with the experimental technique. In all probability, therefore, the second series of experimental results with terrestrial samples is more directly comparable with the meteoritic results than the first. From the isotopic proportions found, one can only conclude that the terrestrial and meteoritic materials are identical within the experimental error.

Summary

The isotopic composition of samples of purified terrestrial and meteoritic iron has been measured with a mass spectrograph. There were no certain differences in composition either among the different samples of each of the two varieties of material or between the two varieties themselves.

The following ratios and percentages of the four iron isotopes were found.

	Ratios	Percentages	
		This paper	Nier
Fe^{54}	6.33	5.81	6.04
Fe^{56}	100.00	91.75	91.57
Fe^{57}	2.34	2.15	2.11
Fe^{58}	0.32	0.29	0.28

These give a mean mass number of 55.911 for iron. The atomic weight calculated with the packing fraction -7.15×10^{-4} and the conversion factor 1.000275 is 55.856. Nier's[5] isotopic percentages given above yield the atomic weight 55.851. The International atomic weight, 55.85, depends on the analyses of ferric oxide,[6] 55.847, of ferric chloride,[7] 55.853, and of ferrous bromide,[8] 55.850.

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(5) Nier, *Phys. Rev.*, **55**, 1143 (1939).

(6) Baxter and Hoover, THIS JOURNAL, **34**, 1657 (1912).

(7) Hönigschmid, Birkenbach and Zeiss, *Ber.*, **56B**, 1473 (1923).

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[CONTRIBUTION FROM THE PHILADELPHIA QUARTZ CO.]

A Phase Study of Sodium Palmitate–Alkaline Electrolyte–Water Systems

BY REYNOLD C. MERRILL AND RAYMOND GETTY

During the past twenty-five years numerous publications on the phase behavior of aqueous soap systems have appeared.[1] Considerable information has also become available on the effects of sodium or potassium chloride on these systems.[2,3,4] Very little is apparently known at present, however, of the effects of other electrolytes, although alkaline salts such as the silicates and phosphates are industrially important as soap builders. A review of the available literature is given in a separate paper which reports a study of the phase behavior of ten commercial mixed sodium soap–water–electrolyte systems.[5] The salts used were sodium chloride, carbonate, tetraborate, trisodium phosphate, tetrasodium pyrophosphate, Calgon ("sodium hexametaphosphate"), sodium metasilicate, sodium silicates of SiO_2/Na_2O ratios by weight of 2.46 and 3.93, and a potassium silicate of SiO_2/K_2O ratio by weight of 2.04. This paper reports a similar study on aqueous sodium palmitate systems with trisodium phosphate, tetrasodium pyrophosphate, sodium metasilicate, and sodium silicates of SiO_2/Na_2O ratios by weight of 2.46 and 3.92. Data are given outlining the regions of existence of isotropic solutions up to 160° and showing the influence of these electrolytes on the transition from hydrated crystalline to liquid crystalline soap.

Work on the sodium palmitate–water system has recently been summarized by McBain and Lee.[1a] The ternary system with sodium chloride has been studied by McBain, Lazarus and Pitter,[6] and more completely at 90° by Vold and Ferguson.[3]

Experimental

Materials.—The sodium palmitate was made by neutralizing to phenolphthalein a hot alcoholic solution of Eastman Kodak Co. best quality palmitic acid, with an alcoholic solution of sodium ethylate and subsequent crystallization of the soap. It was dried to constant weight at 105° before use. The acid recovered from the soap in a yield 99.6% of theoretical melted over the range 61.5–62.0° and had a molecular weight by titration of 260 (calcd. 256). The amounts of impurities present are too small to affect significantly the results on the systems containing less than 50% soap studied in this paper. The impurities are higher and lower molecular weight fatty acids whose effects on solubility tend to counter balance each other.

The phosphates were C. P. chemicals. Analyses of the silicates are given in a separate paper.[5] The most silicious silicate was further purified. In addition to the metasilicate pentahydrate, an anhydrous metasilicate containing about 3% sodium carbonate was used. Both gave essentially the same results.

Method.—All data were obtained by the standard synthetic method. Systems of known composition in sealed

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(1) See, *e. g.*, (a) J. W. McBain and W. W. Lee, *Oil & Soap*, **20**, 17 (1943); (b) J. W. McBain, R. D. Vold and M. J. Vold, THIS JOURNAL, **60**, 1866 (1938); (c) J. W. McBain in Alexander, "Colloid Chemistry," Vol. I, Chemical Catalog Co., New York, 1926, p. 132; (d) R. H. Ferguson, F. B. Rosevear and R. C. Stillman, *Ind. Eng. Chem.*, **35**, 1005 (1943); (e) M. J. Buerger, L. B. Smith, F. V. Ryer and J. E. Spike, *Proc. Natl. Acad. Sci.*, **31**, 226 (1945).

(2) See, *e. g.*, (a) J. W. McBain, R. D. Vold and K. W. Gardiner, *Oil & Soap*, **20**, 221 (1943); (b) J. W. McBain, W. J. Elford and R. D. Vold, *J. Soc. Chem. Ind.*, **59**, 243 (1940); (c) J. W. McBain, K. W. Gardiner and R. D. Vold, *Ind. Eng. Chem.*, **36**, 808 (1944); (d) J. W. McBain, R. C. Thorburn and C. G. McGee, *Oil & Soap*, **21**, 227 (1944).

