light absorbed by an oil film in the region of 320-400 mμ was indicative of the durability of the film upon exposure to accelerated weathering conditions.

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The Hydrolysis of Soap Solutions. III. Values of pH and the Absence of Fatty Acid as Free Liquid or Solid

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SOAPS hydrolyze to form hydroxyl ion and free fatty acid, but the latter is converted into soluble or insoluble undissociated acid soaps. The conversion of free fatty acid into acid soap causes the soaps to hydrolyze far more than the acetates (N/10 sodium acetate hydrolyzes to the extent of 0.007%) though the fatty acids are but slightly weaker than acetic acid. Thus the hydroxyl ion concentration is no longer equal to that of the free fatty acid but is at least an order of magnitude larger, since the corresponding fatty acid is consumed by forming acid soap.

At least three opinions have been expressed as to the presence of fatty acid in soap solutions. McBain has long maintained that, though fatty acid is always formed, there is never sufficient present to saturate the solution. Ekwall (1) holds, however, that there is more than sufficient for saturation only in a narrow range of very dilute solutions, just below the limiting concentration which he describes as the highest concentration in which the free fatty acid can appear before its conversion to acid soap. Powney and Jordan (2), on the contrary, have calculated that, not in the most dilute solutions, but in approximately 0.005 M sodium laurate, 0.001 M sodium myristate, 0.0002 M sodium palmitate, and 0.00003 M sodium stearate at 60°C., the solubility limit of fatty acid is reached and that in a range above these concentrations it is in excess of and may be several hundred times greater than the saturation value.

To confirm one of these views, pH values of potassium and sodium soap solutions were determined, and from them the actual concentration of free fatty acid in solution was calculated. This amount was found to be less than the saturation value, as determined by conductivity measurements, given in the preceding communication.

From the pH values the percentage hydrolysis was also calculated. Estimates of hydrolysis have ranged from negligible to complete hydrolysis, based upon various types of data, including E.M.F. measurements, catalysis, indicators, analysis of ultrafiltrates, extraction with benzene or other solvents, and pH measurements. Much of the earlier work has been done on sodium soaps. Ekwall and Lindblad (3) published pH data obtained by use of the glass electrode for sodium laurate at 20°. Stauff (4) used the hydrogen electrode to measure the pH of sodium soaps at 60°C. and constructed hydroxyl ion activity curves as a function of concentration but did not disclose the pH's. Likewise, Powney and Jordan (2) using the glass electrode determined the pH's of a number of sodium soaps at 25, 40, 60, and 80°C., published hydrolysis-concentration curves but did not give the pH's. Some earlier studies of potassium soaps have involved E.M.F. (5), indicator (6), and extraction (7) methods, but there are but few data on their pH's in the literature. Hence the determination of the pH of sodium and potassium soaps over a range of concentrations is here recorded for 25 and 50°C.

Experimental

Kahlbaum's best acids, and some Lepovsky's purified myristic acid were used in preparing the soap solutions. They were first analyzed by titrating them with alkali in 70-80% aqueous alcohol to determine the equivalent weight. McBain and Van Tuyl (8) showed by the titration curves of lauric and myristic acids in 80% alcohol, using phenolphthalein as indicator, that the equivalence point, the point of inflection, and the color change coincided whereas in aqueous solution the point of inflection required 1.5% excess lauric acid and 6.2% excess myristic acid. In this study titrations were made in aqueous alcoholic solutions using approximately decinormal sodium hydroxide, potassium hydroxide, and sodium hydroxide with a glass electrode; the results of the three titrations agreed closely. Also the results seemed to be independent of the concentration of alcohol, provided that there was sufficient to prevent precipitation.

For the pH determinations stock solutions were prepared by adding the calculated volume of standard alkali to a weighed amount of acid. This was heated on a water bath at approximately 70-90°C. until the acid dissolved, then cooled, and diluted to volume with conductivity water. The sodium hydroxide solutions were made from carbon dioxide-free

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sodium drippings and conductivity water; potassium hydroxide solutions were made from Bakers "Analyzed," after a preliminary rinsing to wash away carbonate from the solid.

A few measurements were made on stock solutions made by another method. Alkali was added to the acid, yielding a soap which was considered to have the same concentration as that of the alkali; e.g. 0.5555 g. of lauric acid was dissolved in 20.09 ml. of 0.1379 N_v potassium hydroxide to give 0.1379 N potassium laurate solution. The error involved in neglecting the volume of the acid would be small in all but the more concentrated solutions. The results of the two methods, used by different persons, did not agree precisely. Most of the values given are those obtained by use of the first method, but some of the second (by P.L.) are also given.

The stock solutions were diluted as follows, boiled out conductivity water being used throughout. The normalities are N_v, or approximately N_v, neglecting the slight volume change on mixing. 2.50 ml. of water were added from a 10-ml. microburette to 10 ml. of 1.000 N solution to give an 0.800 N solution, 6.67 ml. of water were added to 10.00 ml. of 1.00 N to give a 0.600 N solution. Using pipettes, 10.00 ml. of solution were diluted with an equal volume of water. (Thus 0.800 N was diluted to 0.400 N, 0.400 N to 0.200 N, 0.600 N to 0.300 N, 0.300 N to 0.150 N.) 5.00 ml. of 1.000 N were diluted to 50 ml. in a volumetric flask, giving .100 N solution, which was diluted through the range 0.0800 to 0.0100 in the manner given above. 0.100 N was diluted to 0.0100, 0.0100 to 0.00100 N, and these were diluted as above.

For the pH measurements the Beckman pH meter and the blue glass-calomel assembly was used. The meter was checked with a series of buffered solutions made from Burrell buffer tablets. A small meter correction was necessary above pH 9.80. In the tables both corrected and uncorrected pH's are given at 25°C. No correction was applied at 50°C.

