

LXXXVI.—*The Alkalinity of Soap Solutions as measured by Indicators.*

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THE classical experiments of Chevreul ("Recherches chimiques sur les corps gras d'origine animal," Paris, 1823) demonstrated clearly the existence of hydrolysis in aqueous solutions of sodium and potassium soaps, and gave some indication of the products of hydrolysis. Until recently, however, the extent of the hydrolysis was a matter of dispute and of wide divergence of opinion (see, *e.g.*, F. Goldschmidt, "Handbuch der Chemie und Technologie der Öle und Fette," Vol. III, 1911, pp. 405 and 411, where it is stated that this is "still an unsolved problem"). Contributions from the

Bristol Laboratory (McBain and Martin, J., 1914, **105**, 957; McBain and Bolam, J., 1918, **113**, 825; Beedle and Bolam, *J. Soc. Chem. Ind.*, 1921, **40**, 27 T; McBain and Taylor, *Z. physikal. Chem.*, 1911, **76**, 179; McBain and Jenkins, J., 1922, **121**, 2325; McBain and Bowden, J., 1923, **123**, 2417; M. E. Laing, *J. Physical Chem.*, 1924, **28**, 673; McBain and Buckingham, J., 1927, 2679) have established by many independent methods (hydrogen electrode, rate of catalysis, conductivity, ultrafiltration, and electric migration) that all aqueous solutions of the salts and acid salts of the fatty acids are definitely alkaline, although the concentration of hydroxyl ion is only of the order of $N/1000$ or less. Each of these methods has limitations, and the present contribution, in which the use of indicators is described, greatly extends the available data.

The investigation, which was completed at the University of Bristol in 1926, began by a study of the behaviour of all the commercially available indicators in alkaline solution in the absence of soap. Many surprising discrepancies were encountered,* including, for example, a very large salt error caused by the standard Sorensen buffers themselves with such indicators as thymol-blue, phenol-red, and phenolphthalein in alkaline solution. Some of the results of this study have been published by McBain, Dubois, and Hay (*J. Gen. Physiol.*, 1926, **9**, No. 4, 451). The work has been supplemented and confirmed by the use of the hydrogen electrode by Miss Clark and Miss M. E. Laing at Stanford (*J. Gen. Physiol.*, in press).

Very few indicators possess any value for the study of soap solutions; for example, the Universal Indicator, which has been used in several technical circles, yields completely erroneous results.

The two best indicators are alizarin-yellow G ($0.003-0.0005N-OH'$) and phenolphthalein ($0.0008-0.0001N-OH'$). Thymol-blue agrees with these ($0.0007-0.0001N-OH'$), though the colour changes are not so striking; *o*-cresolphthalein also gives the same results as phenolphthalein if the correct concentration of indicator is used, but phenol-red lies in a range of alkalinity so low (below $0.0001N-OH'$) as to be rarely suitable in soap solutions. The special technique employed to minimise or eliminate systematic error is to match the colour given by indicators in standard Sørensen and Palitzsch buffers, glycine-sodium hydroxide and borax-boric acid, at 20° with the same colour given by the indicator in solutions of pure sodium hydroxide at 20° and at 90° , and to use the hydrogen electrode in the dilute solutions of sodium hydroxide to correct

* (*Added to proof.*) Compare McCrumb and Kenny on the shortcomings of the available indicators for alkaline solutions (*J. Ind. Eng. Chem.*, analytical edition, 1929, **1**, 44).

for any effect of the indicators upon the hydroxyl-ion concentration. Thus colours given in the soap solutions at 20° and at 90° could be matched against these buffers at 20°, whilst the colours are directly interpreted in terms of true alkalinity at the temperature of the soap. Results obtained by this method agree with the best established results of the previous methods in the few cases where such comparison is possible.

Previous methods have given somewhat distorted results for soap solutions stronger than $N/10$ or $N/5$. In the *E.M.F.* method, the neglected diffusion potential, difficult to evaluate precisely, must render the apparent hydroxyl-ion concentration too great. On the other hand, it was shown by blank experiments that the catalytic method gave low results for concentrated soaps because of sorption of reacting substance by the soap. The truth lies between these two values, and the results with indicators fall in the expected place. This is seen from Table I, which gives the results for the two soaps for which data by these three methods are available.

TABLE I.

