CCLXXXIV.—*Hydrolysis in Solutions of Potassium Laurate as measured by Extraction with Benzene.*

By JAMES WILLIAM MCBAIN AND MONROE EATON.

THE hydrolysis of soap solutions is a property only of the simple fatty ions, and its extent is largely due to the almost quantitative disappearance of free fatty acid to form acid soap. Thus all soap solutions are alkaline, far more so than would be expected from the dissociation constants of the fatty acids,* and concentrated soap solutions are less alkaline than dilute ones. Likewise, contrary to a still almost universal preconception, soap solutions are always unsaturated with regard to fatty acid, in spite of the low solubility of the fatty acid (McBain, Taylor, and Laing, J., 1922, **121**, 621; McBain and Buckingham, J., 1927, 2679, which see for further references).

The present communication develops the methods employed by McBain and Buckingham (*loc. cit.*) with sodium palmitate, applying them to various solutions of potassium laurate with and without other additions at 25° Reference should be made to the previous paper for a discussion of many of the points at issue and the general nature of the results previously obtained.

EXPERIMENTAL.

The work to be described consists of experiments on the composition of a wide range of solutions of potassium laurate with and without additions of alkali or lauric acid. Additional experiments are described which were designed (1) to show that complete reversible equilibrium is attained,† (2) to find the concentration of lauric acid in benzene that is in equilibrium with unaltered aqueous potassium laurate solutions, (3) to measure the solubility of the various constituents in benzene singly and together, (4) to measure the alkalinity by hydrogen electrode and by indicator, and finally (5) to study the effect of potassium chloride and of carbon dioxide upon the alkalinity and extractability of the aqueous potassium laurate. A few results with aqueous sodium laurate are given for comparison, and some experiments have been carried out with acid

---

* The dissociation constants are known for the saturated fatty acids up to decoic acid, and hence for the next member with an even number of carbon atoms, lauric acid, the dissociation constant must be 1×10^{-5}, which is not so very weak (S. Smiles and P. O. Herzog, "Chemische Konstitution und Physikalische Eigenschafte," p. 526; E. Franke, *Z. physikal. Chem.*, 1895, **16**, 477).

† This was demonstrated for the first time in the experiments of McBain and Buckingham (*loc. cit.*).

potassium laurate, and also with carbon tetrachloride instead of benzene as extracting solvent.

The chief experiments are the determinations of the compositions of aqueous and benzene layers in equilibrium with each other. For the complete interpretation of the data several subsidiary items of information are required. For example, it is found that the approximate solubility of potassium laurate at 25° is 70 g. per 100 g. of water and 0·005 g. per 100 g. of benzene, showing that for the purposes of most of the experiments the soap itself is insoluble in benzene. However, in the section dealing with acid soap it will be shown that when the benzene contains a large proportion of lauric acid the soap is highly soluble in it, forming acid soap. The potassium laurate used was specially made by Kahlbaum but contained 0·5 equiv. % excess of alkali, whereas the sodium laurate contained 1·8 equiv. % excess of lauric acid. They were dried to constant weight at 110°. Kahlbaum's lauric acid was used, and its solubility in 100 g. of benzene at 25° was 186 g.; at 40° there is miscibility in all proportions. The solubility in water at 25° is 0·00017 g. of undissociated lauric acid per 100 g. of water, as determined by conductivity (see p. 2173).

Since the method of analysis of the non-aqueous layer was to evaporate the solution to dryness and weigh the residue of lauric acid, blank experiments were necessary to show that there was no appreciable loss. It was found that when 10 c.c. of a 1·5% benzene solution of lauric acid were evaporated nearly to dryness during ¾ hour and the heating was continued for 4 hours at 80°, the maximum loss by volatilisation was 2% of the total lauric acid originally in the benzene. In the extraction experiments, evaporation was carried only to dryness and the temperature was never allowed to rise above 75°, and in most cases the solutions were far more dilute. Hence the error must have been inappreciable.

The benzene used was dried over calcium chloride or potassium hydroxide and twice distilled. It boiled at 79·5—80·5° and left no residue on evaporation. Boiled-out conductivity water ($\kappa = 2 \times 10^{-6}$ mho) was used throughout. Concentrations are all expressed in weight normality (N_w), *i.e.*, as mols. of solute per 1000 g. of solvent. Kahlbaum's purest potassium chloride was dried at 125° for a day; it was insoluble in benzene.

