CCCLVI.—*The Hydrolysis of Solutions of Sodium Palmitate as measured by Extraction with* p-*Xylene.*

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AFTER long uncertainty and widely conflicting opinions, it is now commonly accepted that the hydrolysis alkalinity of soap solutions is of the order of only $N/1000$ (conductivity: McBain and Taylor, *Z. physikal. Chem.*, 1911, **76**, 179; hydrogen electrode: McBain

and Martin, J., 1914, **105**, 957; catalysis: McBain and Bolam, J., 1918, **113**, 825; Beedle and Bolam, *J. Soc. Chem. Ind.*, 1921, **40**, 27T; ultrafiltration: McBain and Jenkins, J., 1922, **121**, 2325; indicators : McBain and Hay, unpublished). The presence of free fatty acid in all soap solutions is readily demonstrated by shaking them with any suitable solvent such as light petroleum or toluene (Krafft and Stern, *Ber.*, 1894, **27**, 1747, 1755; Krafft and Wiglow, *ibid.*, 1895, **28**, 2566, 2573; Lewkowitsch, *Z. angew. Chem.*, 1907, **20**, 951; Fendler and Kuhn, *ibid.*, 1909, **22**, 107; Holde, *Z. Elektrochem.*, 1910, **16**, 436; S. von Schapringer, Dissert., Karlsruhe, Freiberg, 55—67; Reychler, *Int. Congr. Appl. Chem.*, 1912, **22**, 221), which always extracts fatty acid although the amount is only a small fraction of that which the soap would yield if completely decomposed. As will be seen, such extraction occurs from all soap solutions, whether neutral or containing excess of acid or of alkali. In every case, likewise, the solutions are definitely alkaline even when as much as a complete equivalent of excess of fatty acid has been added to the soap.

Even now, however, the statement is frequently made that soap solutions contain emulsified free fatty acid. This is never true. In spite of the low solubility of the higher fatty acids, there is never enough free fatty acid to saturate the solution, much less to give an excess. If the aqueous layer is saturated with fatty acid, then any non-aqueous layer in equilibrium with it would also be saturated, but in no case has this been observed.

The higher fatty acids must be almost as strong as acetic acid, as is evident from a study of the dissociation constants of the lower acids of the homologous series. The only reason why soap solutions are appreciably hydrolysed is that the free fatty acid formed by hydrolysis is almost wholly removed from solution in the form of acid soap. Such acid soaps form a conspicuous, but often almost unweighable, sediment in dilute soap solutions, and the gross composition of these sediments has often been determined (see McBain and Taylor, *loc. cit.*; Krafft and Stern, *loc. cit.*; McBain, Taylor, and Laing, J., 1922, **121**, 621; McBain and Stewart, this vol., p. 1392), although the elucidation of their exact constitution awaits more rationally planned experiments. There is no similar outlet for the alkali formed by hydrolysis, and it therefore accumulates in the solution. The hydrolysis alkalinity, *i.e.*, the concentration of free hydroxyl ions, is therefore always much greater than the mere trace of free fatty acid present in the solution. Addition of a very small amount of alkali scarcely increases the hydrolysis alkalinity, because it is compensated by removal of acid soap.

It is evident, therefore, that extraction with solvents does not

measure the hydrolysis alkalinity, but that when equilibrium is attained the concentration of the free fatty acid in true solution in the final aqueous layer is indicated. The value of the distribution ratio is such that the concentration of fatty acid in the non-aqueous layer is of the order of 10^6 times greater than that in the aqueous layer. Two kinds of experiments may be carried out, *viz.*, those in which soap solutions are extracted with solvent and therefore changed in composition, and those in which approximately the right amount of fatty acid is previously added to the non-aqueous layer, so that the final equilibrium is determined without appreciable alteration of the aqueous solution. Both methods have here been adopted. When a large excess of fatty acid is added in advance to the non-aqueous layer, it passes into the soap solution, thus again demonstrating the formation of acid soap, since the non-aqueous layer is left unsaturated. It is important that true reversible equilibrium between the two layers was readily obtained in our experiments; the position of equilibrium was obtainable from both sides and did not alter with time at 90°.

EXPERIMENTAL.

All the work was carried out at Bristol University. Mr. H. H. Cole studied toluene, xylene, and deca- and tetra-hydronaphthalene with a view to find a solvent which would fulfil the following conditions : it should be (1) of fairly high boiling point, (2) non-miscible with water, (3) a non-solvent for soap and sodium hydroxide, and (4) only a moderate solvent for fatty acid, which should dissolve as unassociated molecules. He found that the solubility of palmitic acid in twice-distilled p-xylene (b. p. 137—138° under 760 mm. pressure) was 33·8 g. in 100 g. of p-xylene at 50° and 73·5 g. at 90°, and ebullioscopic measurements showed that the fatty acid was mainly present as simple molecules (Found : M, 322, 322, 328, 336. Calc. : 266), but the boiling point constant was found only by calculation. Blank experiments showed that if 9·5 g. of palmitic acid were added to 12 c.c. of xylene, the residue after evaporation showed a loss of only 0·1—0·2 mg. of the acid. Further, xylene was found to dissolve only 0·06% of its weight of sodium palmitate when shaken at 95—97° for 22 hours, thus showing that for the purpose of the present experiments sodium palmitate is insoluble in xylene.