Concentration (N_w) * of hydroxyl ion in soap solutions at 90° as given by indicators (1), *E.M.F.* (2), and catalysis (3).

Sodium palmitate.					
Conc. of soap.	0.042 N_w .	0.5 N_w .	0.8 N_w .		
OH' by (1)	0.0008	0.0010	—		
OH' by (2)	0.0010	0.0019	0.0022		
OH' by (3)	0.0009	0.0002	0.0002		
Potassium palmitate.					
Conc. of soap.	0.019 N_w .	0.042 N_w .	0.1 N_w .	0.3 N_w .	0.85 N_w .
OH' by (1)	0.0010	0.0014	0.0016	0.0015	—
OH' by (2)	0.0011	0.0010	0.00125	0.0019	0.0015
OH' by (3)	0.0008	0.0009	0.0009	0.0006	0.0001

* A curiously arbitrary choice is inherent to the use of either the catalytic or the indicator method. This arises from the fact that concentrated soap solutions are so very much bulkier than the water they contain. For example, at 90° a 1.0 N_w -solution of sodium palmitate contains only 1000 g. of water in 1328.0 c.c. of soap solution. When now, solutions of sodium hydroxide are found which exhibit the same rate of catalysis or the same colour of indicator as a given soap solution, does this mean that the amount of hydroxyl ions in the hydroxide is that which is producing the same effect in the same amount of water in the soap solution (N_w of OH') or in the same total volume of soap solution (N_r of OH')? In this paper it is called N_w . The difference is 32.8%, but this is proportional to the concentration and becomes inappreciable in dilute solution.

The hydrolysis alkalinity in the tables is reckoned on the total concentration of soap according to the formula :

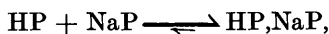
$$\% \text{ Hydrolysis} = (N_w \text{ of OH}' \times 100) / (\text{Total } N_w \text{ of soap})$$

where N_w means equivalents per kg. of water.

Discussion.

The key to the understanding of the hydrolysis of soap solutions is the appreciation of the two factors: (a) that it is a property of the simple fatty ions, and (b) that it is due to the acid soap resulting from hydrolysis. Even the higher fatty acids are not particularly weak, and if it were not for the complexity and frequent insolubility of the acid soaps they would not be appreciably more alkaline than solutions of sodium acetate, which is hydrolysed only to the extent of 0.008% in 0.1*N*-solution at 25°.

The equation of hydrolysis, *viz.*, $P' + H_2O \rightleftharpoons HP + OH'$, refers directly only to the simple fatty ions; P represents a fatty radical such as palmitate, and HP the simple molecules of undissociated fatty acid. The concentrations of HP and of OH' would be equal (and, like those in sodium acetate solution, almost negligibly small) were it not for the almost complete withdrawal from solution of the primary product of hydrolysis, the simple molecules of HP, through formation of acid soap. This shifts the equilibrium as given above to the right, with formation of a far higher concentration of hydroxyl ions:



or, in some cases, $HP + 2NaP \rightleftharpoons HP,2NaP.$

The acid soap, HP,NaP, is formed so completely that there is only the merest trace of free fatty acid left as such. This is conclusively shown by experiments on the equilibria in the presence of a second solvent such as benzene, toluene, or xylene. The low concentration of the fatty acid in the non-aqueous layer, even when the aqueous layer still contains more fatty equivalents of radical than of sodium, is thermodynamically conclusive proof that the aqueous layer is likewise unsaturated with free fatty acid. Thus the aqueous layer of any pure or commercial soap, whether containing excess, or even large deficiency, of sodium, never contains sufficient free fatty acid to saturate the water, in spite of the low solubility of these higher fatty acids. The concentration of hydroxyl ion is of the order $N/1000$, and that of free fatty acid $10^{-8}N$, whereas $10^{-5}N$ would be required for saturation. It is necessary to state these findings precisely, because they refute the opinions even now universally expressed in the literature, where it is taken for granted that free fatty acid occurs in soap solutions as free emulsified liquid or suspended solid. The experimental evidence is summarised in the communications of McBain, Laing, and Taylor (J., 1922, 121, 621), McBain and Buckingham (*loc. cit.*), and McBain and Eaton (J., 1928, 2166; see also, McBain and Stewart, J., 1927, 1392).

The acid soaps are usually insoluble, but when sufficiently soluble they are colloidal electrolytes.