The soap solutions were brought into equilibrium with the benzene layer in horizontal glass tubes about 3 cm. wide and 20 cm. long, which were rotated on their axis at a speed of 11 revs./min. for 48 hours. Even this very gentle stirring tends to emulsify the layers. Hence the tubes were allowed to stand in a vertical position until at least half the benzene layer had cleared. As much as possible of the clear layer was then pipetted out, weighed, and evaporated to dryness at 70°. From this and a knowledge of the original composition of the system it was then possible to calculate the concentrations and the amounts of lauric acid which had passed out of or into the aqueous layer. The original system was always made up by weighing the constituents into a tube which was immediately sealed to minimise evaporation of the benzene.

Extraction of Lauric Acid from Aqueous Potassium Laurate by Benzene.

The three-component systems here described consist of three phases, the aqueous phase, the benzene solution of extracted lauric acid, and the sediment of the acid soap in the aqueous layer. However, it is much more interesting to add lauric acid as a fourth component with a view to find the concentration of lauric acid in benzene which is just in equilibrium with unaltered soap solution, a higher concentration giving up lauric acid to the soap solution and a lower concentration partly extracting it. The extractability was shown to be the same after one month as after a few days.

Table I gives the results of the equilibrium experiments with potassium laurate with and without added excess of lauric acid. Table II records for comparison a few experiments on sodium laurate. It is seen that sodium laurate is distinctly more extractable than potassium laurate even when the fact is taken into account that the specimen used contained excess of lauric acid (see p. 2167).

The very definite result from these two tables is that the benzene layer is unsaturated with respect to fatty acid. Since the benzene layer is in true reversible equilibrium with the soap layer, the latter must be equally unsaturated. Even when a very appreciable excess of fatty acid is added to the system so that the aqueous layer contains more equivalents of fatty radical than of potassium or sodium, the benzene layer is still very far from being saturated with respect to fatty acid.

Almost every writer has assumed that there is excess of fatty acid, free in liquid or emulsified form, in ordinary soap solutions. This belief is definitely shown to be false by the results of these quantitative experiments and those of McBain and Buckingham (*loc. cit.*). All the soap solutions are alkaline and unsaturated with regard to free fatty acid. Hence when excess of free fatty acid is added to the soap solution it disappears through combination with the soap to form acid soap. An aqueous solution even of acid soap containing twice as much fatty radical as of sodium or potassium is still appreciably alkaline. Experiments described later show that when the non-aqueous layer is made nearly saturated with fatty acid, practically all the soap disappears from the aqueous soap solution.

TABLE I.*

Equilibrium experiments in which aqueous solutions of potassium laurate were shaken at 25° with benzene, to which in some cases lauric acid had been added in advance.

		HL in benzene.			
Soap soln. (g.).	Benzene (g.).	Before (g.).	After (g.).	After † (N_w).	N_w of OH′ (aqueous, after).
		0·493N_w-Potassium laurate.			
15·08	10·31	0	0·00122	0·00059	0·005
15·96	10·30	0	0·00152	0·00073	0·004
		0·25N_w-Potassium laurate.			
36·81	10·83	0	0·00185	0·00085	0·005
35·42	10·83	0	0·00161	0·00074	0·006
59·61	18·20	0	0·00327	0·00090	0·005
29·33	11·90	0	0·00224	0·00090	0·005
27·38	8·16	0	0·00192	0·00085	0·005
45·02	12·11	0·0031	0·00322	0·00132	0·003
55·46	11·92	0·0076	0·00302	0·00127	0·003
49·37	16·08	0·0242	0·00614	0·00189	0·002
58·30	17·91	0·0406	0·01438	0·00400	0·001
72·00	15·67	0·0753	0·01444	0·00460	0·0009
54·67	17·82	0·1569	0·02884	0·0081	0·0005
		0·1N_w-Potassium laurate.			
39·78	17·01	0	0·01202	0·0035	0·001
19·27	9·13	0	0·00486	0·0027	0·002
24·64	10·31	0	0·00553	0·0027	0·002
24·75	10·23	0	0·00514	0·0025	0·002
24·69	10·35	0	0·00361	0·0017	0·003
24·66	10·35	0	0·00322	0·0016	0·003
24·73	10·36	0	0·00320	0·0016	0·003
40·02	11·03	0	0·00504	0·0023	0·002
36·87	10·21	0	0·00546	0·0027	0·002
43·02	18·30	0·0031	0·0175	0·0039	0·001
48·23	18·37	0·0110	0·0175	0·0048	0·001
41·01	14·78	0·0057	0·0077	0·0025	0·002
51·43	10·08	0·0066	0·0064	0·0032	0·002
43·83	12·39	0·0186	0·0119	0·0048	0·001
43·90	12·86	0·0230	0·0156	0·0061	0·0009
44·70	12·30	0·0273	0·0210	0·0085	0·0006
43·04	16·96	0·0571	0·0419	0·0123	0·0004
37·63	13·81	0·0782	0·0471	0·0172	0·0003
37·30	13·54	0·1019	0·0646	0·0239	0·0002
40·74	13·58	0·2234	0·1466	0·0545	0·0001
44·00	16·97	0·3424	0·2245	0·0654	0·0001