Before each series of measurements the meter was standardized by use of a pH 7 buffer, and it was checked from time to time against a second buffer of pH 11. To make a measurement 15-20 ml. of the solution were placed in a 50-ml. beaker, brought to 25 or 50°C., suspended in a Dewar flask, and the blue glass-calomel electrode assembly was lowered into the solution. The reading was taken after three to five minutes, when it was usually, but not always, quite constant. During this short period the solutions were in contact with the atmosphere. Otherwise they were kept enclosed. It should be noted that any carbon dioxide taken up by the soap solution would tend to lower pH and favor formation of free fatty acid. However, as is shown, the fatty acid was not enough even to saturate the water in the soap solution. For readings at 50° the temperature regulator of the meter was set at 40°, the meter was adjusted so that it read correctly the pH 7 buffer (6.97 at 50°C.). Then if x is the dial reading at 50°, the pH

$$= 6.97 \frac{313}{323} (x - 6.97).$$

The stock solutions were allowed to stand for a day or more before making the measurements as the pH may vary with the age of the solution. Most of the measurements were made on the diluted solutions 10 minutes to an hour after dilution though some remained for a longer time. With some solutions the variation in pH is appreciable, in others it is slight. The pH of a 0.1 N potassium myristate solution measured 10.95 just after its preparation from the acid and alkali; after 16 hours the value was 10.47. A portion of it diluted to 0.01 N read 10.62 just after dilution, and 10.70 the next day. In general, when solutions were diluted tenfold, a longer time was required to reach a fairly constant pH than when diluted twofold.

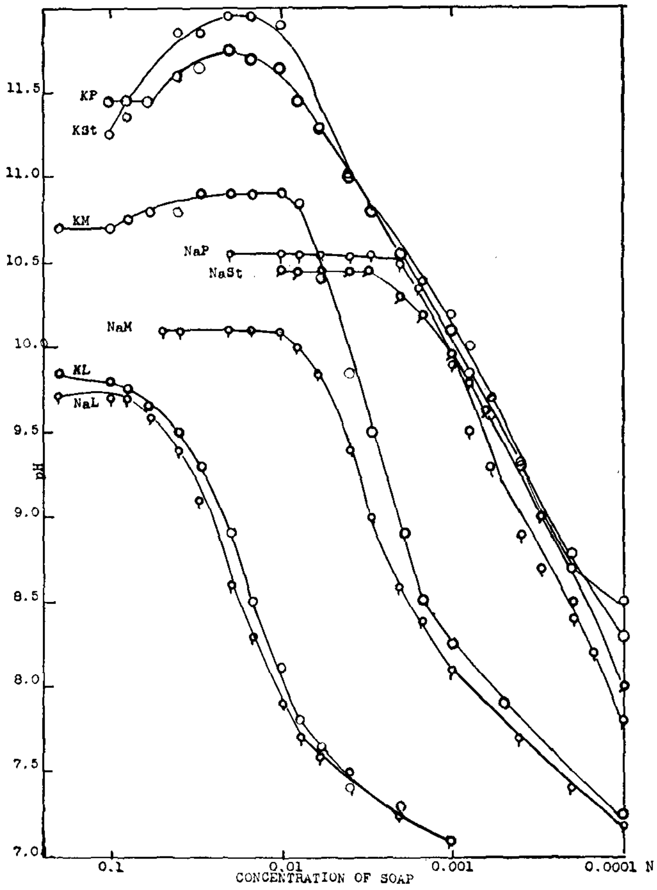

FIG. 1. Comparison of the pH of sodium and potassium soaps at 25°.

For each soap studied a number of solutions were prepared and the pH measured, the average of these results, rounded to the nearest 0.05, or in some cases the nearest 0.1, of a pH unit are given in the tables which follow. From the pH, the hydroxyl ion activity was calculated using for the ionization constant of water 10^{-14} at 25° and $10^{-13.26}$ at 50°C.

To test the effect upon pH of solubilized hydrocarbon about one equivalent of hexane was added to some of the laurate stock solutions and allowed to stand for 24 hours or longer. A small amount of the hexane was solubilized. The solution was diluted in the usual manner, and the pH was determined simultaneously with an untreated solution. A slight lowering of pH and of hydrolysis is due to the solubilized hexane. The pH values listed in the laurates under "corrected pH" have had the meter correction applied and are rounded off to the nearest 0.05 of a pH unit and are sometimes slightly greater or less than the designated pH since other data were also considered. Tables I, II, III, and IV give the pH, the hydroxyl ion activity, and the percentage hydrolysis at 25 and 50°C. for the soaps studied. Table I includes the effect of solubilized hexane on the laurates at 25°C. Table V gives some pH values of soaps prepared by the second method described above.

In Figures 1 and 2 the pH values are plotted as a function of the concentration. They show that the pH of the potassium soap is nearly always somewhat higher than that of the corresponding sodium soap. For the laurates the difference is small at 25°, and also in the more concentrated solutions at 50°C., while in dilute solutions the two curves nearly coincide. For the myristate, palmitates, and stearates at 50° the pH of the potassium salt is usually only a few tenths of a unit higher than that of the sodium salt, but at 25° the difference may exceed one pH unit in concentrations above 0.004 N.

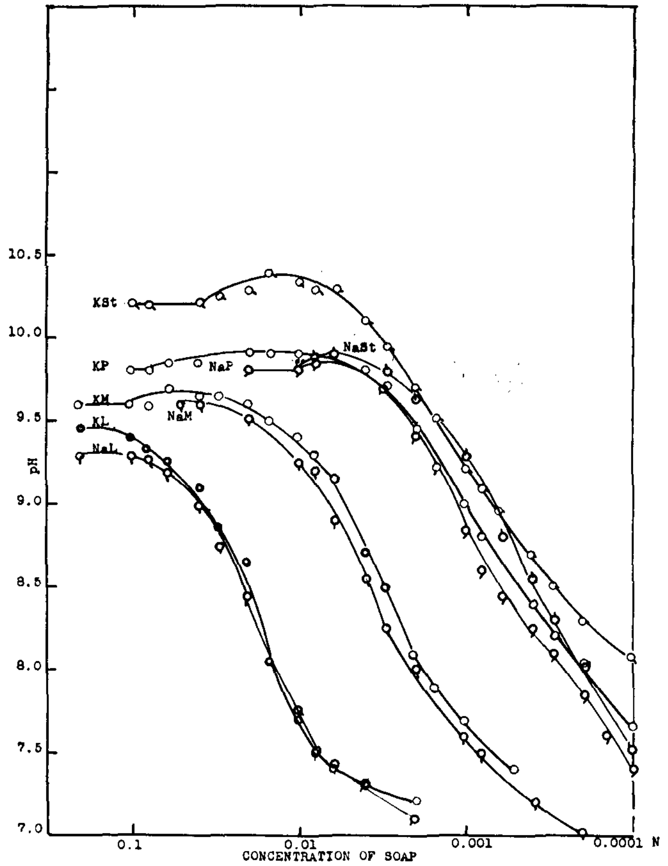

FIG. 2. Comparison of the pH of sodium and potassium soaps at 50°.