To sum up, the substance that hydrolyses is P', the simple fatty ion; the hydrolysis is also conditioned by the locking up of the free fatty acid in the form of acid soap.

In sufficiently dilute solution (*e.g.*, less than $N/20$ at 90°), all soaps are simple crystalloidal salts like sodium acetate. Hence the degree of hydrolysis depends simply on the molecular weight; the higher the soap in the homologous series the greater the hydrolysis. Furthermore, potassium and sodium soaps are nearly identical. This is shown in Table II where also it is seen that in accordance with the greater solubility of the oleates as compared with stearates, the oleates are distinctly less hydrolysed. The oleates (C_{18}^- , unsaturated) are very similar to palmitates (C_{16} , saturated); this is true for the sodium soaps in dilute solution up to $0.02N$, and for the potassium soaps right up to $0.4N$.

TABLE II.

Concentration of hydroxyl ion (N of OH') and hydrolysis (%) in 0.01N_w-soap solutions at 90°.

	Potassium soap.		Sodium soap.	
Laurate, C_{12}	0.00029N-OH'	2.9%	0.00025N-OH'	2.5%
Myristate, C_{14}	0.00033	3.3	0.00045	4.5
Palmitate, C_{16}	0.00074	7.4	0.00075	7.5
Oleate, C_{18}^-	0.00081	8.1	0.00086	8.6
Stearate, C_{18}	0.0015	15.0	0.0013	13.0
Behenate, C_{22}	—	—	0.0029	29.0

In concentrated solutions the simple fatty ions P' are largely replaced by ionic micelles (P'_n) and hence there is less hydrolysis. Thus here it is the highest soaps that are least hydrolysed, and the hydrolysis is less than in dilute solution, not merely relatively, but absolutely. In other words, the hydroxyl-ion concentration increases as soap is gradually added to pure water, passes through a flat maximum and decreases again. The fact that in concentrated solution the highest soaps are less hydrolysed than the laurate (C_{12}) is shown in Table III.

TABLE III.

Concentration of hydroxyl ion (N of OH') and hydrolysis (%) in 0.5N_w-soap solutions at 90°.

	Potassium soap.		Sodium soap.	
Laurate, C_{12}	0.0034N-OH'	0.68%	0.0030N-OH'	0.6%
Myristate, C_{14}	0.00123 *	0.31	0.00092 *	0.23
Palmitate, C_{16}	0.0012	0.24	0.0010	0.2
Oleate, C_{18}^-	0.0012 *	0.3	—	—
Stearate, C_{18}	0.0012 *	0.3	0.0010	0.2

* 0.4N_w-Soap.

The laurates (C_{12}) are crystalloidal up to much greater concentrations than the higher soaps, and hence not only develop a much higher hydroxyl-ion concentration but also do not reach a maximum value for the concentration of hydroxyl ions until in such concentrated soap solution as $0.8N_w$. In contrast with this, the more colloidal palmitates (C_{16}) and oleates (C_{18} , unsaturated) attain maximum alkalinity between 0.07 and $0.2N_w$. Sodium stearate (C_{18}) reaches its maximum alkalinity at $0.05N_w$, whilst that of potassium stearate or sodium behenate (C_{22}) is practically constant from 0.02 to $0.2N_w$. At room temperature, where the laurates are far more colloidal, they attain their maximum alkalinity at $0.2N_w$ of soap; but the oleates have reached it at $0.05N_w$. The soaps of the higher, saturated, fatty acids are all too sparingly soluble to be investigated at 20° .

The change over from the increase of hydrolysis shown in Table II to the decrease shown in Table III is illustrated by the data for $N/10$ soaps at 90° (Table IV), where six out of the ten soaps are equally hydrolysed. In the more concentrated solutions the potassium soaps are very slightly more hydrolysed than the sodium soaps.

TABLE IV.

Concentration of hydroxyl ion (N of OH') and hydrolysis (%) in $0.1N_w$ -soap solutions at 90° .

	Potassium soap.		Sodium soap.	
Laurate, C_{12}	0.00174N-OH'	1.74%	0.0015N-OH'	1.5%
Myristate, C_{14}	0.00123	1.23	0.00123	1.23
Palmitate, C_{16}	0.00172	1.72	0.0018	1.8
Oleate, C_{18}	0.00168	1.68	0.00094	0.94
Stearate, C_{18}	0.00172	1.72	0.0011	1.1

Table V shows how small is the absolute concentration of hydroxyl ions in extremely dilute solution, but how high a percentage hydrolysis this represents. Dilute solutions of a soap such as potassium laurate at room temperature are full of bulky crystalline sediment (acid soap), whereas a concentrated solution of the same soap at the same temperature is as clear as water even in the ultramicroscope.

