be comparable to that observed by Piper, Chibnall, *et al.*,[11] in the case of hydrocarbons, fatty acids, etc., where solubility of a substance of long chain molecules in one of short chain molecules is far less common than the converse.

Summary

Diagrams have been determined showing the phase behavior of the four component system sodium palmitate–sodium laurate–sodium chloride–water at 90° for two constant ratios of sodium palmitate to sodium laurate. From these data a curve has been constructed which permits fairly accurate prediction of the phase rule diagram for any mixture of the two soaps.

Corresponding phase boundaries in the mixed soap system occur at salt concentrations far nearer the values for pure laurate than for pure palmitate. This effect is probably due to interference of the shorter sodium laurate molecules with the degree of regularity in the sodium palmitate micelles.
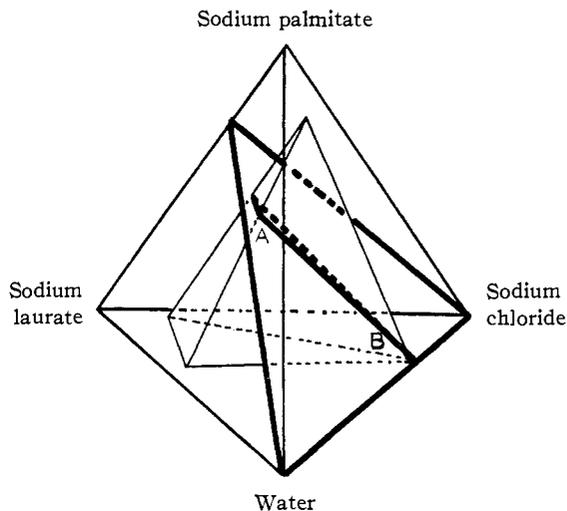
The least soluble phase of sodium palmitate is

Fig. 6.—A possible relation of the phase boundary AB to the tetrahedron representing the quaternary system at constant temperature.

made actually as soluble as sodium laurate by the addition of sodium laurate to the system.

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(11) S. H. Piper, A. C. Chibnall, S. H. Hopkins, H. Pollard, J. A. B. Smith and E. F. Williams, *Biochem. J.*, **25**, 2072 (1931).

Thermodynamic Behavior of Liquid Crystalline Solutions of Sodium Palmitate and Sodium Laurate in Water at 90°

BY ROBERT D. VOLD AND MARJORIE J. VOLD

The liquid crystalline states of aggregation[1] are characterized, as their name implies, by sets of mechanical and physical properties intermediate between those of true crystals and those of true liquids. From the theoretical standpoint, also, these states are intermediate between crystal and liquid. Corresponding to the definition of a crystal as an array of atoms or molecules in regular periodic order in all three coördinate directions and the definition of a liquid as an essentially chaotic or "zero dimensional ordered" array, liquid crystals can be defined as aggregates of atoms or molecules regularly arranged in only one or two directions, and randomly distributed with respect to the remaining coördinate or coördinates.

The most convenient identification of a particular state as truly liquid crystalline makes use of the property of spontaneous optical anisotropy, common to all liquid crystals. The fact that

optically homogeneous regions—"single liquid crystals"—seldom grow spontaneously to a size much greater in any dimension than the wave lengths of visible light, together with the fact that these homogeneous regions are readily deformable, gives rise to a very large variety of marvelously beautiful optical figures observable microscopically using polarized light. Study of the optical properties has given a great deal of information about the structure of various liquid crystals.[2] Still it is important to recognize that these optical properties are all consequences of the anisotropy and deformability of the liquid crystals and are *not* independent characteristics.[3]

(2) See, *e. g.*, A. van Wijk, *Ann. Physik*, [5] **3**, 879 (1929).

(3) A. S. C. Lawrence, *Trans. Faraday Soc.*, **34**, 660 (1938), refuses to classify certain phases of the alkali soaps as liquid crystalline on the ground that the characteristic optical figures cannot be obtained. He attributes the spontaneous optical anisotropy that exists even in completely strain free masses prepared by undisturbed cooling of the isotropic liquid form to the presence of oriented sub-microscopic crystals, an hypothesis which established phase rule diagrams render completely untenable. Moreover, J. W. McBain and W. E. Elford actually have obtained excellent photographs of typical focal conic structures in the case of aqueous potassium oleate. One such photograph has been published [J. W. McBain, *Nature*, **114**, 49 (1924)].