The curves at 50°C., Figure 2, show best the increase in pH though it is not a uniform increase, with increasing carbon content from the laurates to the stearates; for example, the pH's of 0.01 N solutions of potassium salts are: laurate, 7.70; myristate, 9.4; palmitate, 9.9, and stearate, 10.35, and of the corresponding sodium salts: 7.75, 9.25, 9.8, and 9.8. At 25° in the higher concentrations used the sodium stearate curve is slightly lower than that of the palmitate, contrary to what one might expect. Preston (9) in the study of the detergent action of sodium soaps also found the palmitate and stearate order was the reverse of that expected in "whiteness of washed cloth-concentration" curves. However, both of these latter systems were curded mixtures (not all solution) in the higher concentrations used, so sorption may be partially responsible for this order.

Milton A. Lesser (10) in "Pros and Cons of Toilet Soap Irritation" states "The pH range of 1% solutions of toilet soaps was found to be 9-11 by Klander and co-workers (Arch. Dermat. and Syph., 1931, *162*, 517). Sharlitt (New York State J. Med., 1943, *43*, 160) found a pH range of 9-10 for toilet soaps." Our results for pure soaps range from 11.7 for the highest concentrations of the highest soaps, and 9.9 for the highest concentrations of potassium laurate, down to 7.1 for the laurates in 0.001 N and about 8 for the stearates in 0.0001 N. Our results for 1% solutions range from 9.5 for laurates to 11.6 for potassium palmitate and stearate.

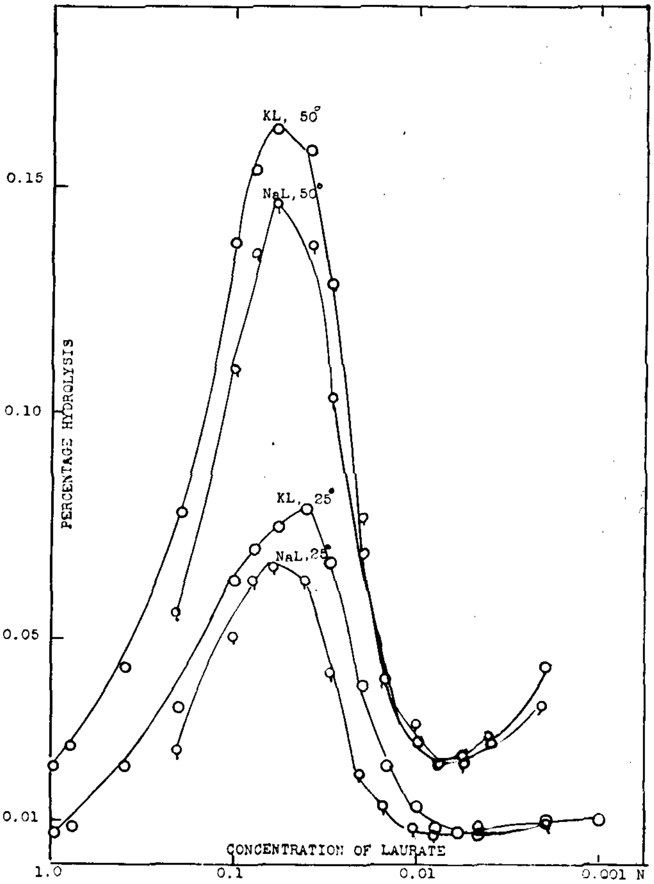

FIG. 3. Percentage hydrolysis-concentration curves for the laurates at 25° and 50°.

Under our data for pH percentage hydrolysis-concentration curves were constructed for each soap. Figure 3 gives those of the laurates at 25° and 50°C. Potassium and sodium laurate are similar in percentage hydrolysis, but in all but the most dilute solutions that of the potassium salt is greater than that of the sodium salt. For the laurates percentage hydrolysis is roughly twice as great at 50° as at 25°. Potassium myristate is hydrolyzed about six times as much as the sodium salt in 0.01 N solution at 25°, the difference is very small at 50°. A maximum occurs in each of the hydrolysis curves, and, if the concentration is sufficiently dilute, a minimum is also present.

The 0.2 N sodium laurate was clear at 25° but readily set to a solid curd when cooled slightly below 25°. At times, beautiful needles separated from 0.1 N solution when the temperature fell to about 20°. An

TABLE I

The pH, Hydroxyl Ion Activity and Percentage Hydrolysis at 25° and 50°C. and the pH in the Presence of Solubilized Hexane at 25° for Potassium and Sodium Laurate