TABLE V.

Concentration of hydroxyl ion (N of OH') and hydrolysis (%) in extremely dilute soap solutions ($0.0005N_w$) at 90° .

Na palmitate, C_{16}	0.00012—0.00007N-OH'	24—14%
Na oleate, C_{18}	0.00011	22
K palmitate, C_{16}	0.00013	26
K oleate, C_{18}	0.00011	22
K stearate, C_{18}	0.00038	76

The effect of temperature is slight in very dilute solution, although more pronounced in concentrated solution, but always in such a direction that hydrolysis is diminished on cooling provided that the soap stays in solution. Soap solutions from which soap has separated out on cooling (curded) are always distinctly more alkaline than the same system wholly in solution at, say, 90°. This accords with the observations of McBain and Martin (*loc. cit.*) with the hydrogen electrode; probably it is due to sorption of acid soap on the extensive surface of the freshly formed curd fibres. Equilibria are not attained here until after long periods. After 3 months, however, the alkalinity appears to be much the same as in the original solution at 90°.

Previous studies have shown that hydrolysis is not completely suppressed until excess of alkali to the extent of 3 or 4 equivalents per cent. has been added to a soap solution. Thereafter the alkalinity is just that of the added alkali. The slight amount of free alkali in a well-finished soap is of wholly negligible importance. Indeed, a small excess of alkali would, furthermore, be completely offset by the carbonic acid in ordinary tap-water. Addition of fatty acid decreases the alkalinity of a soap solution but never entirely removes it. Indicators confirm this. Owing to the insolubility of acid sodium palmitate, even at 90°, addition of palmitic acid renders a solution of sodium palmitate cloudy and heterogeneous.

EXPERIMENTAL.

The soap solutions were carefully prepared from Kahlbaum's purest fatty acid by the method of Bunbury and Martin (J., 1914, 105, 417) after the molecular weight had been determined by dissolving the acid in freshly boiled-out, neutralised alcohol containing phenolphthalein and titrating it against the solution of sodium or potassium hydroxide which was to be used in making the soap.* It was arranged that in this titration the solution at the end-point contained 60—80% of alcohol. *N*/5- and *N*/10-Solutions were prepared and were diluted with freshly boiled-out conductivity water. The sodium hydroxide was carefully made, as described in previous communications, from drippings from metallic sodium free from carbon dioxide. Stopped Jena-glass vessels were employed throughout. Solutions were prepared immediately before use by dilution of the drippings with freshly boiled-out conductivity water.

* This method of working must render negligible any influence of slight impurity in the fatty acid; specifically, the myristic acid was found to have slightly too high a molecular weight.

Two types of buffer mixture were used, Sørensen and Palitzsch's glycine-sodium hydroxide and borax-boric acid (Clark, "Determination of Hydrogen Ions," Wilkins and Williams, 1922). The glycine, sodium chloride, borax, and boric acid were Kahlbaum's purest. After addition of indicator, buffer solutions were kept in closed vessels; and to avoid error due to fading they were not kept more than 2, or sometimes 3, days. Tubes containing buffers with added phenolphthalein were sealed in an atmosphere of nitrogen free from carbon dioxide.

The amount of indicator added, as shown in the tables, was that required to produce maximum colour. The buffers contained 5 drops of 1% neutralised alcoholic solution of phenolphthalein in 20 c.c. of buffer solution. The colour of the solutions was matched by eye under a Sherringham Daylight Lamp in glass test-tubes of equal bore. Details of the standardisation of the colours given by buffers against known concentrations of pure alkali are recorded in previous references (McBain, Dubois, and Hay, *loc. cit.*; Clark and Laing, *loc. cit.*).

Experimental Data giving Hydrolysis Alkalinity (N_w of OH') and Hydrolysis (%).

(Throughout these tables, the concentration of soap is given in terms of weight-normal, N_w , and the column headed " N_w -NaOH" shows the normality of the sodium hydroxide solution required to give a matching colour.)

Solutions of sodium laurate.