(1) For an excellent discussion and classification, see J. D. Bernal and D. Crowfoot, *Trans. Faraday Soc.*, **29**, 1032 (1933). For a detailed theoretical discussion see C. Hermann, *Z. Krist.*, **79**, 186 (1931).

The liquid crystalline phases of the alkali soaps, of which the best known are neat soap and middle soap,[4] can contain large amounts of water in the solution. The purpose of this paper is to make a comparison of the behavior of these aqueous liquid crystalline solutions with that of crystalline solutions on the one hand and true liquid solutions on the other, based on a study of the partial pressure of water vapor as a function of the composition of the soap system at 90°. Use has been made of the measurements of Vold and Ferguson,[5] made in connection with a phase rule study of the system sodium palmitate–water at 90°. Similar measurements on the system sodium laurate–water are reported in this paper.

Experimental

Materials.—The sodium laurate used was prepared from Eastman Kodak Co. best grade of lauric acid by neutralization in boiling ethyl alcohol with sodium ethylate, followed by removal of alcohol and water by drying to constant weight at 105°. The resulting soap contained 0.49 wt. % excess lauric acid. The lauric acid from which the soap was made had the following characteristics: mol. wt. (from titration), 202.6; iodine no. 0.05; m. p. 45°, (the same as a sample of Kahlbaum lauric acid). A few measurements were made using the same sodium laurate stock, No. 102, as had been used in previous phase rule work.[6] This soap gave vapor pressure points lying identically on the same curve as values obtained with the new preparation.

Vapor Pressure Measurements.—The vapor pressure of water as a function of the composition of the soap system was measured by the isopiestic method described by Vold and Ferguson.[5] Only one modification was made in the procedure there described. Formerly air was evacuated from the Y-tubes to increase the rate of attainment of equilibrium by transference of water vapor. In the present series the tubes were not evacuated. True reversible equilibrium was reached in the time allowed (about thirty days), as proved by the fact that systems of different initial composition, equilibrated with the same acid, reached the same final composition. In many cases one member of such a pair of tubes showed a net transfer of water from the soap to the sulfuric acid, while the other showed net transfer of water from the acid to the soap.

Analysis.—In these experiments, as in those of Vold and Ferguson,[5] the water content of the equilibrated soap system was determined by drying to constant weight at 105°. Recently Lawrence[3] has reported that alkali soaps may retain as much as 7% of water at this temperature. A 1-g. sample of sodium palmitate or sodium laurate requires about one hour at 105° to reach constant weight. Direct analysis for soap by decomposition with standard acid, extraction with ether and titration of the recovered

(4) For terminology see J. W. McBain, R. D. Vold and M. J. Vold, THIS JOURNAL, **60**, 1866 (1938).
(5) R. D. Vold and R. H. Ferguson, *ibid.*, **60**, 2066 (1938).
(6) J. W. McBain, G. C. Brock, R. D. Vold and M. J. Vold, *ibid.*, **60**, 1870 (1938).

fatty acid with standard alkali shows that both these soaps are practically completely dried by this procedure. Moreover, dehydration at 105° has become a standard

TABLE I

VAPOR PRESSURE OF SODIUM LAURATE–WATER SYSTEMS AT 90°

Initial wt. % NaL	Composition Final Wt. % NaL	Mole % NaL	H₂SO₄ concn. wt. % H₂SO₄	Vap. press., mm.	P/P_{H_2O}
		Isotropic Solution			
15.0	15.0	1.25	1.63	523	0.9935
25.0	25.2	2.50	3.19	520	.9890
29.7	35.2	4.25	5.20	515	.9795
		Middle Soap			
32.8	39.6	5.15	7.11	510.5	0.9709
41.5	45.3	6.40	8.25	508	.9661
44.9	48.7	7.00	9.85	503.5	.9598
39.8[a]	50.4	7.50	10.42	501.5	.9538
44.6	51.5	7.80	10.22	502	.9547
	Middle Soap and Neat Soap in Equilibrium				
49.8	51.6	7.83	11.83	497	0.9450
54.9	52.2	8.00	11.93	497	.9450
63.4[a]	55.0	9.00	11.88	497	.9450
		Neat Soap			
58.0	59.1	10.05	14.13	489.5	0.9329
62.2	60.3	11.1	14.24	489	.9300
69.9[a]	65.5	13.5	16.73	480	.9129
91.2	69.2	15.4	17.15	478	.9091
72.6	70.7	16.3	20.27	465	.8844
76.0	73.7	18.4	24.29	445.5	.8473
75.7	74.6	19.0	25.86	438	.8330
93.25	75.1	19.5	24.69	443.5	.8435
	Neat Soap and Waxy Soap in Equilibrium				
78.0	76.7	21.0	26.52	433	0.8235
76.0	77.1	21.2	26.76	431.5	.8207
76.6	77.6	21.5	26.45	433	.8235
		Waxy Soap			
79.8	78.7	23.0	26.96	430	0.8178
82.0	80.4	24.8	27.36	427.5	.8131
88.8	81.2	25.8	26.96	430	.8178
87.3	83.0	28.5	27.46	426.5	.8111
83.0	83.4	29.3	27.74	425	.8083
77.2	85.4	32.4	28.03	423	.8045
89.75	86.6	34.5	28.09	422.5	.8036
87.0	87.0	35.2	28.41	420	.7988
	Waxy Soap and Curd Fibers in Equilibrium				
90.0	89.3	40.0	28.62	419	0.7969
		Curd Fibers			
91.90	91.17	45.1	28.90	416.5	0.7920
92.98	91.92	47.4	29.63	411.5	.7826
92.85	93.43	53.3	30.27	406.5	.7731
95.17[a]	94.05	57.0	32.36	391.5	.7446
93.89	95.33	62.0	32.24	392	.7455
94.9	96.38	68.0	35.28	368	.7000
97.48[a]	97.46	75.2	38.78	336.5	.6400
95.42	97.39	74.5	41.02	314	.5973