(3) R. D. Vold and R. H. Ferguson, THIS JOURNAL, **60**, 2066 (1938).

(4) R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, **24**, 1329 (1932).

(5) R. C. Merrill, *ibid.*, **39**, 158 (1947).

(6) J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. physik Chem.*, **A147**, 87 (1930).

Pyrex tubes 13 mm. in diameter by about 70 mm. long were first heated to a homogeneous isotropic solution. As the tubes slowly cooled the temperature, T_i, was recorded at which the first trace of liquid crystal or a second isotropic liquid formed. Observation through crossed polaroid discs facilitated the detection of liquid crystal. After standing at room temperature for several weeks, the temperature, T_c, was determined at which all traces of the opaque white solid just disappeared on slow heating to complete the formation of an isotropic liquid, an anisotropic liquid crystalline phase or a mixture of both. The data are readily reproducible except at high concentrations of the silicious silicate with a SiO_2/Na_2O ratio of 3.93, particularly when two isotropic solutions are formed. There is a tendency for a hydrous gel-like mass, possibly a high ratio silicate, which is very difficult to dissolve to form on cooling in the latter concentration range. Even at these concentrations reproducible data can be obtained with sufficient care.

Results

The influence of each of the five salts on the temperature, T_c, at which the transition occurs from the hydrated solid crystalline soap phase or mixture of phases existing at room temperature to a liquid or liquid crystal phase or both is shown in Fig. 1. The curves at the specified temperatures

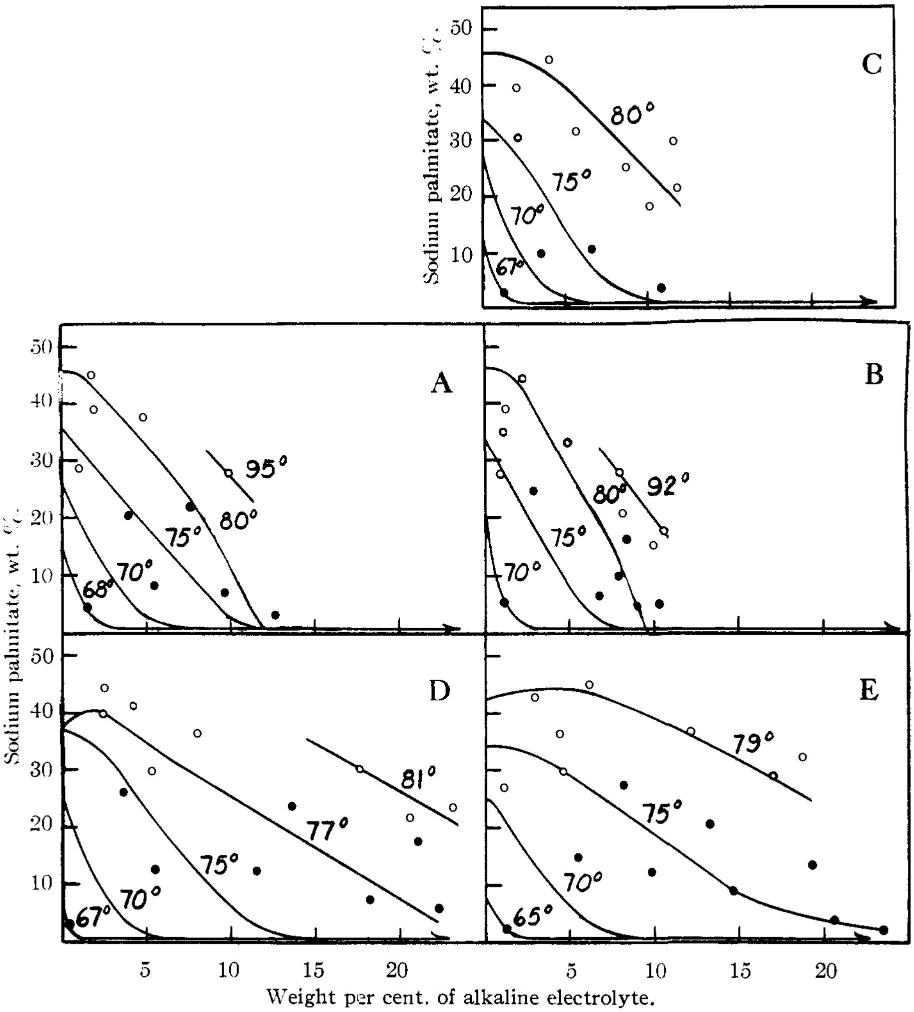
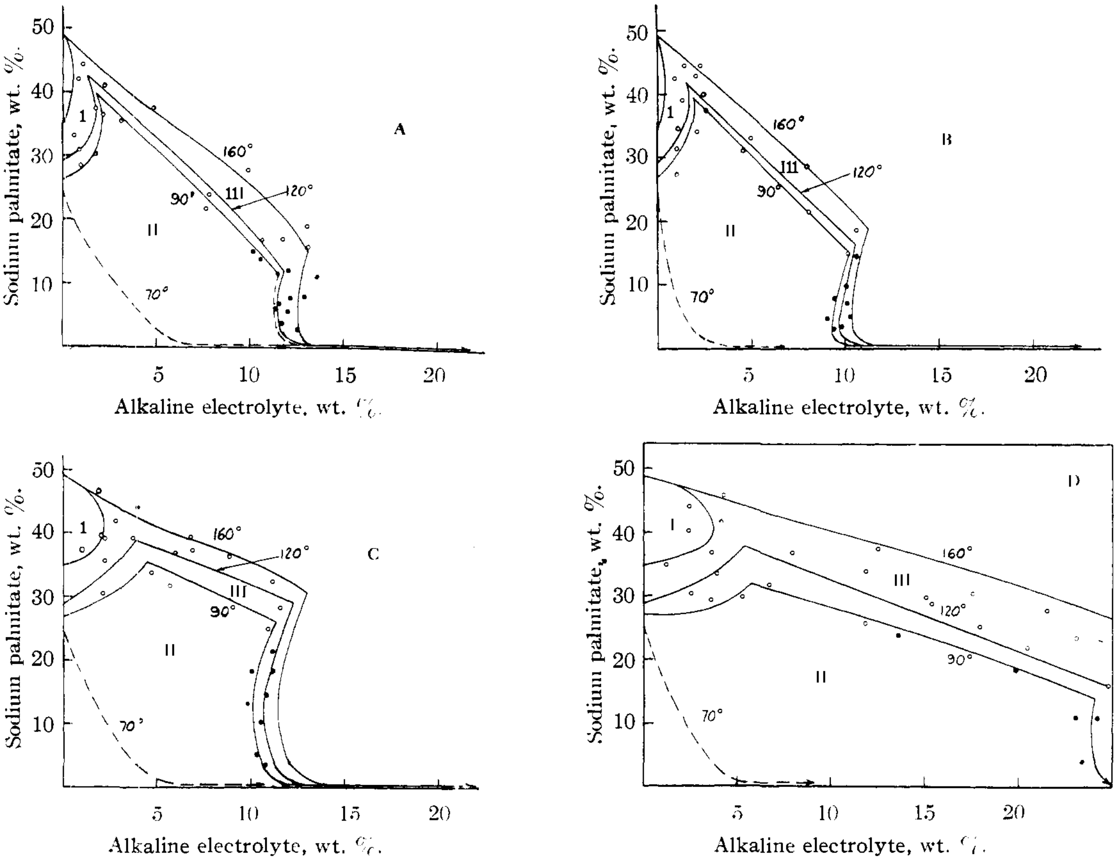