Conc. soap.	At 90°.*			At 20°.		
	N_w -NaOH.	N_w -OH'.	%.	N_w -NaOH.	N_w -OH'.	%.
0.5	0.003†	0.003	0.6	0.0011†	0.0010	0.2
0.2	0.0022†	0.0020	1.0	0.0012†	0.0011	0.55
0.1078	0.0017†	0.0016	1.5	0.0008†	0.0007	0.65
0.1078	0.00175‡	0.0016	1.5	0.0010‡	0.0009	0.8
0.1	0.0015†	0.0014	1.4	0.0010†	0.0009	0.9
0.05	0.00099†	0.00088	1.8	0.00075†	0.00066	1.3
0.05	0.00080§	0.00073	1.5	0.0008§	0.0007	1.4
0.02	0.00048	0.00043	2.15	0.00032	0.00027	1.35
0.02	0.00054§	0.00049	2.45	0.00032§	0.00027	1.35
0.01	0.00025	0.00021	2.1	0.00021	0.00017	1.7
0.005	0.00012	0.00008	1.6	0.00010	0.00007	1.4

* The sodium laurate used for solutions at 90° contained 1.8% equivalents excess of lauric acid.

† Indicator, 9 drops of 0.04% alizarin-yellow G.

‡ ,, , 10 drops of 0.04% alizarin-yellow G.

§ ,, , 10 drops of 1% phenolphthalein.

|| ,, , 3 drops of 1% phenolphthalein.

Solutions of potassium laurate.

Conc. soap.	At 90°.			At 20°.		
	N_w -NaOH.	N_w -OH'.	%.	N_w -NaOH.	N_w -OH'.	%.
0.862	0.003†	0.003	0.35	0.0011†	0.0010	0.12
0.5	0.004†	0.004	0.80	0.0010†	0.0009	0.18
0.5	0.0028†	0.0026	0.52	0.0009†	0.0008	0.16
0.5	—	—	—	0.0008†	0.0007	0.14
0.3	0.0035†	0.0032	1.17	0.0008†	0.0007	0.23
0.2	0.0025†	0.0023	1.15	0.00107†	0.0010	0.50
0.1	0.00174†	0.0016	1.58	0.0008†	0.0009*	0.9
0.05	0.0012†	0.0011	2.2	0.0008†	0.0007	1.4
0.02	0.00036‡	0.00031	1.55	0.0003†	0.0002	1.0
0.02	—	—	—	0.0003§	0.00026	1.3
0.01	0.000285‡	0.00024	2.4	0.00023§	0.00019	1.9

Solutions of potassium laurate containing 0.07% deficiency of alkali.

0.5	0.0015†	0.0014	0.28	0.0004§	0.00036	0.07
0.4	0.00175†	0.00158	0.40	0.0004§	0.00036	0.09
0.294	0.00168†	0.00152	0.52	—	—	—
0.2	0.00168†	0.00152	0.76	—	—	—
0.1	0.0013†	0.0012	1.2	—	—	—
0.048	0.00082†	0.0007	1.5	0.00027§	0.00023	0.48
0.02	0.00023‡	0.00019	0.95	0.00022§	0.00018	0.9
0.01	0.00011‡	0.00008	0.8	0.00013§	0.00010	1.0

* Miss Laing determined the N_w -OH' as 0.0011 by hydrogen electrode.

† Indicator, alizarin-yellow G.

‡ „ „ , phenolphthalein.

§ „ „ „ , 5 drops of 1% phenolphthalein.

Solutions of sodium and potassium myristate at 90°.

Conc. soap.	Sodium myristate.			Potassium myristate.		
	N_w -NaOH.	N_w -OH'.	%.	N_w -NaOH.	N_w -OH'.	%.
0.4	0.00092*	0.00091	0.23	0.00123*	0.00111	0.28
0.2	0.00123*	0.00111	0.56	0.00123*	0.00111	0.56
0.1	0.00123*	0.00111	0.11	0.00123*	0.00111	1.1
0.05	0.00123*	0.00111	2.2	0.00092*	0.00082	1.6
0.02	0.00083†	0.00077	3.85	0.00039§	0.00035	1.75
0.0195	—	—	—	0.00037§	0.00033	1.7
0.015	—	—	—	0.00035§	0.00031	2.1
0.01	0.00048†	0.00043	4.3	0.00033§	0.00029	2.9
0.005	—	—	—	0.00013§	0.00009	1.8
0.0001	0.00005‡	(0.00003)	(3.0)	—	—	—

* Indicator, 10 drops of 0.05% alizarin-yellow G.