[a] Points obtained using preparation No. 102.

method of analysis for a great variety of commercial alkali soaps.[7] It is certain that in most cases the amount of water remaining at 105° is less than 0.5%.

Data

The experimental data are contained in Table I. Column 1 gives the initial composition of the soap system, cols. 2 and 3 the final composition of the soap system, col. 4, the composition of the sulfuric acid solution of the same vapor pressure at 90° and cols. 5 and 6, the vapor pressure and its ratio to that of pure water at 90°. Figure 1 shows graphically the variation of the vapor pressure with the water content. The horizontal portions of the curve represent composition ranges in which two condensed phases are in equilibrium. The terminal points of these "flats" give the limiting compositions for the existence of each of the five phases. These points are determined within 0.5% soap. Table II gives the composition ranges for the existence of each of these phases at 90°.

TABLE II

THE RANGE OF EXISTENCE OF AQUEOUS SODIUM LAURATE PHASES AT 90°

| Phase | Composition range | |
	Wt. % NaL	Mole % NaL
Isotropic solution	0.00– 35.8	0.00– 4.40
Middle soap	38.0 – 52.0	4.80– 7.95
Neat soap	55.4 – 75.0	9.10– 19.5
Waxy soap	77.0 – 88.0	21.2 – 36.3
Curd fiber phase	91.3 –100	45.2 –100

Waxy Soap.—The existence of waxy soap in the sodium laurate–water system[8] at 90° as a phase separate from neat soap on the one hand and curd fiber phase on the other, is proved by the vapor pressure curve in Fig. 1. The flat FG indicates the composition range within which waxy soap is present in equilibrium with neat soap and the flat HI corresponds to the equilibrium between waxy soap and curd fibers. The continuous change of the vapor pressure with composition along the curve from G to H shows that waxy soap at this temperature is a solution phase whose composition can vary continuously from 77.0 to 88.0 wt. % sodium laurate. Had this new phase not been present, neat soap and curd fiber phase would have been in direct equilibrium and the vapor pressures F and I would necessarily have been identical.

(7) A.S.T.M. Preprint (1937), p. 30, Report of Committee D-12 on Soaps and Detergents.

(8) That a waxy soap phase exists in the sodium palmitate system was already known from work described in a paper by R. D. Vold, F. B. Roseveare and R. H. Ferguson, presented at the Chicago meeting of the American Oil Chemists' Society, October, 1938.
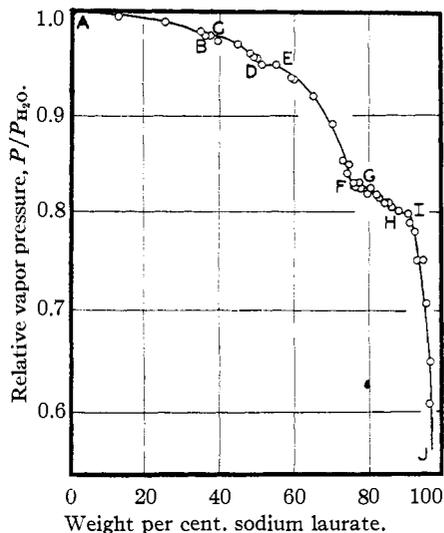

Fig. 1.—Vapor pressure of aqueous sodium laurate systems at 90°.

