphthalein. The mixture was filtered, ground and washed with ethanol to remove excess alkali, washed with acetone, and air-dried. The soap was recrystallized from a mixture of absolute ethanol and benzene, and the sodium carbonate filtered off repeatedly. The product was finally washed with acetone, ground again, and dried at about one millimeter pressure at 150° for several hours. Only with this rigorous drying was it possible to obtain a soap which gave reproducible thermograms. The soap and the carefully dried solvents were handled in a drybox and weighed in sealed containers.

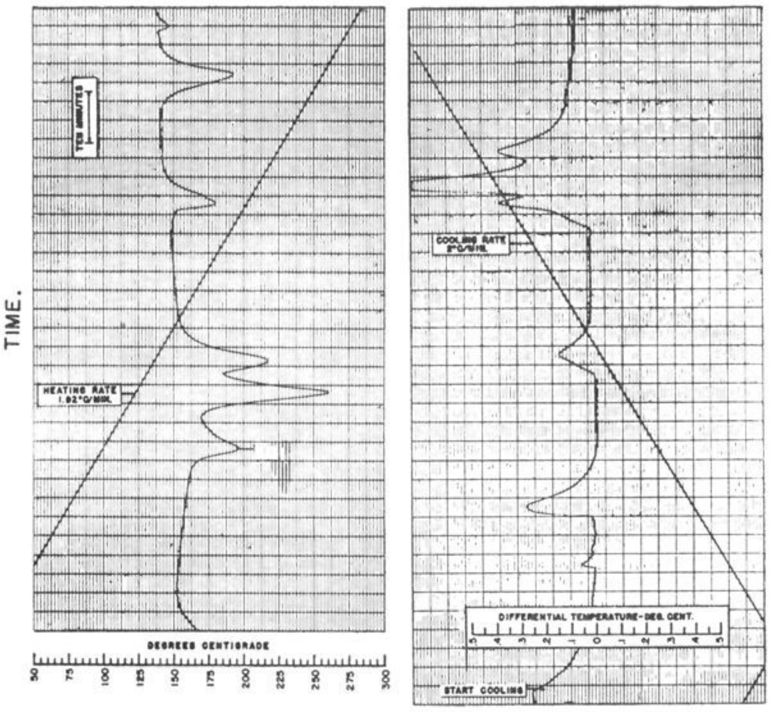

Fig. 2.—Heating and cooling, sodium stearate: (a), temperature of the samples (straight line); (b) temperature difference between active and reference samples (thermogram record).

The visual observation samples also were prepared so as to exclude water as far as possible. For the microscopic preparations, 5-mm. glass tubing was drawn out into flat capillaries, the ends of which were sealed, leaving the capillaries attached to the tubing. After introducing the soap and the solvent into the capillary end and weighing the system, the sample was chilled with Dry Ice and simultaneously evacuated through the glass tubing. Then the capillary was sealed off, so that the sample was contained in an evacuated fairly flat microtube 15–20 mm. long, 2 mm. wide and 1 mm. thick. The observations were made in a Spencer petrographic microscope with a Leitz–Weygand hot-stage capable of reaching 300°.[7] For macroscopic observations, the samples were evacuated and sealed in a glass cell, which could be manipulated by means of a glass rod attached to it. Within the cell there was a glass-encased iron core which could be moved about magnetically from the outside. The cell and the magnets were immersed in a bath[8] which could be heated to about 300° for extended periods of time without disturbing discoloration. The sample was viewed between polarizers by means of a 20-power short-focus telescope.

Results

A phase diagram, obtained by plotting initial transition temperature against concentration, is shown in Fig. 3. Where these temperatures were not sharply enough defined the ranges of maximum change of slope were used. Table I gives the corresponding data and individual heats of transition. In this phase diagram there was no indication of the existence of any "phase islands," neither of the general type ascribed to the sodium stearate–centane system,[9] nor that described by Smith[10] in which the general characteristics of the phase diagrams appeared to be essentially independent of the solvent type in the variety of low molecular weight hydrocarbons used. This result is consistent with the previously reported observations[1] according to which the dry systems failed to show phase islands.

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[5] S. Speil, *et al.*, Tech. Paper 664, p. 7, U. S. Bureau of Mines.

[6] The authors are indebted to Messrs. E. R. White and R. J. Moore of these laboratories for the preparation and purification of the reagents.

[7] This hot-stage was calibrated with pure samples of known melting point.

[8] General Electric 9981 LT NV 40 silicone oil.

[9] Doscher and Vold, *J. Coll. Sci.*, **1**, 299 (1946).

[10] G. H. Smith, *J. Am. Oil Chem. Soc.*, **XXIV**, 353 (1947); also thesis, Stanford Univ., 1947.