Conc'n N_v	25°C.					50°		
	pH	pH Hex.	Corr. pH	a_{OH} $\times 10^4$	Percentage Hydrolysis	pH	a_{OH} $\times 10^4$	Percentage Hydrolysis
			POTASSIUM LAURATE					
1.0	9.80	9.88	9.85	0.708	0.0071	9.60	2.19	0.022
0.8	9.80	9.85	9.85	0.708	0.0088	9.60	2.19	0.027
0.4	9.87	9.85	9.95	0.891	0.022	9.50	1.74	0.044
0.2	9.80	9.85	9.85	0.708	0.035	9.45	1.55	0.078
0.1	9.75	9.68	9.80	0.631	0.063	9.40	1.38	0.138
0.08	9.68	9.62	9.75	0.563	0.070	9.35	1.23	0.154
0.06	9.63	......	9.65	0.447	0.075	9.25	0.997	0.163
0.04	9.48	9.45	9.50	0.316	0.079	9.10	0.692	0.158
0.03	9.20	......	9.30	0.200	0.067	8.85	0.389	0.129
0.02	8.88	8.82	8.90	0.0794	0.040	8.40	0.138	0.069
0.015	8.40	......	8.50	0.0324	0.022	8.05	0.0617	0.041
0.01	8.05	7.94	8.10	0.0126	0.013	7.70	0.0275	0.027
0.008	7.72	7.77	7.80	0.00621	0.0079	7.50	0.0174	0.022
0.006	7.57	......	7.65	0.00447	0.0074	7.40	0.0138	0.023
0.004	7.48	7.42	7.40	0.00251	0.0063	7.30	0.0110	0.027
0.002	7.24	7.07	7.30	0.00200	0.10	7.20	0.00872	0.044
0.001	7.10	......	7.10	0.00126	0.013	......	....	......
			SODIUM LAURATE					
0.2	9.72	9.63	9.70	0.501	0.025	9.30	1.10	0.055
0.1	9.72	9.70	9.70	0.501	0.050	9.30	1.10	0.110
0.08	9.68	9.64	9.70	0.501	0.063	9.30	1.10	0.135
0.06	9.58	9.55	9.60	0.398	0.066	9.20	0.872	0.148
0.04	9.42	9.37	9.40	0.251	0.063	9.00	0.55	0.137
0.03	9.04	9.00	9.10	0.126	0.042	8.75	0.308	0.103
0.02	8.62	8.58	8.60	0.0398	0.020	8.45	0.155	0.077
0.015	8.28	8.28	8.30	0.0200	0.013	8.05	0.0617	0.041
0.01	7.90	7.86	7.90	0.00794	0.0079	7.75	0.0308	0.031
0.008	7.70	7.70	7.70	0.00501	0.0063	7.50	0.0174	0.022
0.006	7.62	7.48	7.60	0.00398	0.0066	7.40	0.0138	0.023
0.004	7.47	7.44	7.50	0.00316	0.0079	7.30	0.0110	0.028
0.002	7.25	7.22	7.25	0.00178	0.0079	7.0	0.0055	0.028
0.001	7.12	......	7.10	0.00126	0.013	......	....	......

0.028 N solution remained quite clear on standing, but in the more dilute solutions acid soap separated. 1.0 N potassium laurate was clear; likewise those down to about 0.04 N, where acid soap appeared. Crystals formed in the more concentrated solutions on standing. All of the laurate solutions were clear at 50°C.

0.05 N sodium myristate readily set to a curd when cooled slightly below 25°, and even at 25° the solutions from 0.05 to 0.01 N tend to set; first many white spherical nuclei appear, then the entire solution crystallizes to curd. The pH of a clear sol of 0.05 N measured 9.97, and after setting the pH was 10.26, corresponding to the separation of some soap.

TABLE II

The pH, Hydroxyl Ion Activity, and Percentage Hydrolysis of Potassium and Sodium Myristate at 25° and 50°C.

Conc'n N_v	25°C.				50°		
	pH	pH Corr.	a_{OH} $\times 10^4$	Percentage Hydrolysis	pH	a_{OH} $\times 10^4$	Percentage Hydrolysis
			POTASSIUM MYRISTATE				
1.0	10.50	10.70	5.01	0.05	9.70	2.75	0.027
0.8	10.50	10.70	5.01	0.063	9.70	2.75	0.034
0.4	10.50	10.70	5.01	0.12	9.70	2.75	0.069
0.2	10.50	10.70	5.01	0.25	9.60	2.19	0.11
0.1	10.50	10.70	5.01	0.50	9.60	2.19	0.22
0.08	10.55	10.75	5.62	0.70	9.60	2.19	0.27
0.06	10.60	10.80	6.31	1.05	9.70	2.75	0.46
0.04	10.60	10.80	6.31	1.6	9.65	2.45	0.61
0.03	10.70	10.90	7.94	2.6	9.65	2.45	0.82
0.02	10.70	10.90	7.94	4.0	9.60	2.19	1.1
0.015	10.70	10.90	7.94	5.3	9.50	1.74	1.15
0.01	10.70	10.90	7.94	7.9	9.40	1.38	1.4
0.008	10.65	10.85	7.08	8.8	9.30	1.10	1.4
0.006	10.30	10.40	2.51	4.2	9.15	0.776	1.1
0.004	9.80	9.85	0.708	1.7	8.70	0.275	0.69
0.003	9.50	9.50	0.316	1.1	8.50	0.174	0.58
0.002	8.90	8.90	0.0794	0.40	8.10	0.0776	0.39
0.0015	8.50	8.50	0.0316	0.21	7.90	0.0436	0.30
0.001	8.25	8.25	0.0178	0.18	7.70	0.0275	0.27
0.0005	7.90	7.90	0.00794	0.16	7.40	0.0138	0.27
0.0001	7.25	7.25	0.00178	0.18	......	....	......
			SODIUM MYRISTATE				
0.05	10.00	10.10	1.26	0.25	9.60	2.19	0.44
0.04	10.00	10.10	1.26	0.31	9.60	2.19	0.55
0.02	10.00	10.10	1.26	0.63	9.50	1.74	0.87
0.01	10.00	10.10	1.26	1.26	9.25	0.977	0.98
0.008	9.95	10.00	1.00	1.25	9.20	0.87	1.1
0.006	9.80	9.85	0.708	1.2	8.90	0.437	0.73
0.004	9.40	9.40	0.251	0.63	8.55	0.195	0.43
0.003	9.00	9.00	0.100	0.33	8.25	0.0977	0.32
0.002	8.60	8.60	0.0398	0.20	8.00	0.0550	0.27
0.0015	8.40	8.40	0.0251	0.17	......	....	......
0.001	8.10	8.10	0.0126	0.13	7.60	0.0219	0.22
0.0008	8.00	8.00	0.0100	0.12	7.50	0.0174	0.22
0.0004	7.70	7.70	0.00501	0.12	7.20	0.0087	0.22
0.0002	7.40	7.40	0.00251	0.12	7.00	0.0055	0.27
0.0001	7.20	7.20	0.00159	0.16	......	....	......