Fig. 1.—Solubility and transition temperature (T_c) isotherms of hydrated crystalline sodium palmitate–alkaline electrolyte–water systems at definite temperatures (curves) as deduced from the T_c determinations (circles) made at intermediate temperatures. Open circles represent compositions forming liquid crystals on heating; filled circles those forming isotropic solutions. In the graphs the isotherm extends to the solubility of the phosphates or metasilicate in pure water at 0% soap on the horizontal axis. [The solubility of tetrasodium pyrophosphate in water increases from 21.83 g. per 100 g. of water (17.91%) at 60° to 30.04 g. at 80° (23.1%) and 40.26 g. at 100°; that of trisodium phosphate from 48.59 g. per 100 g. of water at 70° (32.7%), to 77 g. at 100° (43.5%) (A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed., D. Van Nostrand Co., 1940). The solubility of sodium metasilicate in water increases from 50.05% by weight at 65° to 61.63% at 80°, and then decreases to 47.97% at 90° (C. L. Baker and L. R. Jue, *J. Phys. Chem.*, **42**, 165 (1938)). The solubility of the 2.46 and 3.93 ratio silicates is greater than 30% by weight above room temperature.] A, Tetrasodium pyrophosphate; B, trisodium phosphate; C, sodium metasilicate (SiO_2/Na_2O ratio by weight of 0.97); D, sodium silicate of SiO_2/Na_2O ratio by weight of 2.46; E, sodium silicate of SiO_2/Na_2O ratio by weight of 3.93.



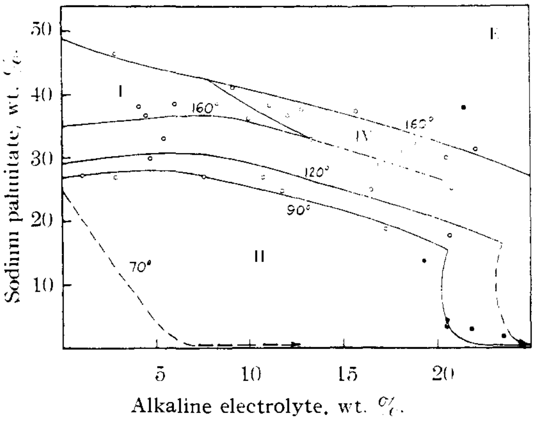


Fig. 2.—Boundaries of the field of aqueous isotropic solutions for sodium palmitate–alkaline electrolyte–water systems at 90, 120 and 160° (curves) as deduced from T_i determinations (circles) made at intermediate temperatures. Open circles represent compositions forming liquid crystals on cooling, filled circles, those forming isotropic solutions: I, middle soap region; II, field of isotropic solution; III, neat soap on nigre region; IV, liquid crystal on isotropic solution.

