[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Phase Rule Studies of Soap. II. The System Sodium Laurate-Sodium Chloride-Water

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In the preceding paper a review has been made of existing phase rule studies of soap systems. This paper, extending the work begun by one of us in collaboration with A. J. Burnett¹ adds the system sodium laurate-sodium chloride-water to the list of those whose behavior has been investigated over a wide range of temperature and composition. In the present work emphasis has been placed on verifying the strict applicability of the phase rule and on ascertaining the experimental conditions necessary for establishing true reversible equilibrium.

Experimental Procedure

Three different standard methods have been employed. The first, the synthetic method, consists of observing the temperatures at which phase changes occur in systems of known composition. The second, the delimiting method, is an isothermal procedure having the consequent advantage that observations on the same tube can be made at intervals over a period of time. It consists of preparing, by trial and error, pairs of systems whose compositions lie very close together, one on each side of the boundary to be determined, and placing the boundary between them. The third method consists of analyzing the separated phases.

The sodium laurate used was a special preparation made for us by Kahlbaum (it contained less than 0.3% excess fatty acid). The soap was dried in an air oven at 105° from time to time and periodic checks made of its water content, which was always taken into account in making up tubes. Kahlbaum dry sodium chloride "for analysis" was used throughout. The water was freshly distilled, and in the case of dilute systems special precautions were taken to exclude carbon dioxide.

In all cases the calculated quantities of salt, water and soap, in the order named, were weighed into heavy-walled Pyrex glass tubes which were sealed off immediately to prevent changes in composition.

For application of the synthetic method the following procedure was adopted. The tube was first heated to a temperature such that its contents formed a homogeneous isotropic solution. A "Mazola" oil-bath was employed for temperatures up to 230°. Temperature was measured by means of a calibrated mercury thermometer. Above 230° an electrically heated oven provided with mica windows was used. Temperature was measured by means of a calibrated thermocouple pyrometer. Then the tube was allowed to cool slowly and the temperature (T_i) recorded at which the first turbidity appeared due to the formation of droplets of a second phase. Finally, the tube was cooled to room temperature and the temperature (T_c) recorded at which, on slow reheating, the last trace of crystal or curd fibers just disappeared.

For application of the delimiting method, the following procedure was found to be most desirable. Spurious results that may be obtained by superficially innocent variations of this procedure are described later. First the tube was heated to homogeneity as described under the synthetic method. It was then cooled to the desired temperature and allowed to stand for a few days, undisturbed except for periodic gentle mixing of the separated phases. The number and nature of the phases present was determined by inspection.

For the analytical work larger samples were used; consequently, because of the increased danger of explosion, these tubes were not heated to homogeneity. The tubes were allowed to stand at 90° for three months. Since the results obtained were in good agreement with those obtained by the other two methods, we are confident that equilibrium was reached. The analyses were carried out in the following manner. A tube was removed from the thermostat and quenched by immersion up to the level of the soap sample in a salt-ice-water freezing mixture. Each of the separated phases was analyzed for soap content by decomposition with a known amount of sulfuric acid, extraction with ether and titration with sodium hydroxide solution of the weighed lauric acid recovered from the ether extract, as well as back titration of the acid in the aqueous layer. Salt content was determined by titrating, with silver nitrate, the neutralized aqueous layer from which the fatty acid had been extracted.

The System Sodium Laurate-Water

In the two component system sodium lauratewater, the observations of temperatures at which phase changes occur can be plotted directly on a temperature-composition diagram. The data obtained are recorded in Table I and Fig. 1. Curve ABCD is drawn through points representing the upper temperature limit of existence of liquid crystalline soap phases (T_i) . Curve EFGHDJO is drawn through points representing the upper temperature limit of the existence of crystalline soap (T_c) .

At all points above the curve ABCDJ the soap system consists of homogeneous isotropic solution. In the composition range from F to G and also that from H to D, the temperature of disappearance of crystalline soap is constant. Consequently, by direct application of the phase rule, four phases are present in each of these regions. These phases are crystalline soap, middle soap,

⁽¹⁾ J. W. McBain and A. J. Burnett, J. Chem. Soc., 121, 1320 (1922).