* In experiments with 1·0N_w-potassium laurate, emulsification was so great that it was only after 2 months' standing that about one-tenth of the benzene layer could be withdrawn for analysis, and the lauric acid in two such samples was too small to be weighable. This is probably due to (*a*) the small concentration of hydrolysable simple laurate ion, and (*b*) the completeness with which any fatty acid formed is combined in this high concentration of soap.

† A saturated solution of lauric acid would have been 9·3N_w.

TABLE I (*continued*).

		HL in benzene.			
Soap soln. (g.).	Benzene (g.).	Before (g.).	After (g.).	After * (N_w).	N_w of OH′ (aqueous, after).
		0·05N_w-Potassium laurate.			
26·00	10·31	0	0·00620	0·00299	0·002
26·59	10·33	0	0·00548	0·00250	0·002
26·17	10·33	0	0·00708	0·00341	0·002
34·21	8·079	0	0·00576	0·00356	0·0015
30·86	8·64	0	0·00508	0·00294	0·001
30·29	7·08	0	0·00455	0·00320	0·001
33·99	9·95	0·0039	0·00723	0·00362	0·001
35·87	8·28	0·0082	0·00855	0·00515	0·001
31·02	6·95	0·0173	0·0148	0·01308	0·0004
30·64	7·26	0·03336	0·02526	0·01737	0·0003
31·10	14·37	0·04703	0·03152	0·01094	0·0005
29·55	8·16	0·06952	0·05672	0·03462	0·00015
30·25	5·97	0·05097	0·03115	0·02595	0·0002
30·47	8·17	0·0997	0·08580	0·0524	0·0001
27·74	9·67	0·1228	0·1077	0·0556	0·0001
32·10	9·39	0·3884	0·3446	0·1832	0·00003
		0·01N_w-Potassium laurate.			
24·68	4·37	0	0·00331	0·00373	0·0003
24·42	12·34	0	0·00456	0·00184	0·0005
24·67	10·32	0	0·00442	0·00214	0·0005
47·92	10·45	0	0·00418	0·00198	0·0006
33·71	12·60	0·0024	0·00819	0·00324	0·0003
48·34	9·55	0·0046	0·01275	0·00667	0·0001
41·32	10·43	0·0094	0·01241	0·00595	0·0002
46·68	15·68	0·0157	0·0174	0·00555	0·0002
57·80	10·56	0·0251	0·0256	0·0121	0·0001
49·90	13·37	0·1156	0·1156	0·0431	0·00003
48·07	12·22	0·2111	0·2036	0·0829	0·00001
		0·005N_w-Potassium laurate.			
24·70	4·29	0	0·00297	0·00346	0·0001
25·13	10·33	0	0·00349	0·00168	0·0003
25·32	10·35	0	0·00356	0·00172	0·0003
25·26	10·35	0	0·00418	0·00202	0·0002
		0·001N_w-Potassium laurate.			
62·30	12·88	0	0·00224	0·00085	0·0002
60·70	12·89	0	0·00311	0·00120	0·0001
71·09	11·72	0	0·00643	0·0027	0·00004
83·49	14·06	0·0123	0·0228	—	—
103·74	21·43	0·0223	0·0279	0·0063	0·00002
60·28	13·34	0·1895	0·1899	0·0710	0·000002
117·47	27·35	0·5388	0·5345	0·0968	0·000001
68·75	13·08	0·3085	0·3043	0·1163	0·000001

* A saturated solution of lauric acid would have been 9·3N_w.