The terminus of each isotherm on the 0% sodium palmitate axis gives the solubility of the electrolyte in pure water (*cf.* legend of Fig. 1): A, tetrasodium pyrophosphate; B, trisodium phosphate; C, sodium metasilicate (SiO_2/Na_2O ratio = 0.97); D, sodium silicate of SiO_2/Na_2O ratio of 2.46; E, sodium silicate of SiO_2/Na_2O ratio of 3.93.

were deduced by linear interpolation from the T_c determinations (circles) made at intermediate temperatures. In both Figs. 1 and 2 the intercepts of the isotherms on the 0% salt axis were obtained from data summarized by McBain and Lee.[1a] Intercepts on the 0% soap or horizontal axis give the solubility of the salt in pure water except possibly for the two silicious silicates. The open circles represent compositions forming liquid crystals on heating; filled circles those forming isotropic solution. The data are given in Table I and are separated according to the number and probable nature of the phase or phases formed above T_c, based upon analogy with the previous work on the corresponding sodium chloride system.[3,6] The use of both weight per cent. and molality (gram-moles per kilogram of water) to express the salt concentration enables comparisons to be made on a molecular as well as a technical basis.

Up to 70° all compositions to the left and below the 70° isotherm change at this T_c temperature from a hydrated crystalline form or forms to isotropic solution only. The T_c isotherms below 70° thus outline the boundaries of the region of isotropic solution. They give the amount of each electrolyte necessary to salt out various concentrations of sodium palmitate at each temperature or, in other words, the solubility of the soap in various concentrations of salt solutions. Between 70 and 80° the crystalline soap forms at the T_c temperature either middle soap, middle soap and isotropic solution, or isotropic solution only. When isotropic solution only is formed, the T_c points define the boundary of the isotropic solution field. The first addition of these electrolytes to systems containing from 27 to 49% soap, which form middle soap on heating, appears actually to lower this transition temperature or at least has very little effect. This is particularly true with the more silicious sodium silicates.

TABLE I

THE THREE COMPONENT SYSTEMS: SODIUM PALMITATE-ALKALINE ELECTROLYTE-WATER. TEMPERATURES AT WHICH SOAP CRYSTALS OR CURD FIBERS COMPLETELY DISSOLVE OR CHANGE TO LIQUID CRYSTAL

% Soap	% Builder	*M* Builder	T_c, °C.	Phase(s) remaining[a]
		Tetrasodium Pyrophosphate		
4.66	1.44	0.058	68	I
8.89	5.57	.245	73	I
20.3	4.00	.199	74	I
28.5	1.05	.056	74	M
6.70	9.66	.434	76	I
22.1	7.72	.414	78	I
39.0	1.91	.121	78	M
44.7	1.82	.128	80	N
37.7	4.86	.318	80	N
2.85	12.6	.558	84	I
28.1	9.94	.603	95	N
		Trisodium Phosphate		
4.89	1.29	0.096	70	I
24.4	2.90	.243	75	I
27.4	1.05	.090	75	M
34.6	1.14	.109	76	M
39.0	1.33	.135	78	M
6.42	6.85	.482	78	I
9.17	7.92	.582	79	I
4.68	9.03	.638	79	I
44.4	2.33	.266	80	N
4.92	10.3	.744	80	I
16.5	8.45	.686	81	I
32.8	4.99	.490	82	N
15.2	10.0	.820	82	N
21.2	8.08	.697	82	N
28.4	8.03	.770	92	N
18.2	10.6	.907	93	N
		Sodium Metasilicate		
2.78	1.35	0.115	67	I
9.79	3.50	.331	73	I
30.5	2.19	.223	76	M
10.7	6.65	.800	76	I
3.46	10.8	1.03	78	I
39.4	2.02	0.282	78	M
31.7	5.74	0.752	79	N
21.3	11.9	1.44	80	N
25.0	8.66	1.07	80	N
18.3	10.1	1.16	80	N
44.0	4.04	0.636	80	N
29.8	11.6	1.62	80	N
		Sodium Silicate, SiO_2/Na_2O ratio of 2.46		
3.47	1.22	0.061	67	I
34.9	1.23	.092	74	M
12.5	5.35	.310	74	I
26.5	3.56	.261	75	I
29.6	5.29	.387	76	M
12.7	11.52	.724	76	I
5.65	22.2	1.47	77	I
40.1	2.41	0.199	77	M
7.64	18.2	1.17	77	I
44.1	2.51	0.224	78	M
23.8	13.6	1.04	78	I
17.5	21.0	1.63	78	I
36.8	8.00	0.691	78	N
41.5	4.21	.369	78	M
22.0	20.5	1.70	79	N
30.4	17.6	1.61	81	N
23.6	23.1	2.06	83	N
		Sodium Silicate, SiO_2/Na_2O ratio of 3.93		
2.28	1.25	0.0435	65	I
27.0	1.10	.0517	72	M
12.4	9.80	.424	74	I
14.9	5.37	.226	74	I
8.83	14.7	.645	75	I
3.87	20.6	.918	75	I
29.8	4.75	.244	75	M
1.95	23.6	1.07	75	I
27.2	7.60	0.392	76	L
20.3	13.3	.674	76	I
36.5	4.43	.252	77	M
13.6	19.3	.965	78	I
28.9	16.9	1.05	79	L
46.3	2.97	0.197	79	N
36.7	12.1	.794	79	L
44.8	6.10	.417	79	N
32.2	18.8	1.29	86	L

