[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

A Phase Rule Study of the System Sodium Myristate-Water

BY R. D. VOLD, R. REIVERE AND J. W. MCBAIN

Sodium myristate is one of the commonly occurring soaps whose phase rule behavior with water has not previously been studied. The data here presented are of value in extending the correlation of phase rule diagrams with the properties of the soap molecule begun by McBain, Vold and Frick.[1]

In general the results obtained tend to show that sodium myristate and water have a phase diagram of the same type as that found for other sodium soaps.[1,2] As the anhydrous soap is heated it passes through a large number of mesomorphic phases before melting to isotropic liquid. These phases maintain their individuality in the presence of small amounts of water (up to about 10% by weight), the water merely lowering the temperatures at which a given phase is first formed. Further addition of water produces different phases which probably cannot exist in the absence of solvent.

Material, Experimental Methods and Data

The myristic acid was specially prepared and purified by Dr. S. Lepkovsky. Its equivalent weight was 227.8 by titration (theoretical value 228.2), and its melting point 55.0°. The sodium myristate was prepared by Dr. M. J. Vold by neutralization (to phenolphthalein) of a hot solution of the acid in 95% ethyl alcohol with sodium ethylate. The soap was freed from alcohol and water by drying in air at 105° with frequent stirring to prevent burning. The final product contained only 0.04 wt.% excess sodium hydroxide. It also contained 0.1 wt.% water as used, an amount which remained constant during the course of the experiments and which was allowed for in weighing out samples. Its transitions are compared in Table I with those of soap from Kahlbaum acid.[3]

TABLE I

TRANSITION TEMPERATURES OF ANHYDROUS SODIUM MYRISTATE

Phase change	Microscopic	Hot wire[a]	Dilatometric[a]	Ref. 3
	..	..	79°	not studied
Curd fiber⇆subwaxy	98(?)	..	113	107
subwaxy⇆waxy	141	134	135	141
waxy⇆superwaxy	177	175	176	176
superwaxy⇆subneat	218	207	204	217
subneat⇆neat	246	251	257	243
neat⇆isotropic liquid	315	309	(312)	310

[a] By Dr. M. J. Vold.

Essentially the same methods were employed in this investigation as in the previous studies of sodium oleate[2] and sodium stearate.[1] The temperatures at which anisotropic material forms on cooling (T_i), and the temperatures at which the last trace of curd fiber phase disappears on heating (T_c), were determined for systems of different compositions. The position of additional phase boundaries was obtained by microscopic study of samples sealed in flattened glass capillaries observed between crossed Nicols at about 100 ×. Dilatometric measurements were made on two aqueous systems (95.0% and 58.6% soap) to check the results of microscopic and visual observations. Finally, eighteen tubes covering the whole composition range were hung in a thermostat and observed at each of several temperatures, their condition being compared with that expected on the basis of the phase diagram as constructed from the preceding data.

Since only a limited quantity of myristate was available most of the visual observations were made on 1-g. systems sealed in Pyrex tubes of 7 mm. i. d. and 1 mm. wall thickness. The T_i of one system was determined first in a long tube and then again after the vapor space had been halved. The value of T_i found was the same within 2°. The results of T_i and T_c determinations are given in Table II. Immediately below T_i the solutions containing more than 50% soap were viscous anisotropic translucent gels. Those containing from 50–30% were very viscous, transparent, anisotropic gels.

TABLE II

VISUAL DETERMINATIONS OF TEMPERATURES OF PHASE BOUNDARIES OF SODIUM MYRISTATE SYSTEMS

Wt. %	T	T_c	Wt. %	T_i	T_c
100.0	316	..	50.5	171	70
92.8	292	..	49.9	165	69
90.4	289	..	48.3	173	68
90.2	290	..	43.9	176	67
88.0	290	..	43.0	175	..
87.4	291	..	40.4		64
81.8	292	102	35.0	138	61
73.6	288	..	32.5	117	61
73.1	288	84	29.5	81	..
70.4	286	83	24.8	..	58
63.8	275	80	17.0	..	56
61.3	273	..	9.5	..	52
61.0	267	78	5.0	..	48
55.4	239	74	1.0	..	41
50.7	174	..			

Some of the results of repeated microscopic observations are shown in Fig. 1, only those results being plotted for which the reality of the change was well established. The microscopic appearance

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

[2] R. D. Vold, *ibid.*, **43**, 1213 (1939).