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TABLE I							
THE TWO	Сомрон	NENT SY	STEM SODIUM LA	URATE	-WATER		
NaL wt. %	Ti	$T_{\rm c}$	NaL wt. %	Tì	Tc		
2.17		24	43.44	145	51		
2.68		25	44.31	144	51		
2.87		26	46.19	149	54		
3.53		28	46.75	149	55		
5.20		32	49.39	139	57		
10.89		38	51.12	141	59		
18.77		41.5	51.29	153	60		
28.77		42	53.21	182	61		
31.19		42	57.34	236	61.5		
31.91		42	58.40	237	62.5		
32.69		42	60.60	242	66		
35.09	85	44	60.89	247	66		
36.80	100	44	62.30	266	—		
42.50	142	50	71.16	290	76		
43.63	144	51	100	310	226		

neat soap and vapor in the case of region FG; and crystalline soap, middle soap, isotropic solution and vapor in the case of region HD.

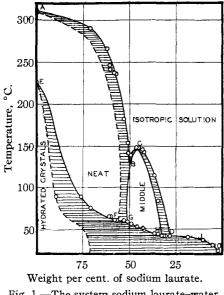


Fig. 1.—The system sodium laurate-water.

These observations make the further course of the diagram clear even though the boundaries that have not been quantitatively determined throughout are drawn with dashed lines. No conclusion concerning the constitution of the crystalline form or forms can be drawn from the work included in the present communication, but it is a definite result from vapor pressure studies at 90° (which will be communicated shortly) that it does not consist of anhydrous sodium laurate. Further vapor pressure measurements designed to ascertain the number and nature of the crystalline phases are now under way in this laboratory. Meanwhile, to facilitate interpretation of the diagram, a tentative boundary has been drawn in (dotted line, Fig. 1).

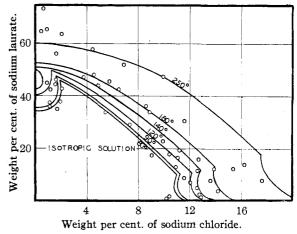


Fig. 2.—The boundaries of the field of aqueous isotropic solutions at definite temperatures (curves), as deduced from T_i determinations (circles) made at intermediate temperatures.

The phase behavior of sodium laurate and water is entirely similar to that of other soap systems.² The nature of the phases and the various equilibria have been described in these earlier communications. At point C middle soap is in equilibrium with an isotropic solution of the same composition (NaL + 14.4 H₂O, or 3.85 N_W solution). This point does not indicate compound formation: it has the same nature as a maximum point of

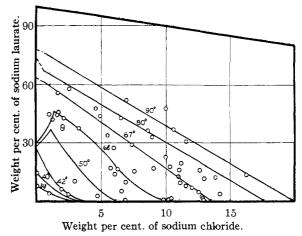


Fig. 3.—The limiting solubilities of hydrated crystalline soap at definite temperatures (curves), as deduced from the T_c determinations (circles) made at intermediate temperatures.

⁽²⁾ McBain, Lazarus and Pitter, Z. physik. Chem., **A147**, 87 (1930); McBain and Elford, J. Chem. Soc., 421 (1926); McBain and Field, J. Phys. Chem., **36**, 1545 (1926).

tangency of an ordinary solidus and liquidus curve.³

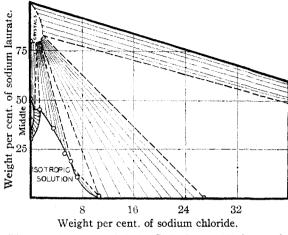


Fig. 4.—The system NaL-NaCl-H₂O: equilibria at 60°

The System Sodium Laurate-Sodium Chloride -Water.—Typical isothermal diagrams, horizontal sections of the right triangular prism neces-