[a] *M* = middle soap or middle soap and nigre remain; N = neat soap and "lye" remain; I = isotropic solution remains; L = a liquid crystal remains.

Above 80° equilibria with other liquid crystalline phases are evolved. While the nature of the liquid crystalline phases involved at the higher builder and soap concentrations cannot be determined from these data, analogy with the corresponding sodium palmitate–sodium chloride system indicates that around 90° the T_c determinations give the neat-lye edge of the triangle neat soap–curd phase–lye.[3,6] The recently discovered "kettle wax" phase may also be involved.[2c,2d]

Figure 1 shows considerable variation in the effects of the different electrolytes on the solubility of the soap in salt solutions and on the transition from hydrated crystal to liquid crystal. Up to 75° the weights of the phosphates or metasilicate which can be added to an aqueous sodium palmitate system before salting out soap or changing it to liquid crystal are not very different. At 80° more metasilicate than either of the phosphates can be added before the T_c transition occurs. The sodium silicate with a SiO_2/Na_2O ratio by weight of 2.46 can be added in considerably larger amounts than either the metasilicate or phosphates before increasing T_c to the same extent. Even larger amounts of the sodium silicate with an SiO_2/Na_2O ratio by weight of 3.93 dissolve before solid soap is formed.

The fields of aqueous isotropic solutions at 90, 120 and 160° for each of the sodium palmitate–builder–water systems are given in Fig. 2. The boundaries were determined by linear interpolation of the T_i determinations in Table II. The T_i values have also been separated in the table according to the probable nature of the phase which separates on cooling. Compositions in the table for which no T_i value is given remained apparently homogeneous on cooling but were sufficiently near to an isotherm to be of assistance in locating it. For comparison the boundary outlining the field of isotropic solution at 70° as determined by T_c measurements is given as a dotted line.

TABLE II

THE THREE COMPONENT SYSTEMS: SODIUM PALMITATE–ALKALINE ELECTROLYTE–WATER. TEMPERATURES AT WHICH ISOTROPIC SOLUTION SEPARATES A LIQUID CRYSTALLINE OR A SECOND LIQUID PHASE. ISOTROPIC SOLUTIONS NEAR A PHASE BOUNDARY

Tetrasodium Pyrophosphate

A. Middle Soap is Formed

% Soap	% $Na_4P_2O_7$	M $Na_4P_2O_7$	T_i, °C.
30.1	1.81	0.132	73
39.0	1.91	.121	78
28.5	1.05	.056	101
30.9	0.97	.044	121
37.2	1.75	.108	136
44.0	1.14	.782	142
33.0	0.65	.037	146
42.2	.87	.058	154

B. Neat Soap is Formed

% Soap	% $Na_4P_2O_7$	M $Na_4P_2O_7$	T_i, °C.
35.6	3.17	0.195	87
24.0	7.90	.436	112
40.9	2.26	.149	122
16.8	10.7	.557	133
17.1	11.8	.625	144
15.9	13.1	.693	160
37.7	4.86	.318	167
19.1	13.1	.726	167
28.1	9.94	.603	172
44.7	1.82	.128	172

C. Two Isotropic Solutions are Formed or Solution Remains Isotropic Near a Phase Boundary

% Soap	% $Na_4P_2O_7$	M $Na_4P_2O_7$	T_i, °C.
36.5	2.06	0.126	...
14.0	10.6	.528	...
6.05	11.4	.521	...
15.1	10.2	.514	...
22.1	7.72	.414	...
3.87	11.5	.508	...
11.7	11.6	.566	...
6.99	11.6	.537	143
12.1	12.1	.600	149
3.96	11.6	.519	151
5.53	12.1	.553	154
7.79	12.2	.573	156
2.85	12.6	.558	159
8.00	12.9	.615	161
11.3	13.6	.680	169

Trisodium Phosphate

A. Middle Soap is Formed

% Soap	% Na_3PO_4	M Na_3PO_4	T_i, °C.
33.9	2.15	0.205	79
27.4	1.05	.090	85
31.4	1.69	.154	88
34.6	1.14	.109	144
39.0	1.33	.135	147
42.9	2.04	.226	148
44.5	1.48	.167	152
42.3	0.99	.106	156

B. Neat Soap is Formed

% Soap	% Na_3PO_4	M Na_3PO_4	T_i, °C.
31.1	4.60	0.436	78
15.2	10.0	.820	84
21.2	8.08	.697	91
40.0	2.49	.264	128
32.8	4.99	.490	147
18.2	10.6	.907	153
28.4	8.03	.770	160
44.4	2.33	.266	176