Referring to the data of Tables I and II, it is evident that the amount of fatty acid extracted from an aqueous soap solution increases with the various factors as expected; *i.e.*, the extractability increases with increasing proportion of extracting solvent, with decreasing alkalinity of the soap, with increasing amounts of fatty acid added to the soap solution, or with increasing dilution of the soap, and hence increased proportion of hydrolysable simple fatty ion.

TABLE II.

Equilibrium experiments in which aqueous solutions of sodium laurate were shaken at 25° with benzene.

Soap soln. (g.).	Benzene (g.).	HL in benzene, (g.).	HL in benzene, (N_w).	N_w of OH′ (aqueous after).*
		0·10N_w-Sodium laurate.		
45·91	15·46	0·02141	0·00692	0·0008
51·06	21·07	0·02662	0·00617	0·0008
		0·05N_w-Sodium laurate.		
45·71	13·39	0·01851	0·00691	0·0008
48·07	21·63	0·02185	0·00503	0·0011
29·52	12·08	0·01380	0·00571	0·0009

* Concentration of L′ has not been measured in solutions of NaL at 25°; it is therefore assumed to be the same as that in a KL solution of the same concentration.

With very dilute soap solutions, the effect of carbon dioxide becomes a serious source of error. Although carbon dioxide is a much weaker acid than any of the fatty acids, we find that if it is passed through an $N/100$-soap solution in the process of extraction, the whole of the fatty acid passes into the benzene layer owing to complete neutralisation of the hydroxyl ion in the aqueous layer by the carbonic acid. The results with solutions below 0·01N_w are increasingly influenced by ingress of carbon dioxide, in spite of precautions taken. In four out of six experiments with 0·0005N_w-potassium laurate, practically all the lauric acid was removed by the benzene. This is to be expected in a solution sufficiently dilute, although a minute trace of free lauric acid must always remain dissolved in the aqueous phase.

In order to evaluate the concentrations of the various constituents in a soap solution in equilibrium with a benzene solution of fatty acid, it is necessary to know the distribution ratio for lauric acid, the dissociation constant of water (K_w), and the dissociation constant of the lauric acid ($K_a = 1 \times 10^{-5}$). The concentration of simple laurate ion in aqueous soap solution is known from previous studies of freezing point and conductivity (McBain and Jenkins, J., 1922, **121**, 2325). Since the concentration of undissociated lauric acid in the aqueous layer is proportional to that in the benzene layer multiplied by the distribution ratio, the equation for hydrolytic equilibrium is :

$$\frac{[\text{L}']}{[\text{OH}'] \times N_w \text{ of lauric acid in } C_6H_6} = K = \frac{K_a}{K_w} \times \text{distribution ratio.}$$

The distribution ratio may be estimated from the results for 0·1N_w-potassium laurate, since this solution was most carefully studied, and, when neutral (that is, having potassium and laurate stoicheiometrically equivalent to each other), was found to be in equilibrium with the benzene layer, which was $0{\cdot}0055N_w$ with respect to lauric acid. If the hydrolysis alkalinity be taken as $0{\cdot}0009N_w$-OH′, and the concentration of simple laurate ion as $0{\cdot}026N_w$, the distribution ratio would be

$$\frac{0{\cdot}026 \times 10^{-14}}{0{\cdot}0009 \times 0{\cdot}0055 \times 10^{-5}} = 0{\cdot}5 \times 10^{-5},$$

whence the hydrolytic constant $K = 5000$.

This distribution ratio ($0{\cdot}5 \times 10^{-5}$) is that employed in the calculation of the results in Table III, although it is four times larger than the ratio of the solubilities of lauric acid in water and benzene. The discrepancy is not surprising in view of the fact that a saturated solution of lauric acid in benzene is $9{\cdot}3N_w$ and contains almost twice as much lauric acid as benzene. There is a closely similar discrepancy in the distribution ratio of palmitic acid between water and xylene at 90° when saturated solutions are compared with ordinary dilutions.