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

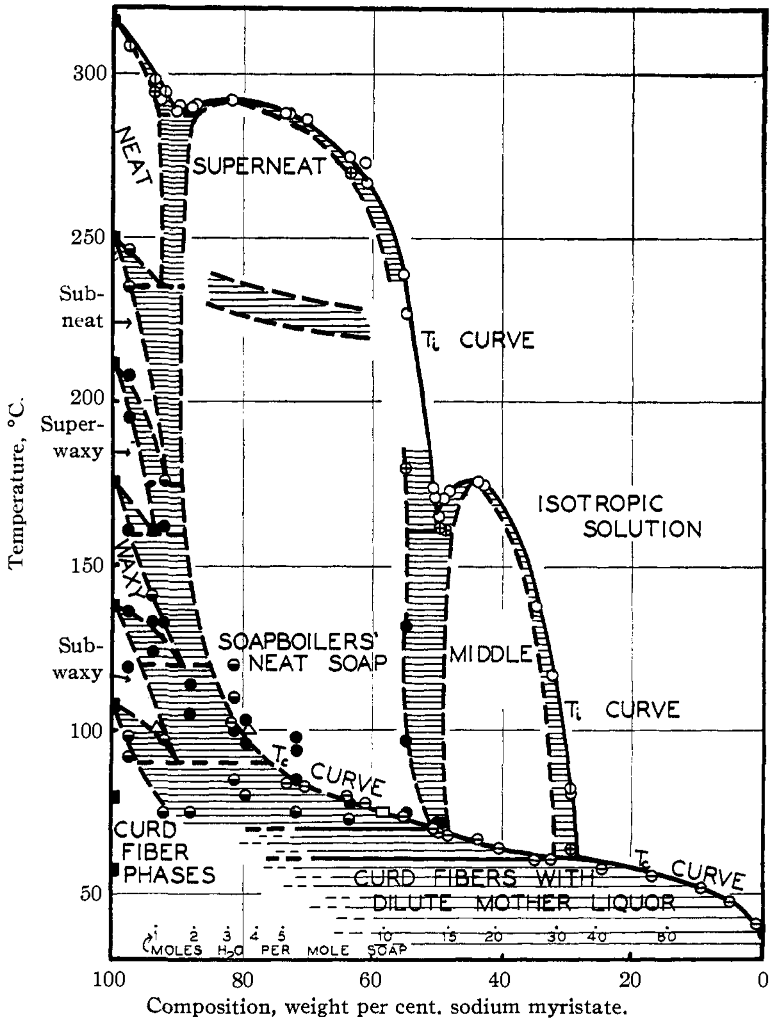

Fig. 1.—Phase diagram of the system sodium myristate–water: O, visual T_i; ◐, microscopic T_i; ⊕, T_o; ⊖, T_c; △, from vapor pressure measurements by W. W. Lee; □, from dilatometric measurements; ■, transition temperatures of the anhydrous soap; ●, microscopic changes; ◒, microscopic changes whose temperatures are less certain.

of the sodium myristate phases is very similar to that of the corresponding sodium oleate phases.[2] Unlike our experience with sodium palmitate,[4] it was possible to detect the change microscopically from subwaxy to waxy soap and from waxy to superwaxy soap in the case of anhydrous sodium myristate.

The macroscopic appearance of the different samples, determined by viewing experiments, served to confirm many of the boundaries shown in Fig. 1. However, in several instances, samples seemed to have a wax-like appearance at temperatures below the T_c curve where according to the diagram they should have contained curd fiber phase. It is not clear whether one of the waxy phases really does persist to temperatures lower than those shown in Fig. 1, or whether the whole phenomenon is due simply to inability always to distinguish curd fiber phase from the waxy phases visually.

Discussion

The phase diagram, Fig. 1, was constructed from all the data. Some of the boundaries are fully determined and are drawn in full lines. Near the superneat maximum the microscopic value of the melting point to isotropic liquid, determined not only on cooling but also on heating, was as much as 12° lower than the macroscopic curve for several samples, possibly due to a more easily induced orientation of superneat soap into a pseudo-isotropic arrangement by the glass of the microscope cell than is the case with the other phases.[5] In these cases T_0 was also found to be unusually low.

The minimum temperature at which isotropic liquid of composition intermediate between soapboilers' neat soap and middle soap can exist is rather well determined by the microscopic evidence that samples of different composition melted at 161°, thereby indicating the existence of a eutectic. Moreover, in the viewing experiments, none of the tubes in this composition range had any isotropic liquid at 160°, whereas isotropic liquid was present at 166°.

In the vicinity of the eutectic between neat soap and superneat soap, and here alone, duplicate determinations of T_i sometimes differed by as much as 5° and many non-reproducible values were obtained at temperatures higher than the confirmed values shown on the curve. A similar effect has also been noticed with other soaps.[1,2,6] It seems possible that it may be caused by a certain degree of residual orientation of clusters of

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(4) R. D. Vold and M. J. Vold, This Journal, **61**, 808 (1939).