TABLE III

The pH, Hydroxyl Ion Activity, and Percentage Hydrolysis of Sodium Palmitate and Stearate at 25° and 50°C.

Conc'n N_v	25°C.				50°		
	pH	pH Corr.	a_{OH} $\times 10^4$	Percentage Hydrolysis	pH	a_{OH} $\times 10^4$	Percentage Hydrolysis
SODIUM PALMITATE							
0.02	10.4	10.55	3.55	1.8	9.8	3.47	1.7
0.01	10.4	10.55	3.55	3.5	9.8	3.47	3.5
0.008	10.4	10.55	3.55	4.4	9.85	3.89	4.9
0.006	10.4	10.55	3.55	5.9	9.85	3.89	6.6
0.004	10.4	10.55	3.55	8.8	9.75	3.09	7.7
0.003	10.4	10.55	3.55	11.9	9.7	2.75	9.2
0.002	10.35	10.5	3.15	15.8	9.4	1.38	6.9
0.0015	......	....	....	......	9.2	0.87	5.8
0.001	9.8	9.85	0.708	7.1	8.85	0.389	3.9
0.0008	9.5	9.5	0.316	4.0	8.6	0.219	2.7
0.0006	9.3	9.3	0.200	3.3	8.45	0.155	2.6
0.0004	8.9	8.9	0.0794	2.0	8.25	0.0977	2.4
0.0003	8.7	8.7	0.0501	1.7	8.1	0.0692	2.3
0.0002	8.4	8.4	0.0251	1.2	7.85	0.0398	1.9
0.00015	8.2	8.2	0.0159	1.1	7.6	0.0219	1.5
0.0001	7.8	7.8	0.00631	0.63	7.4	0.0138	1.4
SODIUM STEARATE							
0.01	10.3	10.45	2.82	2.8	9.8	3.47	3.5
0.008	10.3	10.45	2.82	3.5	9.9	4.36	5.4
0.006	10.3	10.45	2.82	4.7	9.9	4.36	7.2
0.004	10.3	10.45	2.82	7.1	9.9	4.36	10.9
0.003	10.3	10.45	2.82	9.4	9.8	3.47	11.6
0.002	10.2	10.3	2.00	10.0	9.65	2.45	12.3
0.0015	10.1	10.2	1.59	10.6	9.5	1.74	11.6
0.001	9.9	9.95	0.891	8.9	9.3	1.10	11.0
0.0008	9.75	9.8	0.631	7.9	9.1	0.692	8.6
0.0006	9.6	9.6	0.398	6.6	8.8	0.347	5.8
0.0004	9.3	9.3	0.200	5.0	8.55	0.195	4.9
0.0003	9.0	9.0	0.100	3.3	8.3	0.110	3.7
0.0002	8.5	8.5	0.0316	1.6	8.0	0.055	2.7
0.0001	8.0	8.0	0.0100	1.0	7.5	0.0174	1.7

McBain and Hay (6) likewise found that soap solutions from which soap had separated were more alkaline than the same wholly in solution. Ekwall and Lindblad (3) reported that a clear solution of 0.1833 N sodium laurate had a pH of 10.33, which six minutes later fell to 10.15, when it had been converted to a gel! 1.0 N potassium myristate is a clear solution at 25°, in 0.5 N solution a slight deposit separates on

TABLE IV

The pH, Hydroxyl Ion Activity, and Percentage Hydrolysis of Potassium Palmitate and Stearate at 25° and at 50°C.

Conc. N_v	25°C.				50°		
	pH	pH Corr.	a_{OH}' $\times 10^4$	Percentage Hydrolysis	pH	a_{OH}' $\times 10^4$	Percentage Hydrolysis
POTASSIUM PALMITATE							
0.10	11.2	11.45	28.2	2.8	9.8	3.47	0.35
0.08	11.2	11.45	28.2	3.5	9.8	3.47	0.43
0.06	11.2	11.45	28.2	4.7	9.85	3.89	0.65
0.04	11.3	11.6	39.8	9.9	9.85	3.89	0.97
0.03	11.35	11.65	44.7	14.9	......	......	.....
0.02	11.45	11.75	56.3	28.1	9.9	4.36	2.2
0.015	11.4	11.7	50.1	33.4	9.9	4.36	2.9
0.01	11.35	11.65	44.7	44.7	9.9	4.36	4.4
0.008	11.2	11.45	28.2	35.5	9.9	4.36	5.8
0.006	11.05	11.30	20.0	33.3	......	......	.....
0.004	10.8	11.0	10.0	25.0	9.8	3.47	8.7
0.003	10.6	10.8	6.31	21.0	9.7	2.75	9.2
0.002	10.4	10.55	3.55	17.7	9.4	1.38	6.9
0.0015	10.25	10.3	2.00	13.3	9.2	0.87	5.7
0.001	10.0	10.1	1.26	12.6	9.0	0.55	5.5
0.0008	9.8	9.85	0.708	8.8	8.8	0.347	4.3
0.0006	9.6	9.6	0.398	6.6	......	......	.....
0.0004	9.3	9.3	0.200	5.0	8.4	0.138	3.4
0.0003	9.09	9.0	0.100	3.3	8.2	0.087	2.9
0.0002	8.8	8.8	0.0631	3.1	8.0	0.055	2.7
0.0001	8.3	8.3	0.020	2.0	7.65	0.0246	2.5
0.00005	7.6	7.6	0.00398	8.0	7.3	0.011	2.2
POTASSIUM STEARATE							
0.10	11.0	11.25	17.8	1.7	10.2	8.70	0.87
0.08	11.1	11.35	22.4	2.8	10.2	8.70	1.1
0.04	11.3	11.6	44.7	11.2	10.2	8.70	2.2
0.03	11.3	11.6	44.7	14.9	10.25	9.77	3.3
0.02	11.4	11.7	50.1	25.0	10.3	11.0	5.5
0.015	11.4	11.7	50.1	33.4	10.4	13.8	9.2
0.01	11.3	11.6	39.8	39.8	10.35	12.3	12.3
0.008	11.2	11.45	28.2	35.5	10.3	11.0	13.8
0.006	11.0	11.25	17.8	29.7	10.3	11.0	18.3
0.004	10.8	11.0	10.0	25.0	10.1	6.92	17.3
0.003	10.6	10.8	6.31	21.0	9.95	4.90	16.3
0.002	10.4	10.55	3.55	17.7	9.7	2.75	13.7
0.0015	10.3	10.4	2.51	16.6	9.5	1.74	11.6
0.001	10.1	10.2	1.59	15.9	9.2	0.870	8.7
0.0008	9.9	10.0	1.00	12.5	9.1	0.692	8.6
0.0006	9.7	9.7	0.501	8.3	8.95	0.493	8.1
0.0004	9.2	9.2	0.159	4.0	8.7	0.275	8.3
0.0003	9.0	9.0	0.100	3.3	8.5	0.174	5.8
0.0002	8.7	8.7	0.0501	2.5	8.3	0.110	5.5
0.0001	8.55	8.55	0.0355	3.5	8.15	0.077	7.7