This approximate distribution ratio enables us to indicate the approximate concentration of free fatty acid in all the soap solutions studied. The most interesting solutions are those whose composition has not been altered, owing to the exactly requisite quantity of lauric acid having previously been added to the benzene layer, so that the two phases are already in equilibrium when first brought together. The results for the series of concentrations of aqueous solutions of potassium laurate containing equivalent quantities of potassium and total fatty radical are contained in Table III.* The concentration of acid soap (N_w) referred to the water, although part of the acid soap is a sediment, is given in the last column of Table III. It is merely the difference in the normality of the OH′ and of the free fatty acid, since if no fatty acid had disappeared to form acid soap, the concentrations of free fatty acid and OH′ must have been identical.

The most striking feature of Table III is that in all pure soap solutions the concentration of free fatty acid is wholly negligible in comparison with the hydrolysis alkalinity. In other words, as

---

* In calculating the values for N_w of OH′ in Tables I and II, the values for the concentration of laurate ion, L′, as given for unaltered soap solution in Table III are reduced if either lauric acid is extracted from the soap solution by the benzene layer or conversely, forming acid soap. This is allowed for in Tables I and II by multiplying the values for L′ in Table III by the ratio (total laurate radical)/(total potassium), in the aqueous layer, or (total potassium)/(total laurate radical) in the aqueous layer, whichever ratio is less than unity.

TABLE III.

The concentrations of some of the constituents of aqueous potassium laurate solutions at 25°, there being equal equivalents of potassium and laurate radicals in the water, as deduced from the concentration of lauric acid in the benzene layer in equilibrium with the aqueous layer.

Total soap, N_w.	Lauric acid in benzene, N_w.	Laurate ion, N_w.	Lauric acid, $N_w \times 10^{-8}$.	OH′, N_w.	Acid* soap, N_w.
1·0	0·000	0·012	0	—	—
0·25	0·0017	0·021	1	0·002	0·002
0·1	0·0055	0·026	3	0·0009	0·0009
0·05	0·007	0·027	4	0·0008	0·0008
0·01	0·018	0·006	9	0·00007	0·00007
0·001	0·075	0·0009	38	0·0000024	0·000002

* N_w of lauric acid (HL) combined with soap (KL) to form such acid soap as HL,KL.

seen from the practical identity of the last two columns of Table III, the fatty acid set free by hydrolysis goes almost quantitatively to form acid soap.

The solubility of lauric acid in water was determined by conductivity and the mode of calculation used by McBain and Taylor (*Z. physikal. Chem.*, 1911, **76**, 179); the specific conductivity of the saturated solution was $4·54 \times 10^{-6}$, whence the normality of the undissociated lauric acid in saturated solution in water at 25° is $8·8 \times 10^{-6} N_w$.† In pure water, the laurate ion would provide an additional $1 \times 10^{-5} N_w$. This is 300 times greater than the actual concentration of free lauric acid found in a $0·1 N_w$-solution of potassium laurate, illustrating the utter impossibility of fatty acid in the free liquid or solid state existing in a soap solution. As a check upon the possibility that the solubility of fatty acid in water might be enhanced by such solvents as benzene, the solubility of the lauric acid was similarly determined with water saturated in one case with benzene and in the other with carbon tetrachloride. The specific conductivities were $5·23 \times 10^{-6}$ and $4·61 \times 10^{-6}$, respectively, whence it is evident that the solubility is not appreciably enhanced. Hence the distribution ratio of lauric acid must be fairly constant for the more dilute soap solutions studied, especially in comparison with the very large changes in the concentration of the benzene layer.