(5) M. J. Vold, *ibid.*, **63**, 160 (1941).

(6) J. W. McBain, M. J. Vold and J. L. Porter, *Ind. Eng. Chem.*, **33**, in press (1941).

molecules in the isotropic soap solution, which occasionally leads to the persistence of an appearance of small patches of anisotropy at temperatures higher than the true melting point.

It is worth noting that in the lower left-hand portion of soapboilers' neat soap in Fig. 1, the characteristic appearance is not fully attained until temperatures in the neighborhood of the microscopic observations shown in Fig. 1, 5 to 10° higher than the dashed portion of the T_c curve.

The general position of the boundary of the field of homogeneous middle soap is determined by the composition of the maximum in the T_i curve and the compositions at the ends of the two flats in the T_c curve, although the exact values may be in doubt to 2%. All systems within this range of composition had the typical macroscopic appearance and properties of middle soap while systems at the edges obviously consisted of a mixture of two phases. A microscopic sample containing 54.9% soap did not begin to melt to isotropic liquid until 180°, whereas melting would have occurred at 161° if any middle soap had been present at this composition.

That superneat soap and soapboilers' neat soap are actually two distinct phases agrees with slight changes in microscopic appearance at temperatures between 230 and 245°, but is more definitely based upon anomalous changes in apparent viscosity with temperature, which have also been noted with sodium oleate. For instance, an 87.4% sodium myristate system first set to a stiff gel on cooling below T_i, then softened between 240 and 220° to the extent that it again flowed fairly readily on inverting the tube and finally became again immobile at lower temperatures.

That the fields of soapboilers' neat soap and superneat soap are not continuous with anhydrous soap seems clear from the change which occurs in microscopic appearance. Between 120° and T_i systems containing less than about 90% soap undergo very few changes in microscopic appearance and display a much coarser structure than that shown by more concentrated systems.

Systems containing more than about 90% sodium myristate undergo a large number of changes in microscopic appearance on heating, and these resemble closely the phenomena observed with the anhydrous soap. The actual points arrange themselves on the series of tongues shown in Fig. 1. The genotypic transition[7] is shown in Fig. 1 at the melting point of myristic acid, 58°, without further interpretation, as is also done with the transition at 79°.

Effect of Chain Length.—The solubility curves[1,8] defining the field of isotropic liquid for each of the five common sodium soaps and water are shown in Fig. 2. To complete Table IV of Reference 1 the following values for sodium myristate should be added: 39°; 35.8, 61°; 17.0, 176°; 13.9, 161°; 3.1, 292°; 1.4, 287°, these figures being temperatures and compositions at corresponding points.

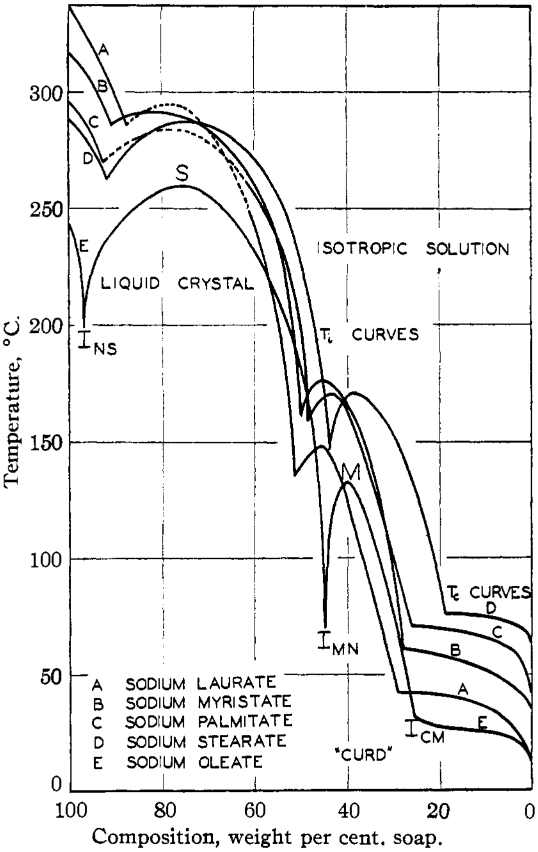

Fig. 2.—Boundaries of the field of isotropic solution in various systems of soap and water.