TABLE I

INITIAL TRANSITION TEMPERATURES AND HEATS OF TRANSITION OF SODIUM STEARATE–CETANE MIXTURES

Wt. % sodium stearate	ΣΔ*H*/ mole, g. cal./mole soap	I. T. T., °C.	Δ*H*/ mole, g. cal./ mole	I. T. T., °C.	Δ*H*/ mole, g. cal./ mole	I. T. T., °C.	Δ*H*/ mole, g. cal./ mole	I. T. T., °C.	Δ*H*/ mole, g. cal./ mole	I. T. T., °C.	Δ*H*/ mole, g. cal./ mole	Run no.
100	10250	86–96 112–118 129–130	7000	198	1170	243–251	1920	271–273	20	280	140	95 100
86	10530	88–94 108–110 128	6600	178–180	1470	241–248 252–255	2460					51
76.6	10950	86–96 107–108 125–126	7200	150–159	1345	226–229	520	248–250	1890			49
63.6	10870	94–100 109–111 126	7650	151–156	950	217–220	450	241–245	1890			52
50.0	10310	93–99 110 125–126	7500	154–156	960	218	250	234–240 257	1600			48
34.9	11070	94–99 106–112 124–126	7020	152–155	1420	210–216 234–241	2630					96
26.4	10590	92–100 104–112 123–126	7150	151–155	1380	210–217	470	235-241	1590			50
9.3	10720	92–98 104–111 122–126	6960	153–156	1170	212–216	820	236–241	1770			111
3.0	[a]	95–100 109–111 121–126		150–152		210		237–241				104
Average 10660												

[a] No good heat measurements available.

Thermal analysis shows that the transitions undergone by the soap at lower temperatures (up to *ca.* 140°) are virtually unaffected by the solvent; no solution occurs, even at the lowest concentrations. At the higher temperatures, however, the transition temperatures of the soap are lowered by the addition of small amounts of solvent. Upon further addition of solvent the transition temperatures tend to become constant, and they can be observed down to very low soap concentrations.

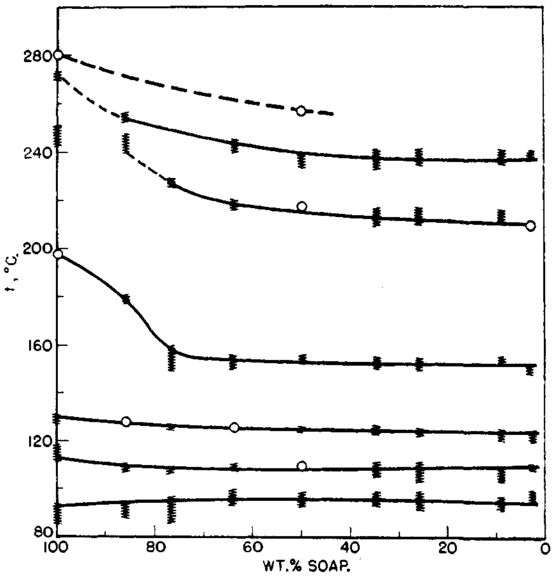

Fig. 3.—Phase diagram, sodium stearate–cetane, thermal data.

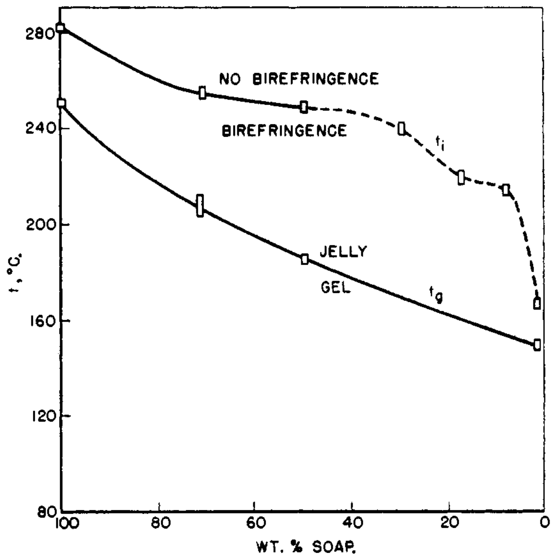

Fig. 4.—Phase diagram, sodium stearate-cetane, visual and microscopic data.

Some visual and microscopic observations were made on systems enclosed in evacuated glass cells and capillaries.[1] Only the t_i points, the temperatures at which, on heating, the optically anisotropic systems become isotropic, could be reproduced repeatedly, and also a few observations below this temperature. The latter (t_g-) points seem to represent transitions from a highly viscous to a much less viscous state, the system however remaining anisotropic. Below the t_g point the magnetically-operated stirrer left a wake which did not heal while above this point healing was increasingly rapid. The observed properties of these states conformed with McBain's definitions[11] of the gel and jelly states, respectively, and they are labeled accordingly in Fig. 4. Although these data should be useful for filling in the missing boundaries of a phase diagram, we feel that we have not sufficient data to construct a complete diagram of this type.