C. Two Isotropic Solutions Are Formed or Solution Remains Isotropic Near a Phase Boundary

% Soap	% Na_3PO_4	M Na_3PO_4	T_i, °C.
37.5	2.55	0.259	...
4.68	9.03	.638	...
7.87	9.47	.698	...
3.03	9.52	.664	111
9.78	10.1	.773	117
4.92	10.3	.744	137
6.96	10.1	.741	142
3.48	9.80	.689	145
14.1	10.7	.868	148

Sodium Metasilicate

A. Middle Soap is Formed

% Soap	% Na_2SiO_3	M $NaSiO_3$	T_i, °C.
30.5	2.19	0.223	94
35.6	2.29	.302	125
39.3	3.75	.540	127
41.8	2.87	.425	151
39.4	2.02	.282	161
37.2	1.04	.137	163

B. Neat Soap is Formed

% Soap	% Na_2SiO_3	M $NaSiO_3$	T_i, °C.
31.7	5.74	0.752	78
24.9	11.0	1.40	80
34.0	4.74	0.633	88
28.2	11.6	1.58	100
36.9	6.02	0.864	120
37.2	6.95	1.15	136
32.4	11.2	1.62	143
36.2	8.91	1.33	157
39.3	6.87	1.05	161
46.5	1.91	0.303	167
44.0	4.04	.636	168

TABLE II (*Concluded*)

% Soap	% Na_2SiO_3	*M* $NaSiO_3$	T_i, °C.
C. Two Isotropic Solutions are Formed or Solution Remains Isotropic Near a Phase Boundary			
5.11	10.4	1.01	...
13.1	9.86	1.05	...
18.3	10.1	1.16	85
3.46	10.8	1.03	102
21.4	11.2	1.36	107
10.2	10.6	1.09	112
18.2	11.2	1.30	116
14.5	10.8	1.18	126
9.86	11.5	1.20	156

% Soap	% $Na_2O \cdot 2.46SiO_2$	*M* $Na_2O \cdot 2.46\ SiO_2$	T_i, °C.
Sodium Silicate, SiO_2/Na_2O ratio of 2.46			
A. Middle Soap is Formed			
29.6	5.29	0.387	85
29.4	3.56	.252	107
30.6	2.57	.183	112
33.5	3.96	.301	116
34.9	1.23	.0918	153
36.8	3.63	.290	158
41.5	4.21	.369	159
44.1	2.51	.224	162
40.1	2.41	.200	164
B. Neat Soap is Formed			
25.8	11.9	0.906	<85
15.4	24.2	1.90	107
31.8	6.74	0.522	118
23.6	23.1	2.06	126
22.0	20.5	1.70	128
25.2	18.0	1.51	130
27.9	21.6	2.04	131
23.3	24.5	2.24	134
29.0	15.4	1.32	135
30.4	17.6	1.61	136
29.9	15.1	1.31	143
34.0	11.9	1.04	145
36.8	8.00	0.691	150
37.2	12.6	1.19	157
45.8	4.31	0.411	>175
C. Two Isotropic Liquids are Formed or Solution Remains Isotropic Near a Phase Boundary			
19.9	18.5	1.33	...
23.8	13.6	1.04	...
11.0	23.1	1.67	~80
4.05	23.4	1.54	~80
11.0	24.1	1.77	107

% Soap	% $Na_2O \cdot 3.93SiO_2$	*M* $Na_2O \cdot 3.93\ SiO_2$	T_i, °C.
Sodium Silicate, SiO_2/Na_2O ratio of 3.93			
A. Middle Soap is Formed			
26.8	2.94	0.141	80
27.0	1.10	.0517	90
29.8	4.75	.244	111
33.1	5.50	.301	146
36.5	4.43	.252	162
38.3	6.09	.369	164
37.9	4.17	.242	167
B. Liquid Crystal (Neat Soap(?)) is Formed			
18.9	17.3	0.912	86
27.2	7.60	.392	95
25.0	11.8	.626	96
17.8	20.7	1.13	108
26.9	10.8	0.580	110
25.0	16.5	.949	140
30.9	18.2	1.20	141
32.2	18.8	1.29	147
25.2	20.8	1.30	151
37.5	12.8	0.872	151
38.3	11.1	.741	151
30.0	20.5	1.40	153
36.7	12.1	0.794	155
41.2	9.13	.618	156
28.9	16.9	1.05	157
32.8	13.3	0.833	160
36.1	9.96	.622	161
46.3	2.97	.197	170
31.4	22.1	1.60	165
37.3	5.7	1.12	>170
C. Two Isotropic Solutions are Formed or Solution Remains Isotropic Near a Phase Boundary			
13.6	19.3	0.965	...
3.87	20.6	.918	...
2.91	21.8	.975	105
4.15	20.4	.908	107
9.12	20.5	.982	109
1.95	23.6	1.07	115

The isotherms in Fig. 2 are qualitatively similar to those obtained previously with various soaps and sodium or potassium chloride,[1c,2,3,4,6] and with a commercial mixed soap and the same builders.[5] Above a concentration of 49% sodium palmitate the salts or builders increase the solution temperature of the liquid crystalline neat soap. Between 27 and 49% sodium palmitate the first addition of salts lowers the solution temperature of the liquid crystalline middle soap. At higher salt concentrations neat soap is formed and the solution temperature again increases. Thus these electrolyte builders "salt in" middle soap and "salt out" neat soap. At lower sodium palmitate concentrations (usually below 15 to 20% at 90° for sodium metasilicate systems) the addition of salts at elevated temperatures causes the formation of two immiscible isotropic liquids. Systems with all of the builders show the characteristic indentation at low soap concentrations known as the "bay region."