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TABLE	11

THE SYSTEM SODIUM LAURATE-SODIUM CHLORIDE-WATER. TEMPERATURES AT WHICH ISOTROPIC SOLUTION SEPARATES

A LIQUID CRYSTALLINE OR A SECOND LIQUID PHASE					
Composition Composition NaL NaCI NaL NaCI					
wt. %	wt. %	T_{i}	wt. %	wt. %	T;
A. Middl	le Soap is I	Formed	C. Neat	Soap is Fo	ormed
37.78	2.00	58	33.72	5.48	70
42.56	2.09	76	29.11	7.37	106
42.74	2.09	77	22.66	9.96	130
37.40	1.15	92	17.65	10.34	108
45.89	1.66	92	15.81	12.67	168
44.37	1.54	107	16.29	11.01	120
42.22	1.20	118	19.39	11.20	137
44.90	0.95	127	44.04	4.90	171
34.7	1.72	51	46.94	3.76	179
_		_	33.88	8.92	175
B. "I	ye" is Fo	med	42.52	6.51	185
1.58	10.41	65	47.96	4.52	192
9.58	11.11	67	36.12	8.61	198
16.90	9.04	71	30.18	11.57	198
0.63	10.20	76	12.87	16.28	226
6.73	12.00	113	7.55	17.65	226
7.97	11.53	93	51.91	6.91	246
4.84	12.54	128	55.85	1.64	247
1.35	12.89	132	47.44	9.92	250
2.14	12.76	133	57.78	4.46	252
7.56	13.6	160	63.68	2.02	267
11.71	12.99	160	64.72	0.46	275
3.73	14.20	161	65.13	0.81	275
12.13	13.89	183	73.35	0.84	290
12.29	15.36	208	78.81	1.21	296
			79.34	0.68	295
			12.59	10.97	93

(3) A. Findlay, "The Phase Rule," Longmans, Green and Co., New York, N. Y., seventh edition, 1931, p. 120.

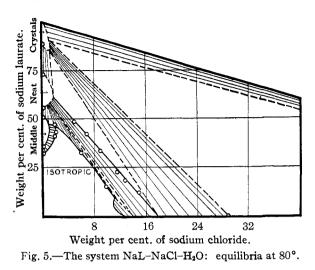
Three	COMPONENT	SYSTEM	SODIUM LA	AURATE-SC	DIUM	
Chlori	de-Water.	TEMPER	ATURES AT WE	IICH SOAP	CRYS-	
TALS OR CURD FIBERS COMPLETELY DISSOLVE						
Composition Composition NaL NaCl NaL NaCl						
wt. %		Te	wt. %	wt. %	T_{c}	
A. I	sotropic Solu	tion	D. N	eat Soap a	nd	
	Remains		•']	Lye" Rem	ain	
0.69	12.93	61	2.04	12.76	66	
1.35	12.89	65	55.85	1.64	66	
0.63	10.20	58	4.84	12.54	67	
0.75	9.85	56	6.73	12.00	67	
0.66	6.85	52	7.97	11.53	67	
1.58	10.41	59	12.59	10.97	72	
4.35		36	7.56	13.60	73	
6.18		42	29.11	7.37	74	
3.41		43	44.04	4.90	74	
10.17		46	47.96	4.52	75	
2.89		48	19.39	11,20	78	
6.57		50	22.66	9,96	77	
17.06	5.73	57	11.71	12.99	77	
14.97	6.03	57	12.13	13.89	78	
16.75	6.26	58	15.81	12.67	78	
27.31	5.97	63	16.29	11.01	78	
9.90	6.91	58	3.73	14.20	78	
37.91	3.25	59	42.52	6.51	79	
B. Mie	idle Soap Re	mains	32.88	8.92	80	
37.6	1.10	58	36.12	8.61	84	
37.4	1.15	50	30.18	11.57	87	
42.20	1.20	54	12.87	16.28	91	
44.37	1.54	59	17.65	10.34	76	
44.90	0.95	55	57.78	2.52	180	
0 NC.		d NI:mus	51.91	6.91	198	
C. Mie	idle Soap and	a Nigre	47.44	9.92	209	
	Remain		33.72	5.48	64	
37.44		55	9.58	11.11	64	
45.89		59	16.90	9.04	6 B	
38.78		56				
42.56	2.09	58				

TABLE III

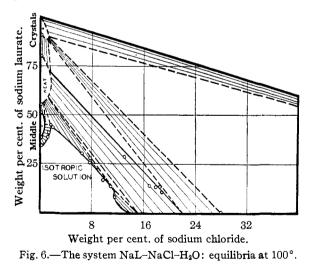
sary for complete representation of the temperature dependence of the phase behavior of a ternary system, are given in Figs. 4 to 9. These diagrams are derived from the data of Tables II and III.