† „ „ „ , 10 drops of 1% phenolphthalein.

‡ „ „ „ , phenol-red.

§ „ „ „ , phenolphthalein.

Solutions of sodium and potassium palmitate at 90°.

Conc. soap.	Sodium palmitate.			Potassium palmitate.		
	N_w -NaOH.	N_w -OH'.	%.	N_w -NaOH.	N_w -OH'.	%.
0.5	0.0010*	0.0010	0.2	0.0012*	0.0010	0.20
0.4	0.00117†	0.0011	0.28	—	—	—
0.3	—	—	—	0.00168*	0.00152	0.51
0.25	0.0020*	0.0018	0.72	—	—	—
0.1	0.0018*	0.0016	1.6	0.00172*	0.00155	1.6
0.09	0.0018*	0.0016	1.6	—	—	—
0.05	0.00092*	0.00082	1.6	0.00172*	0.00155	3.1
0.024	—	—	—	0.00126*	0.00113	4.7
0.02	0.00092*	0.00082	4.1	—	—	—
0.01033	0.00076†	0.00070	6.8	—	—	—
0.01	0.00082†	0.00076	7.6	0.00074§	0.00067	6.7
0.0098	0.00068†	0.00062	6.2	0.0008*	0.0007	7.1
0.005	0.00046†	0.00040	8.0	—	—	—
0.0048	—	—	—	0.00054*	0.00047	9.8
0.002	0.00035†	0.00031	15.5	—	—	—
0.001	0.00019†	0.000158	15.8	0.000148§	0.000144	14.1
0.001	—	—	—	0.000144	0.000108	10.8
0.0005	0.00012‡	0.00009	18.0	—	—	—
0.0005	0.00007†	(0.00004)	(8.0)	—	—	—
0.00047	—	—	—	0.00013	0.00009	19.1

* Indicator, alizarin-yellow G.

† ,, , 5 drops of 1% phenolphthalein in 20 c.c. of solution.

‡ ,, , phenol-red.

§ ,, , thymol-blue.

|| ,, , phenolphthalein.

Solutions of sodium and potassium stearate at 90°.

Conc. soap.	Sodium stearate.			Potassium stearate.		
	N_w -NaOH.	N_w -OH'.	%.	N_w -NaOH.	N_w -OH'.	%.
0.5	0.0010*	0.0010	0.2	—	—	—
0.4	—	—	—	0.0012*	0.0011	0.28
0.296	—	—	—	0.00168*	0.00152	0.51
0.2	0.0010*	0.0010	0.5	0.00168*	0.00152	0.76
0.1078	0.0017*	0.0015	1.4	—	—	—
0.1	0.0012*	0.0010	1.0	0.00172*	0.00155	1.55
0.1	0.0092*	0.00082	0.8	—	—	—
0.065	—	—	—	0.0018*	0.0016	2.5
0.05	0.0018*	0.0016	3.2	—	—	—
0.05	0.00107*	0.0010	2.0	0.0018*	0.0016	3.3
0.029	—	—	—	0.00168*	0.00152	5.2
0.02	0.0016*	0.0015	7.5	—	—	—
0.02	0.00123*	0.00111	5.6	—	—	—
0.015	—	—	—	0.00168*	0.00152	10.1
0.01	0.0014*	0.0013	13	—	—	—
0.01	0.00123*	0.00111	11.1	—	—	—
0.006	—	—	—	0.0013*	0.0012	20.0
0.005	<0.00099*	<0.0009	—	—	—	—
0.005	>0.00054†	>0.0005	—	—	—	—
0.003	—	—	—	0.0013*	0.0012	40
0.002	0.0008*	0.0007	35	—	—	—
0.0015	—	—	—	0.0011*	0.0010	66.6
0.0005	—	—	—	0.00038†	0.00034	68.0

* Indicator, alizarin-yellow G.

† ,, , phenolphthalein.

Solutions of the higher soaps at 20°.