standing. In 0.01 N solution a rather heavy precipitate appears; in 0.001 N there is a light precipitate of acid soap.

The 0.01 N sodium stearate and 0.02 N sodium palmitate were soft curded mixtures at 25°, and even at 50°, most of the curd did not dissolve. At 50°, 0.004 N solution was quite opalescent, and by 0.003 N crystals of acid soap appeared. The 0.0004 N solution was again opalescent. The pH of these curded mixtures was variable, depending upon how the curd separated, the length of time of standing, etc., so the values given are but average values. For 0.01 N stearate, values ranging from 10.0 to 10.6 were obtained at 25°.

0.1 N potassium palmitate contained undissolved crystals, which dissolved when the solution was warmed to about 30°. Crystalline acid soap appeared at 50° in 0.02 N solution, and persisted until the solution was very dilute. The 0.1 N potassium stearate is a greasy viscous white mixture at 25°, but a clear sol. at 50°. At 50° silky crystals were present in 0.04 N solution and continued until a concentration of 0.0008 N, which was clear.

To determine the effect of added salt upon the pH of a soap solution a weighed amount of sodium or potassium chloride was dissolved in some of the stock soap solution, then it was diluted in the usual manner. The pH's of treated and untreated solutions were determined simultaneously. The results are given in Table VI. For potassium laurate solutions at 25° and at 50° the added 0.1 N potassium chloride caused a lowering in pH in concentrations 0.1 to 0.03 N, but from 0.02 to 0.006 N a slight increase was observed and again a decrease from 0.004 to 0.003 N. Sodium chloride added to 0.01 N sodium myristate to make it 0.01 N in sodium chloride had no appreciable effect upon the pH. "Solutions" of 0.01 N sodium palmitate containing 0.1 N and 0.05 N sodium chloride were found to have a much lower pH than the untreated solution. Some salting-out was apparent. Evidently the effect of salt on the pH of a soap solution is rather complex. McBain and Merrill (11) have shown that added electrolyte promotes solubilization and micelle formation at dilutions where there is no evidence for these phenomena without the electrolyte.

Discussion

The pH values of soap solutions supply data for (H^+) in the equation: $\frac{(H^+)\ (A^-)}{(HA)} = K_a$ which expresses the relationship between the components of a solution of a weak acid. The concentration of fatty acid ion (A^-) is in some cases known from osmotic data for soap solution; in other cases it can be estimated. Then one can solve for the concentration of undissociated fatty acid (HA), present in the soap solution.

For solutions of laurate 0.01 N and less, the concentration of free laurate ion (L′), was taken to be equal to the soap concentration, for 0.04-0.1 N solutions, (L′) was taken as 0.026 N, and for 1.0 N solution, (L′) was 0.12, the latter values being approximately those given by McBain and Eaton (7). The same values were used for the myristates, though they are actually somewhat lower. Palmitate and stearate ion concentrations were taken to be the same as those of the soap, except for 0.006 to 0.02 N palmitate, where (P′) was taken as 0.0032 N [the critical concentration, as given by Ekwall (12)].

Beginning with the more concentrated solutions, the calculated amount of undissociated fatty acid decreased with decreasing soap concentration, passed through a minimum, and then a maximum in the case of the laurates and myristates. Perhaps the concentrations used were not sufficiently dilute to reach the maximum for the palmitates and stearates. For potassium laurate the concentration of undissociated lauric acid increased as the concentration of laurate changed from 0.1 to 0.006 N, then decreased in concentrations from 0.006 to 0.001 N. In 0.006 N solution it was about 93% of the saturation value;

TABLE V

The pH of Various Soap Solutions at 25° and at 50°C. Prepared by the Second Method Mentioned in the Text *

Soap Conc.	K Laurate
	25°
1.142	10.1
0.57	10.1
0.28	10.2
0.07	10.0
0.057	9.98
0.028	9.0
0.014	8.8
0.0057	8.25
0.0014	7.6
0.00028	7.3
0.00014	7.1
Water	6.4

Soap Conc.	K Laurate	K Myristate
	50°	50°
0.1379	9.23	9.60
0.07	9.28	9.71
0.035	8.99	9.76
0.01379	8.16	9.60
0.007	7.68	9.42
0.0035	7.29	9.32
0.001379	7.29	8.40
0.0007	......	7.97
Water	7.5	7.68

Soap Conc.	Sodium Laurate	
	25°	50°
0.2	......	9.71
0.1	9.78	9.67
0.05	9.52	9.42
0.010	8.4	8.31
0.005	8.0	7.68
0.001	7.8	7.48
Water	7.5	......