Comparison of Figs. 2A and 2B shows that, although the formula weight of the pyrophosphate is 60% greater than that of the trisodium phosphate, about the same weight of each is in equilibrium with the liquid crystalline phases at each temperature. More pyrophosphate than trisodium phosphate is required on a weight basis to salt out dilute soap systems into two isotropic solutions but less on a molal basis. The metasilicate salts in middle soap less and neat soap more than the phosphates. About the same weight of metasilicate as of the phosphates is required to form two isotropic solutions.

Sodium silicates with a SiO_2/Na_2O ratio greater than about 2 are colloidal electrolytes, although probably of a different type than the soaps. Both silicate and soap micelles are negatively charged. It is of particular interest therefore that the diagrams with the 2.46 and 3.93 ratio silicates are qualitatively similar to those with the non-colloidal metasilicate and phosphates. However, much larger amounts of the silicious silicates than of metasilicate or the phosphates are required to salt out isotropic soap solutions into neat soap, two isotropic solutions (nigre–lye), or hydrated crystalline soap. Their "salting in" action on middle soap is also considerably smaller, particularly with the 3.93 ratio silicate. As expected, the 3.93 ratio silicate has much less effect on the liquid crystalline phases than the 2.46 ratio silicate. This makes somewhat uncertain the exact location of the 160° isotherms surrounding middle soap compositions of higher T_i temperatures (*i. e.*, to the left and between the 160° boundaries given). It also introduces some uncertainty regarding the liquid crystalline phase at high silicate concentrations. Further work by other methods is needed to settle this point.

Surprisingly, the field of isotropic solutions at 90° and above is, at a given temperature, smaller for the 3.93 ratio silicate than for the 2.46. This means that a silicate with an optimum SiO_2/Na_2O ratio between 0.97 (metasilicate) and 3.96 has the least effect in salting out isotropic solutions to the liquid crystalline phase, neat soap, or two isotropic solutions at 90° and above. This is not true at 70° and below where the isotropic solution is in equilibrium with crystalline soap and the amount of silicate which can be added before salting out soap increases with the SiO_2/Na_2O ratio (Fig. 1). The *salting in* of the liquid crystalline phase, middle soap, apparently increases with decreasing SiO_2/Na_2O ratio and no optimum is indicated. Whether there is an optimum ratio for the amount of silicate which can be added to neat soap before forming the two phase system, neat soap on lye, must be determined by further work.

There are apparently differences among the various builders in the lowest temperature at which two isotropic solutions (nigre-lye) form. The lowest T_i observed at which a second isotropic liquid separated from the tetrasodium pyrophosphate system was 143°. Systems containing only about 0.2% less pyrophosphate remained homogenous until solid soap crystallized. A second isotropic solution separated at temperatures as low as 80° in corresponding systems containing silicates.

Differences also exist among the builders in their temperature coefficient of salting out. The additional salt necessary to salt out 27% sodium palmitate (neat soap) at 160° over that required at 90° is 2.4% for trisodium phosphate, 3.2% for tetrasodium pyrophosphate, 13% for the 2.46 ratio silicate and 17% for the 3.93 ratio silicate. The value for sodium metasilicate at 27% soap is not comparable with the others since two isotropic liquid layers are formed at the higher temperature. Five and three-tenths % more metasilicate is required to salt out 31.5% sodium palmitate into neat soap at 160° than is required at 90°. This latter value should be directly comparable with those at 27% soap, even though some metasilicate must be present before the soap completely dissolves at 90°. Similarly the difference in the solubility of sodium palmitate in various 9% builder solutions between 90 and 160° is 6.9% for the trisodium phosphate, 7.3% for the metasilicate, 8.6 for the tetrasodium pyrophosphate, 12% for the 2.46 ratio and 15.7% for the 3.93 ratio sodium silicate.

Discussion

The salting out of gases, ordinary electrolytes, non-electrolytes and even proteins is due mainly to reduction of the solvent water by hydration of the added ions and is influenced largely by the ionic strength. Unfortunately the present data do not provide a good test of the hypothesis that this is true for soap solutions since reliable values for the concentration of each ionic species involved are not available for these alkaline builders at elevated temperatures. However, it appears that the effect of the builder on the equilibria between free ions and the micelle must also be considered and may be more important for soap solutions than hydration. The addition of electrolytes to a soap solution increases the size and proportion of micelles until they adhere to each other and form a precipitate. Since the average micelle contains neutral molecules, steric effects of the added ions on the micelle may be involved in salting out.