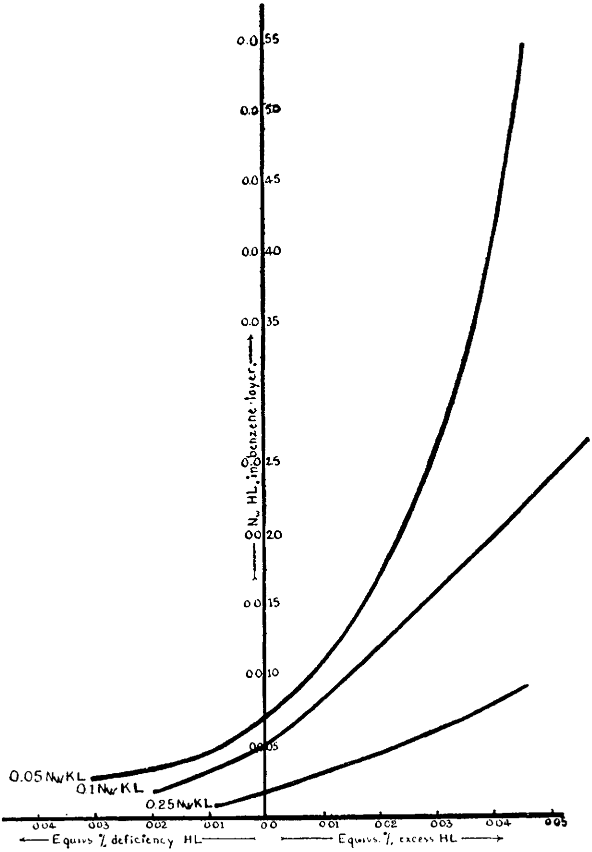
In dilute soap solutions, the percentage of hydrolysis is at a maximum (*e.g.*, it is 9% in $0·001 N_w$-soap) though the absolute concentration of all constituents is least. In very concentrated

---

† Lauric acid is therefore much less soluble than silver laurate, although a saturated aqueous solution of lauric acid gives a just noticeable turbidity on addition of excess of silver nitrate.

solution, on the other hand, the crystalloidal constituents including the laurate ion are practically all replaced by colloid except for the sodium or potassium ions also present. The hydrolysis alkalinity therefore passes through a maximum because the colloid serves merely as a reserve from which hydrolysable laurate ion can be formed. However, even the colloidal undissociated soap may play a rôle in the formation of the acid soap. Acid soap itself is a colloidal electrolyte though often of low solubility, hence the extent of its formation does not closely follow the law of mass action. For example, taking a series of benzene solutions of lauric acid sufficiently concentrated for lauric acid to pass from the benzene into the soap

FIG. 1.



The concentration of lauric acid in the benzene layer in equilibrium with solutions of potassium laurate containing deficiency or excess of lauric acid.

layer, the formation of acid soap does not increase as rapidly as the concentration of the benzene layer.

Fig. 1 of the paper of McBain and Buckingham (*loc. cit.*), which referred to 0·1N_w-sodium palmitate at 90°, shows that fatty acid may be extracted from any soap solution even in the presence of excess of alkali; and likewise that any soap solution is alkaline even when excess of fatty acid has been added. Fig. 1 of the present paper, taken from the results in Table I, shows the similar relations with potassium laurate when excess of alkali or acid is present; it gives the concentration of lauric acid in the benzene layer in equilibrium with aqueous soap layer of the composition indicated. The soap solutions on the alkaline side are those from which some of the laurate radical has been extracted by the benzene layer in the form of lauric acid. The designations of the three curves refer to the total concentration of potassium throughout.

Finally, a few experiments may be noted in which it appears that the relative extracting power of benzene and carbon tetrachloride goes parallel with the solubility of lauric acid therein, as expected (Table IV).

TABLE IV.

Solutions of 0·05N_w-potassium laurate.

Soap soln. (g.).	Solvent (g.).	Lauric acid in solvent.		
		Before (g.).	After (g.).	After (N_w).*
		Benzene.		
30·86	8·64	0·0	0·00508	0·00294
34·21	8·079	0·0	0·00576	0·00356
		Carbon tetrachloride.		
56·05	24·61	0·0	0·00624	0·00127
32·60	18·73	0·0	0·00389	0·00104

* A saturated solution of lauric acid in benzene would be 9·3N_w, and in carbon tetrachloride 5·1N_w.

Acid Soaps.

As we have seen, pure benzene scarcely dissolves potassium laurate, but it is far otherwise when a large amount of lauric acid is simultaneously present in the benzene. When mixtures of benzene, lauric acid, and potassium laurate are heated together, the whole system becomes homogeneous, and on cooling, crystallisation occurs. In four such experiments the single liquid layer was removed for analysis at 25°, with the following results, potassium laurate being determined as carbonate after ignition :

HL in benzene, N_w	0·042	0·451	3·56	9·28
KL in benzene, N_w	0·0002	0·020	0·065	0·192

The crystals deposited from the above solutions were found by analysis to have the exact composition KL,HL, thus again showing that the solubility of potassium laurate in benzene containing lauric acid is attributable to the formation of acid soap. A crystalline acid soap of this composition was described by Oudemann (*Jahresber.*, 1863, 331) as resulting from warming the potassium laurate and lauric acid in this proportion with aqueous alcohol, but subsequent writers have been unanimous in assuming that acid soap of a definite composition did not occur (see, however, McBain and Stewart's recent description of the definite crystalline acid oleate, KOl,HOl; J., 1927, 1392).