Soap Conc.	Na Myristate	K Myristate
	50°	25°
0.0216	9.81	10.28
0.0108	9.62	10.20
0.0054	9.23	9.72
0.00216	8.50	9.15
0.00108	8.06	8.80
0.00054	7.72	8.10
0.00027	......	7.90
0.000216	7.73	7.85
0.000108	7.15	......
0.000054	7	......
Water	6.7	7.0

Soap Conc.	Na Palmitate
	50°
0.0197	10.10
0.0098	10.10
0.0049	10.10
0.00197	9.91
0.00098	9.42
0.00048	8.94
0.00197	8.60
0.000098	8.16
0.000049	7.77
Water	6.9

Soap Conc.	K Palmitate
	50°
0.0655	9.81
0.0328	9.71
0.0164	9.66
0.0065	10.05
0.00328	10.24
0.00164	9.71
0.00082	9.32
0.00041	8.74-8.94
0.0002	8.60
Water	7.5

Soap Conc.	K Stearate
	50°
0.001311	10.05
0.00065	9.81
0.00032	9.56
0.000131	9.13
0.000065	8.79
0.000032	8.31

* These measurements represent single trials made on stock solutions whose concentration was taken as that of the added alkali.

in 0.001 N about 67%; and in 0.01 N it was slightly more than 50% saturated at 25°. Ekwall (13) considered that in sodium laurate solutions at room temperature free fatty acid separates in concentrations from about 0.004 to 0.0065 N. At 50° the highest lauric acid concentration reached lies in the region 0.006-0.008 N when it is about two-thirds the saturation value. This might be compared with the calculations of Powney and Jordan which are given for sodium laurate at 60°. They state that in 0.005 M solution the approximate solubility limit is reached (given as 12×10^{-6} M), and in 0.01 M the concentration of lauric acid is about 3 times this value, and in 0.1 M nearly 31 times this value! They have given the approximate solubility limit at 60° as 4×10^{-6} M for stearic acid and 12×10^{-6} for lauric acid. By conductivity measurements at 50° the concentration of undissociated lauric acid is nearly 80 times that of stearic acid (total solubility is about 20 times as great).

TABLE VI

The Effect of Added Salt on the pH "Solutions" of Sodium Palmitate and Solutions of Sodium Myristate and Potassium Laurate

Conc.	pH of Sodium Palmitate		pH of Sodium Palmitate		pH of Sodium Myristate	
	Alone	0.1 N NaCl	Alone	0.05 N NaCl	Alone	0.01 N NaCl
	25°	25°	25°	25°	25°	25°
0.01	10.30	8.72	10.58	9.13	9.97	9.95
0.008	10.40	8.68	10.50	9.18	9.94	9.98
0.006	10.40	8.90	10.50	9.38	9.78	9.78
0.004	10.40	9.04	10.50	9.45	9.38	9.42
0.003	......	......	10.40	9.54	9.05	9.10
0.002	10.30	9.38	10.37	9.65	8.55	8.57
0.001	9.82	9.25	9.80	9.64	8.26	8.28
0.0008	9.42	9.13	9.55	9.45	8.20	8.16
0.0006	9.28	8.93	9.30	9.30	......	......
0.0004	8.82	7.90	8.90	8.60	7.84	7.84
0.0003	8.70	7.60	8.70	8.41	......	......
0.0002	8.45	7.20	8.40	8.22	7.58	7.46
0.0001	......	......	7.63	7.96	7.28	7.38

Conc.	pH of Potassium Laurate		pH of Potassium Laurate	
	Alone	0.1 N KCl	Alone	0.1 N KCl
	25°	25°	*50°	*50°
0.1	9.82	9.73	9.48	9.36
0.08	9.80	9.65	9.42	9.30
0.06	9.67	9.60	9.30	9.25
0.04	9.53	9.50	9.22	9.10
0.03	9.46	9.38	8.90	8.68
0.02	8.90	9.10	8.43	8.53
0.015	8.55	8.70	8.08	8.20
0.01	8.10	8.22	7.73	7.80
0.008	7.82	8.03	7.50	7.68
0.006	7.68	7.72	7.38	......
0.004	7.60	7.48	7.30	7.25
0.003	7.50	7.43	7.18	7.12

* Temperature correction was not made.

The concentration of undissociated fatty acid reaches a higher per cent of its saturation value in the laurates than in the other soaps over the concentration range calculated. The highest calculated centration for palmitic acid was in 0.0001 N sodium palmitate and in 0.00005 N potassium palmitate where it was 0.12×10^{-6} M at 25°, or 20% saturated; at 50° it was about 40% saturated in sodium palmitate and 26% saturated in potassium palmitate of the above concentrations. The highest stearic acid concentration was in 0.0001 N sodium stearate where it was 26.6% saturated, and in 0.0002 N potassium stearate, 11% at 25°C.; at 50° the percentage saturation for the same concentration was 31 and 16, respectively. These calculations confirm the concept that in soap solutions containing exactly equivalent amounts of alkali metal and fatty acid radical, hydrolytic fatty acid is insufficient to produce saturation; therefore free fatty acid does not separate out unless the solution is acted upon by an excess of acid, such as carbon dioxide.

Percentage Hydrolysis

Percentage hydrolysis is defined in terms of concentration of hydroxyl ion in relation to the total stoichiometric concentration of soap. A comparison of the present values obtained for percentage hydrolysis of soap solutions with those found in the literature shows that, in general, earlier measurements are considerably higher. However, the pH of a solution is not invariable, but (assuming pure materials) depends upon the methods of preparation and the age of the solution, temperature effects, and sorption if excess neutral or acid soap is present. The pH of dilute solutions is much less constant than that of more concentrated solutions. In practice there is the effect of atmospheric carbon dioxide to cope with. It is not surprising, therefore, to find considerable variation in recorded pH's. Calculations show that an increase of 0.2 in pH corresponds to approximately 50% increase in hydrolysis, and an increase of 0.35 to nearly 100% increase. Hence percentage hydrolysis calculated from pH measurements must be subject to a range of variation, depending upon many factors, as age of the solution, etc.

Some conclusions, however, may be set down with considerable assurance. The hydrolysis of the laurates is very much less than that of the higher soaps, not exceeding a few tenths of 1% at 25°, and in most concentrations it is much less than this. At 50°C. it is approximately twice that at 25°. Percentage hydrolysis for the myristates will not exceed a few per cent, except for a small range of concentrations of the potassium salt, and in most concentrations it is much less than 1%. The hydrolysis of the palmitates and stearates is much higher.