Waxy soap is an opaque dull white solid. It is frequently impossible to distinguish it from curd phase by visual observation. It will not flow under gravity, but is sufficiently soft to be deformed by pressing with a stirring rod. It is optically anisotropic as shown by the fact that it is brilliantly illuminated in the polarizing microscope between crossed nicols.

Presumably the aqueous phase here described is related to the waxy phase of anhydrous sodium laurate which preliminary dilatometric observations indicate is formed when curd fiber phase is heated above temperatures around 108°. Experimental work is under way which will make apparent the relation of waxy soap to the phase rule diagrams included in our recent paper on the sodium laurate system.[6]

Activity Calculations and Results

Each of the five phases of aqueous sodium laurate systems and of the four phases of aqueous sodium palmitate systems at 90° is a solution phase. The variation of the properties of these solutions with concentration within each phase, and also the variation in properties from one phase to the next, can be associated with the changes that occur in the spatial distribution of the soap molecules, from complete dissociation into randomly distributed ions up to the practically perfect regularity of the crystalline solution, curd fiber phase. In order further to develop this point of view, it is desirable to express the results of the vapor pressure measurements in terms of a

quantity that refers primarily to the soap, rather than to the water, but that retains as nearly as possible the same complete independence of any kinetic models of the solutions as does the vapor pressure itself. The thermodynamic activity is such a quantity, giving as it does the free energy change per mole accompanying transfer of an infinitesimal amount of soap from a carefully defined standard state to the real solution of given concentration. The sole assumption made is that in some limiting concentration, here, as usual, infinite dilution, the behavior of the real system approaches that of the standard state.

The standard state is defined to be a condition such that the soap is completely dissociated into single free ions which are distributed entirely at random through the solution and which have no interactions with each other or with the solvent water molecules. It is further necessary for complete specification to assign a concentration to this hypothetical solution. It is convenient to define this concentration to be unity in terms of the particular concentration unit employed. Were the calculations confined to the relatively dilute isotropic liquid solution of soap in water, the most convenient unit would be the molality. Since the calculations are to be carried into quite concentrated systems, the mole ratio (moles of soap per mole of water) has been used instead. The
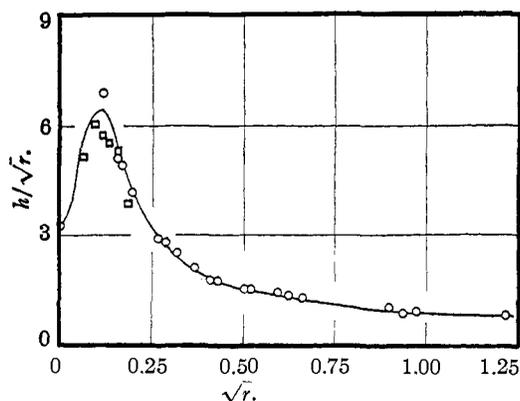

Fig. 2.—$h/\sqrt{r}$ as a function of $\sqrt{r}$ for sodium palmitate at 90°: □, points from work of McBain and Barker;[10b] ○, points from work of Vold and Ferguson.[5]

ratio $a_2^{1/2}/r$, where a_2 is the activity of the soap and r its mole ratio, then approaches unity at infinite dilution.

For the calculation of the activity of the soap from the vapor pressure of the water, use has been

made of the Randall and White[9] modification of the Gibbs equation

$$N_1 \, d \ln a_1 + N_2 \, d \ln a_2 = 0 \qquad (1a)$$

N_1 and N_2 are the mole fractions and a_1 and a_2 the activities of the two components of a binary system. If the Randall and White divergence function is defined for this case as

$$h = \frac{\ln a_1}{2r} + 1 \qquad (1b)$$

where r is the ratio N_2/N_1, then equation (1a) can be written

$$\ln \frac{a_2^{1/2}}{r} = -h - 2 \int_{r=0}^{r=r} \frac{h}{\sqrt{r}} \, d(\sqrt{r}) \qquad (1c)$$

The writing of this equation in integrated form involves the assumption that $a_2^{1/2}/r$ approaches a finite value at infinite dilution. (The value is made unity by suitable choice of concentration for the standard state.) Randall and White[9] give also the limit to which $h/\sqrt{m}$ approaches at 25°. Randall, McBain and White[10] give the value of this limit at 90°. Since m, the molality of soap, and r, the mole ratio of soap to water, differ by the constant factor 55.51, the limit to which $h/\sqrt{r}$ approaches at 90° is readily seen to be 3.28.