Conc. soap.	N _w -NaOH.	N _w -OH'.	%.	Conc. soap.	N _w -NaOH.	N _w -OH'.	%.
Sodium palmitate.				Sodium stearate.			
0.005	0.00040*	0.00030	(6.0)	0.005	0.00075*	0.00066	13.2
0.002	0.0008†	0.0007	35	0.002	0.0011*	0.00100	50.0
0.001	0.00031†	0.00027	27	0.002	0.00011†	0.00008	4.0
0.0005	0.00038†	0.00034	68	0.003	0.00025†	0.00021	7.0
Potassium palmitate.				Potassium stearate.			
0.0098	0.0015*	0.0014	14.0	0.0005	0.00034†	0.00030	60.0
0.00047	0.00028†	0.00024	51.0				

* Indicator, alizarin-yellow G.

† „ „ , phenolphthalein.

Solutions of sodium oleate at 90° and 20°.

Conc. soap.	At 90°.			At 20°.		
	N _w -NaOH.	N _w -OH'.	%.	N _w -NaOH.	N _w -OH'.	%.
0.3634	0.00038‡	0.00034	0.09	—	—	—
0.2	0.00092†	0.00082	0.41	—	—	—
0.1	0.00082†	0.00072	0.72	—	—	—
0.1	0.0012†	0.0010	1.0	—	—	—
0.1*	0.00080†	0.0007	0.7	0.00028§	0.00024	0.24
0.07	0.0012†	0.0010	1.4	—	—	—
0.05	0.0012†	0.0010	2.0	0.0009†	0.0008	1.6
0.02	0.00107†	0.0010	5.0	0.00062†	0.00054	2.7
0.01	0.00082§	0.00076	7.6	0.0012†	0.0010	10.0
				0.0009†	0.0008¶	8.0
0.01	0.00092†	0.00082	8.2	0.0005§	0.00045	4.5
0.005	—	—	—	0.00039‡	0.00034	6.8
0.0049	—	—	—	0.00035‡	0.00031	6.3
0.003	0.00038‡	0.00034	11.3	0.00036‡	0.00031	10.3
0.000286	0.00035‡	0.00031	10.8	—	—	—
0.00186	—	—	—	0.000345‡	0.00030	16.1
0.001	0.00029‡	0.00024	24.0	0.00029‡	0.00024	24
0.00097	0.000265‡	0.00023	23.7	0.000265‡	0.00023	24
0.0007	0.00165‡	0.00014	20	0.00024‡	0.00020	28
0.0005	0.00011‡	0.00008	16	0.00018‡	0.00014	28
0.00044	0.00011‡	0.00008	18	0.00015‡	0.00011	25
0.0003	—	—	—	0.00010‡	0.00007	23

* Solution prepared separately.

† Indicator, 10 drops of 0.05% alizarin-yellow G.

‡ „ „ , 5 drops of 1% phenolphthalein.

§ „ „ , 10 drops of 1% phenolphthalein.

|| Before heating.

¶ After heating.

Solutions of potassium oleate at 90° and 20°.

Conc. soap.	At 90°.			At 20°.		
	N_w -NaOH.	N_w -OH'.	%.	N_w -NaOH.	N_w -OH'.	%.
0.413*	0.0012†	0.0011	0.27	0.000108†	0.000054	0.01
				0.00034†	0.00030	0.08
0.2067	0.00168†	0.000152	0.735	0.00022†	0.00017	0.08
0.1018	0.00168†	0.00152	1.49	0.0003†	0.0002	0.20
0.0517	0.00168†	0.00152	2.94	0.0008†	0.0007	1.35
0.03995	0.00154†	0.00139	3.48	0.0007†	0.0006	1.5
0.0185	0.0012†	0.0011	5.95	0.0008†	0.0007	3.8
0.0102	0.0008†	0.0007	6.86	0.0003†	0.0002	2.0
0.00976	0.00082†	0.0007	7.2	0.0003†	0.0002	2.1
0.005088	0.00054†	0.00047	9.2	0.0003†	0.0002	3.9
0.0048	0.00054†	0.00047	9.8	0.0003†	0.0002	4.2
0.0031	0.00054†	0.00047	15.2	0.00022†	0.00017	5.5
0.001	0.0024†	0.00020	20	0.000265†	0.00023	23
0.001	0.00014†	0.00010	10	—	—	—
0.0007	0.00015†	0.00011	16	0.00024†	0.00020	29
0.0005	0.00011†	0.00008	16	0.00018†	0.00014	28

* Prepared by Mr. Stewart; the other solutions were prepared by dilution from this.