Table II gives the temperatures, T_i , at which, on cooling, tubes having the indicated composition first separated a second phase. The table has been subdivided according to the nature of the separating phases. The data in this table determine the boundary of the field of isotropic solution except at temperatures and compositions such that the isotropic solution is in equilibrium with a crystalline soap phase. In Fig. 2 all these data have been plotted on a single triangular diagram.⁴ The number of points is sufficient to permit drawing in the isotherms. Since such a procedure in-

(4) The right triangle used in place of the more customary equilateral triangle retains all the geometrical properties of the latter except that the water content is derived by subtracting from 100 the sum of the percentages of soap and salt.



volves a certain degree of arbitrary choice, as does any purely graphical method, a uniform method of extrapolation was devised and used in the construction of the isotherms appearing in Fig. 2. A given isotherm is made to pass as closely as possible through all points obtained by linear interpolation or extrapolation from the compositions of pairs of points found to lie on the same boundary, although at somewhat different temperatures. For example, as is indicated in Fig. 2,



a tube containing 12.5% soap and 11% salt separates neat soap at 93° ; a tube containing 17% soap and 9.1% salt separates neat soap at 71° ; consequently the neat-nigre boundary at 80° passes through the point 15.2% soap, 9.9% salt. Even where the experimental points are quite widely separated, the isotherms can be drawn in correctly. For example, it can be seen that a nigre-lye bay must exist in this system even at 250° .

The course of the neat-nigre boundary at salt contents up to 9%, which is accurately determined by the experimental points, precludes the possibility of nigre's containing, for example, 18% each of salt and soap existing in equilibrium with a neat soap of any composition whatsoever, since the

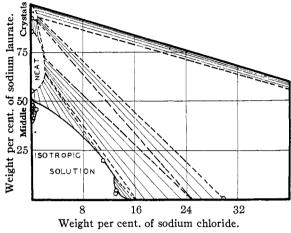


Fig. 7.—The system NaL-NaCl-H₂O: equilibria at 140°.

line corresponding to such an equilibrium cannot reach the soap axis below 100% soap without cutting across the established field of homogeneous solution.

Table III gives the temperatures, T_c , at which, on slow heating, the last trace of crystal just dissolves in systems of indicated composition; the

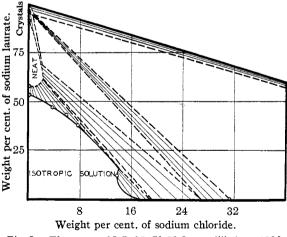


Fig. 8.—The system NaL-NaCl-H2O: equilibria at 180°.

points have been sorted according to the number and nature of the phases remaining. All these data have been plotted on a single triangular diagram in Fig. 3. The isotherms are of three types. Below 42° the solubility isotherms are identically the isotropic solution boundaries. Above 61° the solubility isotherms trace out the neat-lye edge of the triangle, hydrated crystal-neat soap-lye, and a part of the neat soap boundary. At temperatures between 42 and 61° the crystalline soap phase dissolves to form either middle soap or middle soap and isotropic solution. The isotherms were constructed in the same manner as those of Fig. 2.

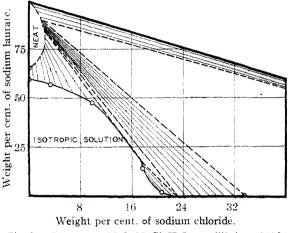


Fig. 9.—The system NaL-NaCl-H2O: equilibria at 250°.

On the basis of the data derived from Tables II and III, the diagrams appearing in Figs. 4 to 9 were constructed. Boundaries that have not been delimited experimentally are dotted in. The authors wish to emphasize the tentative nature of the boundaries given for the crystalline soap region. They are based entirely on analogy with the course of this boundary in the case of sodium palmitate at $90^{\circ 5}$ and the determination by Mc-Bain and Salmon⁶ of the water content at the apex of the triangle, salt-lye-crystalline soap, at 90° .