The actual behavior of very dilute soap solutions is complicated by the hydrolysis of the soap ion and the precipitation of slightly soluble acid soaps. However, as has been pointed out,[9] this complication need not be considered since all measurements were made at concentrations where hydrolysis is negligible.
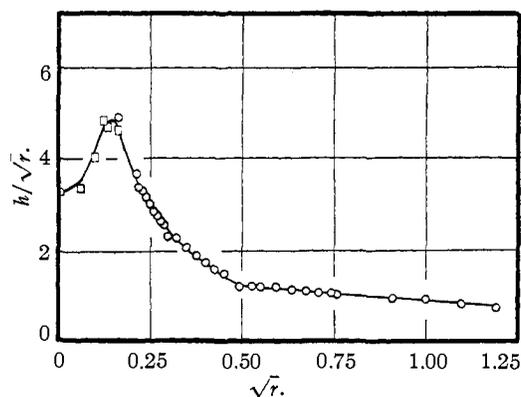

Fig. 3.—$h/\sqrt{r}$ as a function of $\sqrt{r}$ for sodium laurate: □, from work of McBain and Barker;[10b] ○, points from data of Table I.

Figures 2 and 3 show the way in which $h/\sqrt{r}$ varies with $\sqrt{r}$ for sodium palmitate systems and

(9) M. Randall and A. M. White, THIS JOURNAL, 48, 2514 (1926).
(10) M. Randall, J. W. McBain and A. M. White, ibid., 48, 2517 (1926); J. W. McBain and M. Barker, Trans. Faraday Soc., 31, 149 (1935).
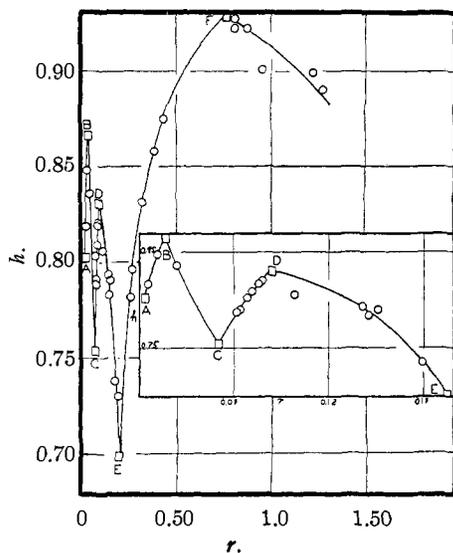
Fig. 4.—h as a function of r for sodium palmitate. □, points from ends of phase fields; AB, isotropic solution–middle soap; BC, middle soap; CD, middle soap–neat soap; DE, neat soap; EF, neat soap–curd fibers; F, curd fibers. Insert shows enlargement of curve AE. ○, other points from data of Vold and Ferguson.[5]

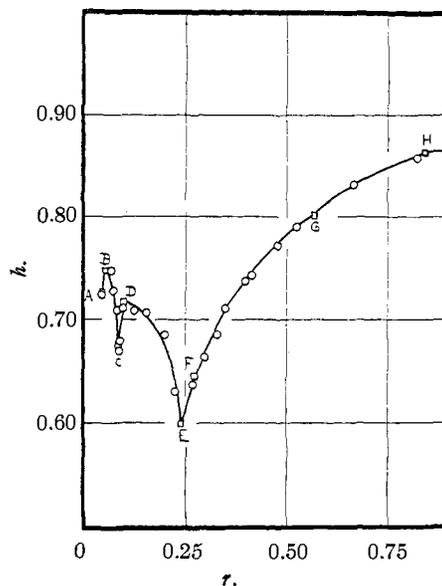Fig. 5.—h as a function of r for sodium laurate: □, points from ends of phase fields; AB, isotropic solution–middle soap; BC, middle soap; CD, middle soap–neat soap; DE, neat soap; EF, neat soap–waxy soap; FG, waxy soap; GH, waxy soap–curd, fibers; H, curd fibers; ○, other points from data of Table I.

sodium laurate systems, respectively. Figures 4 and 5 show the variation of h as a function of r. The discontinuities marking phase boundaries are much more apparent in the latter curves The function is also extremely sensitive to experimental error. For evaluation of a_2 by means of equation 1c, values of h were read off from Figs. 4 or 5 and values of the integral obtained by determination of the area under the corresponding portion of the curves of Figs. 2 or 3. Any inaccuracy in these latter curves, especially in dilute solutions, affects equally the numerical value of all activities obtained at higher concentrations and cannot affect conclusions drawn from the form of the activity–concentration curve.