The 3.93 ratio silicate, as well as the metasilicate, has a greater salting out action on isotropic solutions above 90° than the 2.46 ratio silicate. This may be due to a high ionic strength caused by polyvalent silicate micelles or to the formation of sparingly soluble "complexes" between the silicate micelles and the soap. Calgon, which likewise contains negatively charged micelles, salts out soap at much greater dilutions, possibly for the same reasons.[5]

Summary

A phase study has outlined the regions of existence of isotropic solutions up to 160° for five sodium palmitate-builder–water systems. The effect of the builders on the transition temperature from hydrated crystalline to liquid crystalline sodium palmitate was also determined. The builders were trisodium phosphate, tetrasodium pyrophosphate, sodium metasilicate, and sodium silicates of SiO_2/Na_2O ratios by weight of 2.46 and 3.93.

The results resemble qualitatively those previously obtained with a commercial soap and

various builders, and with sodium or potassium chloride and other soaps.

More of the silicious silicates than of the metasilicate or phosphates is required to "salt in" liquid crystalline middle soap or to "salt out" liquid crystalline neat soap. The silicious silicates have less effect than the phosphates on the transition temperature from crystalline to liquid crystalline soap systems.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarographic Oxidation of +4 Vanadium

BY JAMES J. LINGANE AND LOUIS MEITES, JR.

The fact that +4 vanadium in 1 N sodium or potassium hydroxide produces a well developed anodic wave, representing oxidation to the +5 state, was recently reported.[1] The present paper presents the results of a systematic study of various factors on the oxidation of +4 vanadium at the dropping electrode.

Experimental

Polarograms were recorded with a Sargent–Heyrovsky Model XI Polarograph calibrated according to the usual techniques.[2] Diffusion current constants were measured with a manual instrument incorporating a calibrated Leeds and Northrup Type HS galvanometer.

An H-cell[3] provided with a saturated calomel electrode whose potential was periodically checked against other reference electrodes was used. The dropping electrode assembly included a vertical stand-tube connected to a mercury reservoir and to an automatic m-measuring device.[4]

Since alkaline solutions of +4 vanadium are rapidly oxidized by air, we employed both hydrogen and sulfite ion to remove oxygen from the solutions. A stock solution of +4 vanadium was prepared by reduction with sulfur dioxide of a suspension in 10 M sulfuric acid of a sample of specially purified ammonium metavanadate whose preparation we have previously described.[5] The completely reduced solution was freed from sulfur dioxide by prolonged boiling and sweeping out with carbon dioxide. It was then cooled, filtered and diluted to volume. Other chemicals were reagent grade and were not further purified.

A water thermostat was used to maintain a temperature of 25.00 ± 0.01°. A Beckman glass electrode pH meter was used for all pH measurements.

Data and Discussion

Seven determinations of the half-wave potential of the anodic wave of +4 vanadium in 1 N sodium hydroxide containing 0.08 M sodium sulfite (curves I, Fig. 1) led to a mean value of -0.432 ± 0.004 v. *versus* the saturated calomel electrode. These measurements were made from large-scale plots of $E_{\mathrm{d.e.}}$ against $\log (i/i_{\mathrm{d}} - i)$, and their mean is in good agreement with a previous measurement.[1]

Table I presents data on the diffusion current constant, $i_{\mathrm{d}}/Cm^{2/3}t^{1/6}$, of this wave. The supporting electrolyte was protected by both purified hydrogen and sulfite, and the acidic vanadyl solution was saturated with sulfur dioxide to prevent local oxidation on addition to the alkaline supporting electrolyte. The measurements were made at -0.20 v. *versus* the saturated calomel electrode. Diffusion currents have been corrected for the residual current. No gelatin or other maximum suppressor was present. The diffusion current is not appreciably changed by varying the sodium hydroxide concentration between 0.3 and 3 N.

TABLE I

DIFFUSION CURRENT CONSTANT OF +4 VANADIUM IN 1 N SODIUM HYDROXIDE–0.08 M SODIUM SULFITE

$m^{2/3}t^{1/6} = 2.425$ mg.$^{2/3}$ sec.$^{-1/2}$

+4 Vanadium, millimolar	i_{d} microamp.	$\frac{i_{\mathrm{d}}}{Cm^{2/3}t^{1/6}}$
0.1900	−0.677	−1.465
.346	−1.240	−1.466
.374	−1.334	−1.469
.548	−1.940	−1.463
.667	−2.378	−1.468
.719	−2.540	−1.464
.880	−3.131	−1.467
.966	−3.44	−1.468
1.038	−3.67	−1.462
1.190	−4.24	−1.468
1.245	−4.45	−1.469
1.338	−4.75	−1.464
1.480	−5.29	−1.469
1.619	−5.74	−1.462
		Mean −1.466 ± 0.002

Curves II of Fig. 1 demonstrate the deleterious effect of gelatin on the polarograms of +4 vanadium in 1 N sodium hydroxide–0.08 M sodium sulfite. The half-wave potential in the presence of 0.01% gelatin is -0.35 v., or 0.08 v. more positive than in the absence of gelatin. Although careful measurements have shown that the diffusion cur-

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