The phase behavior of the system at 90° is given in Fig. 10. For this one temperature, the exact courses of the crystalline soap boundary and upper neat soap boundary are the only uncertainties. The additional data available at this temperature are summarized in Tables IV and V. The results of the delimiting experiments fix the position of the triangle, neat-nigre-lye. They also substantiate the validity of the neat-nigre boundary obtained by the synthetic method. The analytical results confirm the correctness of the composition of lye in the triangle, neat-nigre-lye, found using the delimiting method, and also establish the directions of the tie lines in the neat-lye region. The

		Experiments at 90°
Compo NaL	NaCl	Phases present
wt. %	wt. %	at equilibrium
5.01	10.2	Nigre
9.95	11.1	Nigre
2.92	10.6	Nigre
2.96	10.8	Nigre
14.0	10.2	Nigre
20.0	9.10	Nigre
5.01	11.02	Nigre and lye
10.1	11.3	Nigre and lye
2.96	12.0	Nigre and lye
3.02	12.45	Nigre and lye
2.96	12.8	Nigre and lye
4.87	12.30	Nigre and lye
7.53	11.92	Nigre and lye
7.47	11.52	Nigre and lye
20.0	9.42	Neat and nigre
28.0	7.51	Neat and nigre
14.1	12.6	Neat and lye
14.1	12.78	Neat and lye
14.1	12.93	Neat and lye
14.0	12.0	Neat and lye
14.0	12.30	Neat and lye
14.0	11.51	Neat and lye
9.92	12.33	Neat and lye
3.01	13.6	Neat and lye
7.48	12.6	Neat and lye
14.0	11.02	Neat, nigre and lye
9.95	11.45	Neat, nigre and lye
9.95	11.70	Neat, nigre and lye
9. 97	12.0	Neat, nigre and lye
7.50	12,20	Neat, nigre and lye
7.45	12.35	Neat, nigre and lye
13.95	10.8	Neat, nigre and lye
28.0	8.00	Neat, nigre and lye

TABLE IV

TABLE V

RESULTS OF ANALYSIS OF SEPARATED PHASES

Total s	ystem	Neat soa	ip layer ^a	Lye layer
NaL wt. %	NaCl wt. %	NaL wt. %	NaCl wt. %	NaC1 wt. %
14.0	11.51	52.2	3.24	14.2
14.0	12.01	51.3	3.60	15.15
14.10	12.78	53.9	3.89	15.90
14.05	12.93	53.8	3.86	16.17
14.0	13.4	65.4	1.69	16.69
14.0	13.9	68.3	1.23	17.28
14.0	14.4	65.9	1.83	17.78
14.0	15.3	68.5	1.52	18.79
14.02^{b}	11.02			14.07

^a These points lie on the tie-lines but usually not on the neat soap boundary because of incomplete separation of phases. ^b This tube contained 3 layers, neat, nigre and lye. Only the lye layer could be obtained free from contamination. In addition to salt, it was found to contain only 0.2% soap.

compositions of the two phases and that of the total system lie in each case on a straight line, as is required if the analyses are accurate; the slope of

⁽⁵⁾ R. D. Vold and R. H. Ferguson, to be published.

⁽⁶⁾ J. W. McBain and C. S. Salmon, J. Chem. Soc., 119, 1374 (1921).

the tie lines is consistent with the slope of the neat-lye edges of the triangles, neat-nigre-lye and neat-crystalline soap-lye.

The work at 90° shows how well results obtained by entirely independent experimental methods fit together in complete harmony on a standard phase rule diagram, and gives further weight to the assertion⁷ that the phase rule does in fact apply to soap systems.

Experimental Tests of the Applicability of the Phase Rule.—We have emphasized⁷ that the applicability of the phase rule to any system is conditioned by whether or not the state of the system is completely fixed by temperature, pressure and composition, independent of time and of the previous history of the particular specimen examined. The experiments of Ostwald and Erbring,8 of Lester Smith,9 and of Ferguson,10 as well as some results obtained in this Laboratory, had led to the supposition that such a reversible equilibrium might not be realizable in all soap systems. The work of Smith was concerned with metastable equilibria that exist in systems supersaturated with respect to curd fibers. Both Ostwald and Erbring and Ferguson were concerned with the nigre-lye bay and the triangle neat-nigrelye at temperatures around 90°. The following experiments also deal with these latter regions.