Tables III and IV give the numerical results of these calculations for sodium laurate and sodium palmitate, respectively. Cols. 1 and 2 give the concentration; col. 3, the activity itself; col. 4, the ratio $a_2^{1/2}/r$, the familiar activity coefficient for an electrolyte; and col. 5, the ratio a_2/N_2.

Discussion

The activity–concentration curves for the various soap phases exhibit three qualitatively different types of behavior. The activity coefficient $a_2^{1/2}/r = \gamma$ decreases rapidly in the isotropic solu-

tion.[9,10] The corresponding value of a_2/N_2 shows a net increase (it is zero at infinite dilution), in sharp contrast to the behavior of the other four phases. The ratio of activity to mole fraction a_2/N_2 decreases uniformly for both waxy soap and curd fiber phase as the soap concentration increases. The net change in a_2/N_2 for each of the liquid crystalline phases, middle soap and neat soap, is very slight, but (except for sodium palmitate middle soap) the values go through a distinct minimum. The purpose of this discussion is to examine, at least qualitatively, the factors responsible for this difference in behavior between liquid, liquid crystalline and crystalline solutions.

The behavior of the isotropic solution already has been discussed by Randall, McBain and White[10a] and McBain and Barker.[10b] The real soap solution differs greatly from the model used for the standard state, and the value of the activity coefficient is correspondingly very small. The factors responsible for this small value are, first, that the ions are partly associated into molecules and, second, that both molecules and fatty acid ions are associated into colloidal aggregates. The work of McBain[11] and his collaborators has

(11) "International Critical Tables," Vol. V, 1929, pp. 446 ff.

TABLE III

ACTIVITIES OF SODIUM PALMITATE AT 90°

Composition mole fraction NaP (N_2)	$10^5 a_2$	$a_2^{1/2}/r = \gamma^a$	$10^5 a_2/N_2$
		Isotropic Solution[b]	
0.0224	0.445	0.0916	19.85
		Middle Soap	
0.0329	0.445	0.0620	13.5
.0384	.482	.0548	12.5
.0476	.566	.0476	11.9
.0566	.655	.0426	11.56
.0583	.673	.0418	11.52
		Neat Soap	
0.0825	0.673	0.0288	8.16
.0909	.702	.0265	7.74
.0992	.736	.0247	7.43
.107	.770	.0231	7.19
.115	.802	.0218	6.87
.123	.848	.0208	6.89
.130	.900	.0200	6.92
.138	.955	.0193	6.92
.145	1.022	.0188	7.06
.152	1.109	.0187	7.28
.1542	1.158	.0186	7.50
		Curd Fibers	
0.437	1.158	0.00446	2.65
.500	1.277	.00357	2.55
.524	1.309	.00329	2.50
.546	1.347	.00306	2.47

[a] $a_2^{1/2}/r$ of this calculation is identical with $a_2^{1/2}/m$ of Lewis and Randall "Thermodynamics," McGraw–Hill Book Co., Inc., New York, N. Y., 1923, p. 328, since the concentration of the standard state is taken as unity in terms of r rather than m. [b] Activity coefficients for the isotropic solutions of these and other soaps have been calculated by Randall, McBain and White and by McBain and Barker.[10]

TABLE IV

ACTIVITIES OF SODIUM LAURATE AT 90°

Composition mole fraction NaL (N_2)	$10^5 a_2$	$a_2^{1/2}/r = \gamma$	$10^5 a_2/N_2$
		Isotropic Solution	
0.0440	1.756	0.0913	39.9
		Middle Soap	
0.0481	1.756	0.0831	36.5
.0521	1.840	.0801	35.4
.0566	1.927	.0731	34.0
.0610	2.016	.0692	33.0
.0654	2.098	.0654	32.1
.0697	2.162	.0621	31.0
.0741	2.362	.0607	31.9
.0795	2.621	.0589	33.0
		Neat Soap	
0.0910	2.621	0.0512	28.8
.1072	2.959	.0454	27.6
.1228	3.249	.0406	26.4
.1380	3.434	.0367	24.9
.1525	3.832	.0344	25.1
.1667	4.251	.0326	25.5
.1802	4.747	.0313	26.3
.1950	5.550	.0509	28.5
		Waxy Soap	
0.212	5.550	0.0272	25.8
.231	5.610	.0249	24.3
.259	5.700	.0213	22.1
.286	5.776	.0190	20.2
.310	5.806	.0169	18.7
.333	5.929	.0154	17.8
.355	5.960	.0141	16.8
.363	5.991	.0136	16.5
		Curd Fiber Phase	
0.452	5.991	0.00937	13.3
.500	6.022	.00776	12.02
.545	6.053	.00649	11.1
.583	6.100	.00552	10.5
.615	6.147	.00497	10.3
.643	6.289	.00456	9.79
.667	6.432	.00401	9.65