For each soap one can select a tenfold, or in a few cases a hundredfold range where hydrolysis is much greater than elsewhere (except perhaps in very dilute solutions). Table VII summarizes this range of concentration with its corresponding range of hydrolysis together with the maximum hydrolysis and the concentration in which it occurs.

TABLE VII

Tenfold of Concentration in Which Hydrolysis Is Greatest With the Corresponding Range in Hydrolysis, Also Maximum Hydrolysis

Soap	Tenfold of Conc.	% Hydrolysis Range	Maximum Hydrolysis and Its Conc.			
			25°		50°	
NaSt	0.004-0.0004	7.1 -5.0	10.6% at	0.0015N	12.3% at	0.002N
KSt	0.04 -0.0004	11.2 -4	39.8	0.01	18.3	0.006
NaP	0.008-0.0008	4.4 -4.0	15.8	0.002	9.2	0.003
KP	0.04 -0.0004	9.9 -5.0	44.7	0.01	9.2	0.003
NaM	0.04 -0.004	0.31 -0.63	1.25	0.008	1.1	0.008
KM	0.04 -0.004	1.6 -1.7	8.8	0.008	1.4	0.008
NaL	0.2 -0.02	0.025-0.02	0.066	0.06	0.148	0.06
KL	0.2 -0.02	0.03 -0.04	0.079	0.04	0.163	0.06

Summary

The pH of the laurates, myristates, palmitates, and stearates of sodium and potassium at 25° and 50°C. was determined by use of a glass electrode. pH:concentration curves were constructed, and hydroxyl ion activity was calculated. In general, the concentration of hydroxyl ion ranges from 0.001 to 0.0001 N; for the less dilute solutions of the higher soaps, the upper limit is exceeded by several fold, and in the more dilute solutions the concentration may fall beneath the lower value. Solubilized hexane reduced the pH of potassium and sodium laurate but very slightly. Potassium or sodium chloride reduced the pH of soap solutions over a certain range but caused a slight increase in a narrow intermediate range.

Using the pH values obtained, the actual concentration of fatty acid in the soap solutions was calculated, and was found to be *less* than the saturation concentrations obtained by conductivity measurements through the entire range investigated. Free fatty acid therefore never separates as such from pure soap solutions unless acted upon by excess of acid such as carbon dioxide.

Percentage hydrolysis was calculated and curves were constructed. In general, the potassium soaps are hydrolyzed more than the corresponding sodium soaps; the difference is slight for the laurates but is considerably greater for the myristates, palmitates, and stearates in higher concentrations at 25°C. The difference is appreciably smaller at 50° than at 25°. Percentage hydrolysis for the laurates is very much less than for the higher soaps.

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Silicates in Soaps

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SILICATES of soda were added to soaps before 1835. Soaps containing substantial quantities of silicate became popular in this country during the Civil War when the shortage of fats and rosin in the North caused manufacturers to add silicates to their soap in order to extend the supply. The wartime and present shortage of fats is reemphasizing the value of silicates for this purpose. It is estimated that the soap industry of the United States consumes more than 200,000 tons annually of silicates calculated to the 41° Baumé solution equivalent. Most commercial soaps now contain some silicate and some contain it in very large proportion.

At first silicates in soap were regarded simply as fillers which had little or no effect on the washing action of the soap. It is now well established both from careful laboratory studies and continued practical use under a wide variety of conditions over many years that silicates definitely improve the washing action of soaps under conditions of use. Silicates of soda are themselves detergents just as are soaps and the numerous types of new synthetic detergents. Mixtures of soap and silicates in the proper proportions are usually better than either alone.

Types of Silicate. Sodium silicates are composed of varying proportions of sodium oxide (Na_2O), silica (SiO_2), and water. More than 50 products varying in the ratio of these three components are commercially available as well as several potassium silicates. The characteristics of those of most interest to the soap and detergent manufacturer are summarized in Table I. The sesqui- and metasilicates are white crystalline, readily soluble, definite chemical compounds of fixed composition. "GC" has a silica to alkali ratio of 2.0 and is an amorphous hydrated powder. "SSC" is an essentially anhydrous solid of the same ratio. The "GC" silicate is spray dried and the "SSC" powder finely ground to provide rapid solubility. Commercially available silicates with a silica to alkali ratio greater than about two are glasses whose silica to alkali ratio may vary continuously from two to about four, which is now the practical upper limit. Although quite soluble, these silicates can be dissolved satisfactorily only by steam under pressure so are sold as solutions as concentrated as practicable. The silicate now most commonly used by soapmakers has a specific gravity of 41° Baumé and a silica to alkali ratio of 3.2. The chemistry of the soluble silicates is discussed elsewhere (1, 10).

Detergency of Silicated Soaps

pH and Buffering Action. The phenomenon of detergency is complex and involves several factors whose relative importance varies with conditions. One important factor involves the neutralization of the organic acids, sweat, and other acidic materials in dirt and the saponification of fats, oil, and greases since these are a substantial fraction of many dirts. These materials are converted to water soluble sodium salts, which are readily removed by rinsing. Likewise, proteins and oil paints are usually more readily removed by alkaline solutions. This requires a high pH and high available alkalinity, which should be maintained over a wide range of concentrations and temperatures by effective buffering action. Both of these are obtained by using a suitable soluble silicate.

In addition to removing certain types of dirt by neutralization and saponification, the alkalinity of the silicates prevents the formation of acid soaps and/or free fatty acids by reaction of the soap with less alkaline materials. Such materials include bicarbonates in water softened by ion exchange methods, and carbon dioxide absorbed from the air as well as acidic dirts. Acid soaps are generally regarded as having little or no detergent action in aqueous systems.

Silicates, like other electrolytes, decrease the concentration at which micelles begin to form in soap solutions. This may be important for, as data presented by Preston (2) indicate, a marked increase in detergent action occurs at about the concentration at which micelles begin to form. Silicates by themselves do not solubilize water-insoluble dyes. This makes it possible to obtain good cleaning without fading dyed goods. The addition of silicates to a soap solution,