The results given in Table I are not affected by the information just tabulated, since the concentration of lauric acid in the benzene layer was usually well below $0{\cdot}1N_w$. McBain and Buckingham refrained from employing solutions of palmitic acid in xylene exceeding $0{\cdot}25N_w$ in equilibrium experiments with sodium palmitate, because they had observed that with very high concentrations of palmitic acid in xylene the residue on evaporation was greater than the original palmitic acid, and this is now seen to be due to sodium palmitate having entered the xylene layer. They stated that the formation of acid soap was indicated by the soap layer becoming absolutely opaque.

A series of experiments shown in Table V was carried out using a saturated solution of lauric acid in benzene, and the aqueous phase was taken for analysis after filtering off any sediment of acid soap. There was very little emulsification, and most of the acid soap dissolved in the non-aqueous layer. With $0{\cdot}1N_w$-aqueous potassium laurate, both layers were finally almost as clear as water. This is in marked contrast to the experiments reported in Table I, where the aqueous layer became clouded with acid soap when the concentration of lauric acid in the benzene exceeded $0{\cdot}01N_w$.

TABLE V.

Effect of saturated solution of lauric acid in benzene ($9{\cdot}3\mathrm{N}_w$) *upon aqueous solutions of potassium laurate at* 25°.

Benzene soln. (g.).	Aqueous soln. (g.).	Aqueous soln. before (N_w).	N_w of total laurate radical left in aqueous layer.
3·701	4·956	0·100	0·0026
4·352	9·444	0·100	0·0051
4·873	6·095	0·250	0·0086
3·591	5·487	0·250	0·0111
8·947	6·442	0·493	0·0039

It is seen from Table V that the soap is almost quantitatively removed from the aqueous solution by contact with a saturated solution of lauric acid in benzene. The aqueous solution must at last be on the acid side because the lauric acid in the benzene so greatly exceeds the amount of soap in the system. In other words, an aqueous soap solution whose p_H is less than 7 can hardly be prepared. The slight residue of laurate radical in the aqueous layer is probably colloidal acid soap not removed by filtration but materially decreased by increasing the proportion of the benzene layer.

Solid potassium laurate is also capable of largely removing lauric acid from benzene solution, as is shown by the following tabulation of two experiments at 25° in which benzene solutions of lauric acid were used which were too dilute to dissolve much acid soap.

KL, before (g.).	Benzene (g.).	Ratio, total L to total K.	HL, before (g.).	HL left in benzene (g.).	HL removed (%).
3·658	49·37	2·0	3·120	0·423	86·5
0·7336	19·52	1·5	0·3427	0·0048	98·5

Another illustration of the formation of acid soap is given by the action of carbon dioxide upon soap solutions. When a small amount of carbon dioxide is passed over the surface of a soap solution, crystals gradually appear in the upper part of the solution. These crystals are not removed from the solution by extraction with benzene, hence they are not lauric acid. They cannot be potassium laurate, since the solutions are only about 1/30 saturated and the crystals are not dissolved by shaking. We may conclude, therefore, that the first product of the action of carbon dioxide on potassium laurate solutions is acid soap. Soap solutions which have been left exposed to the air for some time show a similar behaviour.

In order to demonstrate the formation of crystalloidal acid soap in aqueous potassium laurate solutions in contact with benzene solutions of lauric acid, an experiment was performed in which the solutions were allowed to stand without shaking. A $0{\cdot}5N_w$-solution of potassium laurate was run into a tube under a saturated solution of lauric acid in benzene. The tube was then sealed and allowed to stand for 2 days. A cake of crystalline acid soap $\frac{1}{4}''$ thick was formed between the benzene and water layers. From the lower side of the cake, long needles could be seen radiating from various points into the aqueous layer. The crystals were insoluble in water and benzene.

Since potassium laurate is very soluble in water and lauric acid is very soluble in benzene, the formation of a solid solution of potassium laurate in lauric acid under the conditions observed in this experiment is more improbable than the formation of a definite chemical compound. The proof of the existence of definite crystalline acid laurates and palmitates will shortly be published.