Experiment 1.-Salt, water, and soap were weighed into tubes in the order named, the salt being all dissolved before the soap was added. The tubes were then sealed off, mixed thoroughly and suspended in a thermostat at 90°. After three hours, during which they were twice mixed gently, the nature of the phases present was entirely in accord with the equilibrium diagram (Fig. 10). The tubes were then allowed to stand undisturbed, except for periodic momentary removal from the thermostat for observation, for a period of three weeks. During this period the volume of the nigre layer in some systems lying within the triangle changed gradually, and a layer of neat soap formed on the surface of all systems lying within the nigre-lye two phase region. Their final condition could not be made to harmonize with any equilibrium phase diagram. Hence further experiments were planned to elucidate the behavior.

Experiment 2.—Our diagram for the phase behavior of the system sodium laurate-sodium chloride-water at 100° showed that Tube No. 14 (Table VI) should consist of homogeneous nigre. At 90° it consisted initially of nigre over lye and had acquired a small surface layer of neat soap on standing for three weeks. It was found that the neat soap layer persisted for at least a day at 100° , but that

it could be destroyed by gentle mixing with the nigre and, once destroyed, did not form again at 100°.

Experiment 3.—The lesson of Experiment 2, that the highly viscous neat soap, once formed, can persist over long periods, suggested that the changes observed in Experiment 1 might have been due to the formation of a small amount of neat soap from nigre in the brief interval during which the tubes were removed from the thermostat for observation, with the gradual accumulation into a visible layer of the neat soap formed during successive observations. All tubes were therefore subjected to periodic gentle mixing carried out with the tubes out of the thermostat for not longer than ten seconds. The neat soap layers that had formed disappeared, and all the tubes returned to their original condition. No further change in the nature or relative volumes of the phases took place over a period of ten days.

It appears that neat soap forms easily from nigre, and disappears only with difficulty. This single simple fact may be in large measure responsible for the results reported above,^{8.10} to the effect that variations with time occur and that results of analysis of separated phases are not in accord with the boundary determined by the delimiting method.

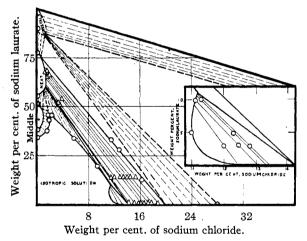


Fig. 10.—The system NaL-NaCl-H₂O: equilibria at 90°. (\odot), Points derived from the data of Tables I, II and III. (\triangle), Points from Table V. Insert: the nigre-lye bay. Tie lines plotted from Table VI.

Experiment 4.—The technique described in Experiment 3 as "gentle mixing" was adopted primarily to minimize the formation of foam. However, the final equilibrium state is completely independent of the mechanical treatment of the sample as long as adequate mixing is achieved, as is proved by the following result. Gentle mixing was replaced by violent vertical shaking which produced complete emulsification of the separated phases in each other and filled the tubes with a macroscopically homogeneous foamy mass. Although there were considerable differences in the rates of settling out of different phases, every tube returned within twenty-four hours to the same state¹¹ as

⁽⁷⁾ J. W. McBain, R. D. Vold and M. J. Vold, This Journal, 60, 1866 (1938).

⁽⁸⁾ Wo. Ostwald and H. Erbring, Kolloidchem. Beihefte. 31, 291 (1930).

⁽⁹⁾ E. Lester Smith. J. Phys. Chem., 36, 2455 (1932).

⁽¹⁰⁾ R. H. Ferguson, private communication,

⁽¹¹⁾ In tubes such as No. 14 containing nigre nearly saturated with respect to neat soap, the foam proved very persistent. When it did finally collapse, a small ring of neat soap was deposited on the glass above the nigre meniscus. This trace of neat soap could be dissolved in the nigre by patient gentle agitation.

was reached under "gentle mixing" conditions both with respect to the phases present and their relative volumes.

Experiment 5.—It was demonstrated that in every tube (23 in all) the same final state was reached on cooling to 90° from such a temperature (160°) that the contents had formed a single homogeneous isotropic liquid, as was reached on heating to 90° from room temperature.