Comparison of Figs. 3 and 4 shows that at soap concentrations below 50%, addition of solvent depresses the visual t_i points markedly without having a corresponding effect on the ultimate transition temperature observed in the thermal analysis. An experiment made with a similar system[12] shows that structural anisotropy, at low concentrations, can exist up to the ultimate transition temperatures, where optical anisotropy no longer exists.

Small amounts of water affect not only the transition temperatures, but also the visual aspect of the system. At lower soap concentrations, the substantially anhydrous systems separate on cooling, at temperatures of 100° and below, into a soap curd and virtually pure cetane; the addition of water ($\sim$0.1%) will cause these mixtures to appear as turbid white gels, which completely retain the cetane. There is a marked difference between the anhydrous and the damp systems when they are viewed between crossed polarizers. The system containing traces of water exhibits a somber yellowish-red glow up to temperatures in the neighborhood of 125°; the anhydrous system shows very bright yellow coarse granules with variegated edges. Valid conclusions regarding the phase diagram can be drawn only from observations made on rigorously dried substances.

The latent heats of the individual phase changes have been evaluated by means of differential thermal analysis. In spite of the only moderate accuracy of the measurements, it can be seen from Table I that the latent heats of the phase changes are fairly constant throughout the concentration range studied. The probable error of the individual latent heats is ±5 to 8% depending on the sharpness of the peak. Where several peaks were superimposed, the individual heats could not be resolved and appear lumped together in the table. The sum of the heats of transition from the solid state at room temperature to the solution in cetane at the t_i point amounts to an average of 10,700 gram calories per mole of soap.

EMERYVILLE, CALIF. RECEIVED DECEMBER 18, 1950

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(11) J. W. McBain, K. J. Mysels and G. H. Smith, *Trans. Faraday Soc.*, **42B**, 173 (1946).

(12) Mr. R. J. Moore of these laboratories has followed the viscosity-temperature relation with a Brookfield viscosimeter at a concentration of about 9% soap in a light oil, and has found the viscosity to decrease sharply with temperature until the temperature corresponding to the ultimate transmission observed by differential thermal analyses was reached. At this point the temperature coefficient of viscosity suddenly decreased, and the viscosity decrease of the system became essentially that of the oil.

[CONTRIBUTION FROM THE DIVISION OF ANALYTICAL CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

A Method for the Preparation of Rhenium(VI) Oxide[1]

BY H. NECHAMKIN[2], A. N. KURTZ AND C. F. HISKEY

Rhenium(VI) oxide is formed by the thermal decomposition of a neutralization product of rhenium(VII) oxide and dioxane. The dioxane complex appears to be $Re_2O_7 \cdot 3C_4H_8O_2$. Exact quantitative studies of the rhenium(VI) oxide disproportionation have been made and confirm a previously reported reaction.

Rhenium(VI) oxide was first prepared by Biltz and Lehrer[3,4] who interacted the metal and yellow rhenium(VII) oxide at 300°. By repeated cooling and grinding of the reagent mixture it was possible to get the reaction to go to completion in a number of days. Even then the product was not uniform, but had compositions ranging between $ReO_{2.4}$ and $ReO_{3.13}$.

A red rhenium(V) oxide also has been reported by Briscoe, *et al.*,[5] confirmed by Roth and Becker[6] and even described in Druce's recent monograph.[7] It now seems certain however that this substance was also the (VI) oxide and that this error has come into the literature largely because these authors did not have analytical methods sufficiently precise to distinguish between Re_2O_5(82.3% Re) and ReO_3(79.5% Re). Biltz's claims for ReO_3 however rest upon more satisfactory analytical evidence, including a crystal structure determination by X-ray diffraction.

In view of the indefiniteness of composition of Biltz's preparations, it was decided to develop an

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(1) Based on the thesis research of Howard Nechamkin for the Degree of Master of Science in Chemistry at the Polytechnic Institute of Brooklyn, June, 1949. Some of this material was presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Atlantic City, N. J., September 19, 1949.

(2) Department of Chemistry, Pratt Institute, Brooklyn, N. Y.

(3) W. Biltz, A. A. Lehrer and K. Meisel, *Nachr. Ges. Wiss. Gottingen, Math.-Physik. Klasse*, 191 (1931).

(4) W. Biltz, A. A. Lehrer and K. Meisel, *Z. anorg. allgem. Chem.*, **207**, 113 (1932); **214**, 225 (1933).

(5) H. V. A. Briscoe, P. L. Robinson and A. J. Rudge, *J. Chem. Soc.*, 3087 (1931); *Nature*, **129**, 618 (1932).

(6) W. A. Roth and G. Becker, *Z. phys. Chem.*, **A159**, 27 (1932).

(7) J. G. F. Druce, "Rhenium," Cambridge University Press, 1948, p. 32.