At relatively low temperatures (below 150°) the saturated solution is dilute on a molecular basis, and any soap molecule finds itself in a largely aqueous environment. Consequently, it is not surprising that in this region the solubility decreases with increasing length of the hydro-

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

(8) J. W. McBain, L. H. Lazarus and A. V. Pitter, *ibid.*, **A147**, 87 (1930); J. W. McBain, G. C. Brock, R. D. Vold and M. J. Vold, THIS JOURNAL, **60**, 1870 (1938).

carbon chain. At high temperatures (greater than 270°), however, the saturated solution is concentrated and the environment of a given soap molecule is not so "unfriendly." Here the order of solubility seems to be related to the strength of the neat soap "structure" and is the same as the order of melting points.[3] Consequently, an isotropic solution of sodium myristate in which neat soap just forms is more concentrated than is the corresponding solution of sodium laurate, the effect of increasing chain length here being just opposite to that at lower temperatures.

Summary

A large portion of the phase diagram of the system sodium myristate–water has been constructed from data obtained by visual and microscopic observations of the temperatures at which phase changes occur, supplemented by a few dilatometric determinations and by viewing experiments at selected temperatures. The phase behavior of this system is qualitatively similar to that of systems of the other saturated soaps and of sodium oleate with water.

The effect of the chain length of the soap molecule on the phase diagram involves at least two opposing factors, the longer chain soaps being less soluble at low temperatures and low concentrations of soap while at higher temperatures and high concentrations of soap the shorter chain soaps are the less soluble.

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The Solubility Curve of Sodium Deoxycholate in Water

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Determinations of the solubility of sodium deoxycholate in water at different temperatures have been made and used to establish the type of interaction of this substance with water.

An important physiological function ascribed to the bile acids—a generic term which also includes their sodium salts—is to promote transfer of water-insoluble materials.[1] In addition to emulsification, two other mechanisms have been suggested for this process. One[2] (p. 110) is the formation of addition compounds between the bile salt and the water-insoluble substance, the so-called choleic acids. Recently[3–7] it has been recognized that the action may be much less specific, the bile salts simply acting like soap solutions which can solubilize water-insoluble materials by retention on or in the colloidal micelles.[8,9]

The present work was undertaken to determine whether a representative bile salt would form addition complexes with water and whether it would give a phase rule diagram similar to that of the soaps, since both these substances have the same solubilizing action in dilute aqueous solution.[5–7] Sodium deoxycholate was chosen for this study since physico-chemical measurements have been made on its solutions[5] and since it, together with sodium apocholate, has the greatest tendency to form coördination compounds (ref. 2, p. 122) in the solid state.

Experimental

Material.—Sodium deoxycholate purchased from Riedel-de Haen in 1939 was used without purification. It contained 10.5% water[10] as judged by the loss of weight at 105°. The specific rotation, $[\alpha]^{20}\text{D}$, of a 2.57% solution was 39.40° comparing with Josephson's value of 45.70° for a 2.5% solution.[11] The pH of a 2.57% solution was 9.63 while that of a 26.5% solution was 10.04. The melting point of the anhydrous material was 357–365° (cor.). The failure to melt sharply may be due to impurities or to decomposition during melting, since repeated melting of the same sample resulted in progressive lowering of the melting point with eventual formation of a non-crystallizable glass.

Although the sodium deoxycholate was a white powder, the solutions were yellowish in color. Solutions prepared

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(1) B. Moore and D. P. Rockwood, *J. Physiol.*, **21**, 58 (1897); B. Moore and W. H. Parker, *Proc. Roy. Soc.* (London), **B68**, 64 (1901); F. B. Kingsbury, *J. Biol. Chem.*, **29**, 367 (1917); A. C. Frazer, *Analyst*, **63**, 308 (1938).

(2) H. Sobotka, "The Chemistry of the Sterids," Williams and Wilkins Co., Baltimore, (1938). Also see H. Sobotka and A. Goldberg, *Biochem. J.*, **26**, 555 (1932), for the "choleic acid principle."

(3) J. W. McBain, *J. Chem. Education*, **17**, 109 (1940).

(4) J. W. McBain, R. C. Merrill and J. R. Vinograd, THIS JOURNAL, **62**, 2880 (1940).

(5) J. W. McBain and S. A. Johnston, to be communicated to THIS JOURNAL.

(6) R. R. Roepke and H. L. Mason, *J. Biol. Chem.*, **133**, 103 (1940).

(7) M. L. Anson, *J. Gen. Physiol.*, **23**, 239 (1939).

(8) J. W. McBain and M. E. L. McBain, THIS JOURNAL, **58**, 2610 (1936); J. W. McBain and T. M. Woo, *J. Phys. Chem.*, **42**, 1099 (1938).

(9) G. S. Hartley, *J. Chem. Soc.*, 1968 (1938).

(10) All concentrations are given in terms of weight per cent.; that is, g./100 g. total system, unless otherwise stated.

(11) Ref. (2), p. 134.