shown that the formation of colloidal aggregates is virtually complete in isotropic solutions less concentrated than those saturated with respect to middle soap. Consequently, this process can be neglected as a factor in the interpretation of the further variation in activity observed in the liquid crystalline and crystalline soap phases,

The probable source of the difference in properties between these phases on the one hand and isotropic solution on the other is the following difference in internal constitution. The isotropic solution is made up of units which, though highly organized in themselves,[12] are nevertheless too small to be visible in the ultramicroscope and are randomly distributed. The organization of the soap molecules in the liquid crystalline and crystalline phases extends over regions rather larger

(12) K. Hess and J. Gundermann, *Ber.*, **70**, 1800 (1937).

than, or at least of the order of, the wave lengths of visible light.

The change in partial molal free energy, $RT \ln a_2$, accompanying dilution of any of these solution phases with water is, of course, made up of changes in both heat content and entropy, and the latter in turn depends partly upon the interaction of the different molecules and partly on the regularity of their spatial distribution. In an ideal solution where the two species of molecules are distributed entirely at random, the free energy of dilution is $RT \ln N_2/N'_2$, where N_2 and N'_2 are the mole fractions in the more concentrated and more dilute solutions, respectively.

For such a solution a_2/N_2 is constant. (It is unity if the standard state is the pure liquid.) However, constancy of a_2/N_2 does not necessarily mean that the solution is ideal. The actual departures of a_2/N_2 from constancy in each of the four phases, middle soap, neat soap, waxy soap and curd fiber phase is far less than would be expected if such departure were a measure of their deviations from ideality.

The interpretation of the activity concentration curves for curd fiber phase would be facilitated by a knowledge of its detailed structure, which, unfortunately, is incomplete. There are several types of possible behavior. One is that the water is randomly distributed among the hydrophilic points of the soap lattice. Its presence there would have a distorting effect on the lattice. The consequent variation of activity with concentration would be strongly dependent on the nature of the interaction of the water and soap molecules and would be entirely unpredictable from statistical considerations alone. A second possibility is that aqueous curd fiber phase has essentially the same lattice as the crystalline anhydrous soap except that all the sites are not occupied by soap molecules. If the empty sites were randomly distributed and if each created a cavity that could be filled by one and only one water molecule, then the solution would have the same configurational entropy as a simple mixed crystal.[13] In other words, a_2/N_2 would be constant. If the empty sites could be occupied by more than one molecule of water a_2/N_2 would show negative deviations from constancy. A third possibility is that water and soap are not molecularly dispersed in curd fiber phase, but that water is held on the surface of very thin fibers, perhaps only two molecules in thickness. Here again it is impossible to derive the activity–concentration curves without knowledge of the interaction energies.

Unfortunately, at present none of these three hypotheses lends itself readily to an even qualitative description of the two principal characteristics of the observed curves, namely, that a_2/N_2 varies as slowly as it does, and that the observed change is a decrease with increasing soap concentration.

The activity–concentration curve for waxy soap is qualitatively similar to that of curd fiber phase and not to that of middle soap or neat soap.

(13) J. H. Hildebrand, THIS JOURNAL, **59**, 794 (1937).

This fact, while not conclusive, indicates that waxy soap may be a second crystalline solution of water in soap, rather than yet a third mesomorphic form.

Within each of the liquid crystalline phases, neat soap and middle soap, the variation of a_2/N_2 is surprisingly small. The curves are qualitatively different from those for waxy soap or curd fiber phase in that, except for the middle soap of sodium palmitate, they all show a definite minimum.

If the ratio of activity to mole fraction is constant for a single phase, it is possible to redefine the standard state in such a way that the new activity with respect to the new standard state is actually equal to the mole fraction. Kinetically, this new standard state would correspond to a pure soap in the given liquid crystalline condition, in the same way as the standard state for liquid solutions is taken as the pure liquid. The significance of a constant ratio of activity to mole fraction is then that for each phase separately, over its own limited range of existence, Raoult's law holds.