Acid soap is a better emulsifying agent than neutral soap, as is evident from the observation made during the experiments of Table I. Miss Laing (*Proc. Roy. Soc.*, 1925, **105**, 28) found that unless the soap solution contains a small excess of alkali the material adsorbed in soap films is acid soap. It may also be mentioned that ready emulsification occurs when a potassium laurate solution, too dilute to contain colloidal soap, is mixed with benzene containing lauric acid.

Effect of Salt upon Extraction and Hydrolysis.

McBain and Buckingham (*loc. cit.*) found that the presence of various salts diminishes the extractibility of aqueous sodium palmitate, in very similar fashion. They pointed out that this was ascribable to repression of the dissociation of the soap into simple laurate ion which is the hydrolysable constituent, and they surmised that the hydrolysis alkalinity was likewise lessened, in accordance with the findings of McBain and Martin (J., 1914, **105**, 957), who used the hydrogen electrode. That a salt greatly decreases the extractability in the case of potassium laurate also is clearly shown in Table VI.

TABLE VI.

Effect of potassium chloride on extractibility of 0·1N_w*-potassium laurate by benzene at* 25°.

Soap soln. (g.).	KCl (N_w).	Benzene (g.).	HL in benzene. Before (g.).	HL in benzene. After (g.).	HL in benzene. After (N_w).
40·02	0	11·03	0	0·00504	0·00230
49·67	0·0114	10·21	0	0·00215	0·00104
52·41	0·0220	20·28	0	0·00465	0·00112
64·13	0·0499	14·52	0	0·00135	0·00064
35·47	0·2272	5·88	0	0·00079	0·00067

The hydrolysis alkalinity of the final solution in Table VI cannot be calculated, because the concentration of hydrolysable laurate ion is also being diminished. On the other hand, it is possible that formation of acid soap might be facilitated through increase in undissociated potassium laurate and through lowering of the solubility of acid soap by salt, both of which factors act in the direction of increasing the hydrolysis alkalinity. However, it seems probable that the dominant factor is repression of laurate ion with consequent lowering of hydrolysis alkalinity on addition of salt. Direct determinations of the hydrolysis alkalinity are required for a complete answer to this problem.

In Table VII a series of experiments is recorded in which the soap was maintained at $0{\cdot}1N_w$ and the potassium chloride at $0{\cdot}143N_w$; also the weight of soap solution was always 3·5 times that of the benzene, but varying amounts of lauric acid were added.

TABLE VII.

Concentration of lauric acid in the benzene layer at 25° in the five-component system where only the amount of added lauric acid is varied.

HL in benzene, before, g.	0·0021	0·0085	0·0243	0·0708
„ „ after, g.	0·00301	0·00546	0·00876	0·01117
„ „ „ , N_w	0·00161	0·00234	0·00404	0·00517

Comparison of the results given in Table VII with those of Table I or Table III shows that, whereas unaltered $0{\cdot}1N_w$-potassium laurate is in equilibrium with a $0{\cdot}0032N_w$-solution of lauric acid in benzene, the equilibrium concentration in presence of the salt is lowered to $0{\cdot}0023N_w$. In every case salt lowers the extractability, and, for a given addition of lauric acid, increases the amount of acid soap produced in the system.

Summary.

1. The compositions of benzene solutions of lauric acid in equilibrium with various solutions of potassium laurate at 25° have been determined, and the experiments extended to solutions containing various additions.

2. Unaltered soap solutions contain the merest trace of free fatty acid—only a few units per cent. of that capable of dissolving in water. The fatty acid corresponding to the hydrolysis alkalinity is almost quantitatively combined as acid soap.

3. Acid soap forms as a sediment whenever carbon dioxide gains access to the soap solutions. Solid potassium laurate, as well as its aqueous solution, extracts lauric acid from its concentrated solutions in benzene, forming acid soap. The definite crystalline compound, acid potassium laurate, KL,HL, is found to exist, and it is fairly soluble in hot benzene. A concentrated solution of lauric acid in benzene almost quantitatively removes soap. Presence of salts promotes the formation of acid soap but diminishes the extractability of aqueous soap solution.

Our thanks are due to Dr. M. E. Laing for constant assistance.

STANFORD UNIVERSITY, CALIFORNIA. [*Received, June* 11*th*, 1928.]