Discussion

The isothermal diagrams shown in Figs. 4 to 10 are for representative temperatures over the complete range from 60° to the melting point of anhydrous sodium laurate. Similar diagrams at any desired temperatures could be drawn on the basis of the data given in Tables II and III. The changes in phase behavior that occur as the temperature is raised have been described fully^{2a} for the case of sodium palmitate. The behavior of sodium laurate is entirely similar as can be seen directly from the diagrams.

In experiments 1 to 5 the fact that the number and relative volumes of the separated phases was determined only by temperature and composition was regarded as sufficient proof of the applicability of the phase rule to this portion of the system. However, the measurements of relative heights of the different phases can be used in an approximate calculation verifying in further detail the conformity of the observed behavior to the requirements of the phase rule.

In the two phase "bay" the relative weights of the nigre and lye are inversely proportional to the distances measured along the tie line from the point representing the total composition of the system. Consequently, since the phases have nearly the same density, the relative volumes of nigre and lye can be used to deduce the direction of the tie lines in this region. Systems no. 14 and no. 23 happen to lie on nearly the same tie line. That the relative volumes of nigre and lye are in accord with the number calculated from the delimiting curve can be taken as verification of conformity with the requirement of the phase rule that systems lying on the same tie line must separate into phases of the same composition. An enlarged section of the "bay" is inserted in Fig. 10, and the numerical data on which the tie lines are based appear in Table VI.

From any point in a three-phase triangle, such as neat-nigre-lye, the relative weights of the three phases can be calculated from the compositions of the corners. Since the neat-nigre-lye triangle is very narrow, the values of the relative weights are

TABLE VI

TIE LINES IN THE NIGRE-LYE BAY

No.	NaL	system NaCl wt. %	Nigr NaL wt. %	e (A) NaCl wt. %	Lye (B) NaCl wt. %	$\frac{Wt, A}{Wt, B}$ Calcd.	Vol. A ^a Vol. B Obsd.
14	10.0	11.3	10.9	11.13	13.36	12.5	12
23	3.0	12.80	10. 9	11.13	13.36	0.34	0.25
R6	4.9	12.30	10.8	11.12	13.23	.81	.68
22	3.0	12.45	10.3	11.1 0	12.96	.39	.34
21	3.0	12.00	9.0	11.06	12.38	.43	.45

^a The relative volumes of the **phases wer**e estimated by measuring their heights in the tube.

extraordinarily sensitive to very small changes in composition. Nevertheless, these calculated relative weights are in accord within the limits of experimental error ($\pm 0.1\%$ in salt content) with the relative volumes observed, as can be seen in Table VII.

TABLE VII COMPARISON OF CALCULATED AND OBSERVED VOLUMES^d OF NEAT, NIGRE AND LYE^d

Total NaL wt. %	system NaCl wt. %	Vol. Calcd.	neat Obsd.	Vol. Calcd.	nigre Obsd.	Vol. Calcd.	lye Obsd.
10:0	11.45	0.024	Trace	0.88	0.78	0.10	0.22
10.0	11.7	.047	0.068	. 67	. 53	.27	. 41
10.0	12.0	.15	.12	. 01	. 17	. 83	.71
14.0	11.0	. 18	.15	.27	.32	. 54	. 53
7.5	12.2	.024	.07	. 51	.34	. 46	. 59
7.5	12.35	.071	. 10	.26	. 20	.67	.70

^a The relative volumes of the phases were estimated by measuring their heights in the tube.

^b The compositions of the triangle corners are (a) neat: 60.0% sodium laurate, 1.50% sodium chloride, (b) nigre: 11.15% sodium laurate, 11.15% sodium chloride, (c) lye: 0.20% sodium laurate, 14.07% sodium chloride.

Summary

1. Diagrams have been constructed showing the phase behavior of the two component system, sodium laurate-water, and of the three component system, sodium laurate-sodium chloride-water, at various representative temperatures from 60° to the melting point of anhydrous sodium laurate (310°). Data are tabulated that make possible construction of the diagram at any intermediate temperature.

2. Results obtained by synthetic, delimiting and analytical methods are in quantitative agreement.

3. It has been shown experimentally that true reversible equilibrium independent of time is reached in this system, and that this equilibrium is described exactly by the phase rule.

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