That Raoult's law should hold, even in this limited sense and with maximum deviations of only 17% for a system made up of such widely different substances as soap and water, and which is not even a true liquid, but is an anisotropic liquid or liquid crystalline solution, seems at first sight very extraordinary. In a recent paper Hildebrand[13] has pointed out that Raoult's law would be expected to hold for solutions of hydrocarbons of very different chain length. He shows how the term in the free energy equal to $RT \ln N$ comes from the fact that there are more spatial configurations for the solution than for the pure substances. The quantitative discussion is based on a solid solution in which there is a definite crystal lattice but an argument is given to show that the results can be carried over to the case of liquid solutions. The same argument certainly permits their application to liquid crystalline solutions.

Using Hildebrand's result, one can say that if for each of the liquid crystalline phases there exists a definite structural framework which is maintained intact over the whole range of existence of the phase, the only effect of dilution being to diminish the soap population of the "lattice," then, as a first approximation, a_2/N_2 should be constant. As already has been pointed out in the discussion of curd fiber phase, the possibility

that more than one water molecule may occupy a position in the "lattice" vacated by a soap molecule leads to negative deviations of a_2/N_2 from constancy. a_2/N_2 for the liquid crystalline phases except for the middle soap of sodium palmitate, does go through a minimum, but it is quite possible that factors other than those here considered are responsible for this behavior. As in the case of curd fibers, any attempt at a more quantitative formulation of the behavior of these liquid crystalline solutions must wait until more has been learned about their internal structure.

Although Raoult's law is a fair first approximation for the liquid crystalline solution, the equation for regular solutions[14] which has as its principal feature a correction term to Raoult's law arising from dissimilarity in the molecular fields of the components, is not applicable. This failure may be due to the fact that a fundamental step in the derivation of the equation is the counting of the number of pairs of interacting spheres—an approximation that cannot be valid for soap-water systems. It seems likely that an equation derived in a similar manner in which differences

(14) J. H. Hildebrand and S. E. Wood, *J. Chem. Phys.*, **1**, 817 (1933).

in geometrical form of the molecules and in their arrangement in the solution are considered, might be satisfactory. Note that a different basic model may be required for each phase in contrast to the behavior of regular solutions, where a single model is applicable over the whole concentration range even though two liquid phases may be formed.

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Summary

The vapor pressure of aqueous sodium laurate at 90° has been measured as a function of its concentration and the existence of waxy soap as a separate phase has been confirmed.

The activities of sodium palmitate and sodium laurate have been calculated for each of the phases present in aqueous systems at 90°. Possible models of each of these phases are described. The models proposed account qualitatively for the experimental activity concentration curves of middle soap and neat soap.

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. VIII. Extrapolations in 82% Dioxane Mixtures and Standard Potentials

By HERBERT S. HARNED, FLETCHER WALKER[1] AND CALVIN CALMON

In the previous communications in this series, the standard potentials of the cells, H_2 $HCl(m)$, Dioxane(X), $H_2O(Y)$ | AgCl–Ag in mixtures containing 20,[2,4,5] 45[2,3,6] and 70%[2,7,8] dioxane have been evaluated. In addition, the thermodynamic properties of hydrochloric acid in the mixtures have been determined from 0 to 50° and throughout wide acid concentration ranges. These mixtures possess dielectric constants of approxi-

(1) This communication contains some of the experimental material from a dissertation presented by Fletcher Walker to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.
(2) Harned and Morrison, THIS JOURNAL, **58**, 1908 (1936).
(3) Harned and Calmon, *ibid.*, **60**, 334 (1938).
(4) Harned, *ibid.*, **60**, 336 (1938).
(5) Harned and Donelson, *ibid.*, **60**, 339 (1938).
(6) Harned and Donelson, *ibid.*, **60**, 2128 (1938).
(7) Harned and Calmon, *ibid.*, **60**, 2130 (1938).
(8) Harned, Donelson and Calmon, *ibid.*, **60**, 2133 (1938).

mately 60, 40 and 20. In this communication, similar results have been obtained in a dioxane–water mixture containing 82% by weight of dioxane which has a dielectric constant of approximately 10. Measurements were obtained at acid concentrations from 0.001 to 0.01 M, inclusive, and at 5° intervals from 5 to 45°.

The evaluation of the standard potential in solutions of dielectric constant as low as these cannot be carried out at the present time with the certainty obtainable in the media of higher dielectric constant. There are a number of reasons for this. The Gronwall, La Mer and Sandved extension of the Debye and Hückel theory is not satisfactory in media of dielectric constant of the magnitude, 10. This is due to the fact that the second term of the extended term series is large,