† Indicator, 10 drops of 0.08% alizarin-yellow G.

‡ „ „ 5 drops of 1% phenolphthalein.

*Solutions of sodium behenate at 90° and 20°.**

Conc. soap.	State of system.	N_w -NaOH.	N_w -OH'.	%.
0.2	90°, True jelly.	0.0073	0.0068	3.4
0.1	90°, „	0.0073	0.0068	6.8
0.05	90°, Viscous liquid.	0.0073	0.0068	13.6
0.02	90°	0.007	0.0065	32.5
	20°	0.010	0.009	45
0.01	90°, Almost clear liquid.	0.0029	0.0027	27
	20°, Milky liquid.	0.0073	0.0068	68

* Indicator, alizarin-yellow G.

*Solutions of sodium palmitate with added excess of palmitic acid.**

Conc. N_a (N_w).	Conc. C_{16} (N_w).	Excess palmitate (%).	At 90°.		At 20°.	
			N_w -NaOH.	N_w -OH'.	N_w -NaOH.	N_w -OH'.
0.4001	0.4001	0.00	0.00117	0.0011	—	—
	0.4041	1.00	0.000604	0.000549	—	—
	0.4201	5.0	0.000109	0.000073	—	—
	0.4669	16.7†	(0.00003)	(0.00003)	—	—
0.005	0.005	0.0	0.000458	0.0004	—	—
	0.00525	5.0	0.000417	0.000371	—	—
	0.00584	16.7	0.000376	0.00033	—	—
	0.00667	33.3	0.0003	0.00026	0.00031	0.00026
	0.0075	50.0	0.0002	0.00016	0.00026	0.00022
	0.010	100.0	0.000109	0.000073	0.00014	0.00011
	0.0125	150.0	0.000077	0.000028	0.00059	0.00054
0.01033	0.01033	0.0	0.00076	0.00070	—	—
	0.01085	5.0	0.000458	0.000412	0.0003	0.00026
	0.01206	16.7	0.000376	0.00033	0.000198	0.000158
	0.01377	33.3	0.000376	0.00033	—	—
	0.02066	100.0	0.000144	0.000108	0.0003	0.00026

* Indicator, 5 drops of 1% phenolphthalein in 20 c.c. of solution.

† Not homogeneous.

*Solutions of potassium oleate with added excess of oleic acid.**

Conc. K (N_w).	Conc. oleate (N_w).	Excess oleate (%).	At 90°.		At 20°.	
			N_w -	N_w -	N_w -	N_w -
			NaOH.	OH'.	NaOH.	OH'.
0.04	0.04	0.0	0.00154	0.00139	0.0008	0.0007
0.0406	0.07267	78.98	0.00036	0.00031	0.0008	0.0007
0.025	0.025	0.0	0.00134	0.0012	0.00074	0.00068
0.02558	0.03887	50.00	0.00037	0.00033	0.00022	0.00018
0.0185	0.0185	0.0	0.0012	0.0011	0.0007	0.00069
0.01761†	0.02639	49.85	0.0008	0.0007	0.00035	0.00031
0.014	0.014	0.0	0.0010	0.0010	0.00045	0.00041
0.0139‡	0.0288	107.2	0.00033	0.00029	0.000115	0.00008

* Solutions prepared by Mr. Stewart. Indicators alizarin-yellow G, phenolphthalein.

† Cloudy.

‡ Very cloudy.

Summary.

1. Very few indicators are of any value for the study of the alkalinity of soap solutions, and even with them certain precautions must be observed. Determinations are recorded for solutions of pure potassium and sodium soaps at 20° and 90° over a wide range of concentration.

2. All the results harmonise with the recognition of two factors: (1) that hydrolysis is a property of the free, simple, fatty ion, not of any other ion, molecular species, or colloid; (2) that hydrolysis is chiefly due to the fatty acid formed being almost completely removed to form acid soap. Hence, all soap solutions are alkaline and none contains even the minute amount of free fatty acid required to saturate the water.

3. The results obtained support the conception that soap solutions are crystalloidal when sufficiently dilute, and colloidal in higher concentrations. For example, on the addition of soap to water the hydroxyl-ion concentration rises, passes through a flat maximum, and diminishes again as the soap solution becomes concentrated and the simple fatty ions are replaced by ionic micelles. The more colloidal the soap the sooner is the maximum hydrolysis alkalinity attained.

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