The method here employed is substantially that developed by Miss A. M. King. The greatest practical difficulty is due to the extreme readiness with which these soap solutions become more or less permanently emulsified with the xylene layer, so that separation for analysis becomes impossible. This was finally avoided by carrying out the extraction in horizontal sealed tubes, about

23 cm. long and 1·3 cm. in diameter, tied parallel to the axis of a slowly rotating horizontal stirrer making 20—60 revs. per min. Even under these conditions, if the tubes contained a very large excess of fatty acid or nearly enough salt to salt out the soap, frothing occurred extensively. Between 7000 and 8000 revs. were allowed for attainment of equilibrium, and after 15 minutes' further standing the xylene layer was usually quite clear. Thereupon, the top of the tube was cut off without removal from the thermostat, and as much as possible of the xylene layer was drawn off and weighed; the xylene was then evaporated at 80°, a tube attached to a filter-pump being kept near the surface of the solution in an evaporating dish to renew the air. After 2 hours' drying the residue of fatty acid was weighed.

Two specimens of sodium palmitate, specially made for us by Kahlbaum, were employed. Specimen A contained 4·5% of water and an excess of alkali amounting to 0·0001 equiv. of sodium per equiv. of soap. Specimen B contained 3·47% of water and 0·0008 equiv. excess of sodium. These amounts of alkali and water are allowed for in recording the composition of the solution. All solutions were made with boiled-out conductivity water (1×10^{-6}) in Jena glass flasks. In experiments involving excess of fatty acid or alkali, palmitic acid (" Kahlbaum ") or drippings from sodium, free from carbon dioxide, were used, respectively. The salts used were Kahlbaum's " for analysis," dried at 120—130°. Sodium carbonate was heated to bright redness in a platinum crucible for 3 hours. In each case it was found that the salts were insoluble in xylene. All solutions were made up by weight, and concentrations are expressed in weight normality (equivs. per 1000 g. of solvent, water, or xylene). About 7 c.c. of soap solution were used in each experiment. In all cases the temperature was 90° ±0·1°.

Results.

Proof that True Equilibrium is attained.—In order to attach significance to the results, it is necessary to demonstrate that true reversible equilibrium is attained between the two phases. This is conclusively shown by the experiments in Table I, in which identical results were obtained from two series of experiments approaching equilibrium from opposite sides. In the first series, a $0·0774N_w$-solution of sodium palmitate was shaken with an approximately equal quantity of pure xylene. In the second series, a $0·0774N_w$-solution of sodium hydroxide was shaken with an equivalent quantity of palmitic acid dissolved in xylene. In the first series, after equilibrium had been attained, 17·1% of the total palmitate radical in the system was present in the xylene layer as

palmitic acid.   In the second series, 17·3% of the original palmitic acid was finally left in the xylene layer, the remainder having gone into the aqueous layer to react with sodium hydroxide.   Thus for the first time it is shown that true equilibrium can be attained in suitably planned experiments on the extraction of soaps.

TABLE I.

Proportion of total palmitate radical extracted when equal weights of $0.0774N_w$-aqueous solution of sodium palmitate and p-xylene are brought into equilibrium at 90°.

Aqueous layer.			Xylene layer.		
N_w-Soap * before.	N_w-NaOH before.	N_w-NaOH † after.	N_w-HP ‡ before.	N_w-HP § after.	% Total HP extracted.
0·0774	0	0·01326	0	0·01262	17·28
0·0774	0	0·01384	0	0·00841	18·01
0·0774	0	0·01257	0	0·01659	16·33
0·0774	0	0·01056	0	0·01397	17·33
0·0774	0	0·01338	0	0·01587	17·43
0·0774	0	0·0100	0	0·01650	16·43
0	0·0774	0·0138	0·0774	0·0138	17·81
0	0·0774	0·0129	0·0774	0·0129	16·69

    * Specimen A.   ‡ HP = palmitic acid.

    † The numbers recorded do not include the hydrolysis alkalinity due to the soap, but only the excess of sodium hydroxide left in the soap solution corresponding with the palmitic acid extracted.   The total final alkalinity is not the sum of the original and that shown, because some of the acid extracted comes from acid soap.

    § A saturated solution would be $2.93N_w$-palmitic acid.

In order to determine the effects of varying the concentration of soap and the amounts of the aqueous and xylene layers, data are given in Table II for the proportion of the total palmitate radical present in the system which is finally found as palmitic acid in the xylene layer when neutral soap solutions are shaken with xylene.

In all the foregoing experiments the soap solution is robbed of part of its palmitic content by the xylene.   Hence the experiments in Table III were carried out by adding excess of palmitic acid to the original xylene, various concentrations being tried until palmitic acid was neither given up to nor extracted from the soap solution. This not only yields the concentration of palmitic acid that is in equilibrium with the unaltered soap solution, but it also affords conclusive proof that true reversible equilibrium was attained in these experiments.   The results are plotted in Fig. 1.

Increased experimental difficulties are encountered when the concentration of palmitic acid in xylene exceeds $0.25N_w$, *i.e.*, 6% : it was difficult to effect complete evaporation of the xylene if the

TABLE II.

Proportion of total palmitate extracted as palmitic acid when p-*xylene is shaken with aqueous solutions of sodium palmitate at 90°.*

N_w-NaP * before.	Soap soln. (g.).	N_w-NaOH † after.	Xylene (g.).	N_w-HP ‡ in xylene.	% HP extracted.
0·1388	5·2069	0·00684	9·0303	0·01145	4·92
0·1388	6·8610	0·00716	9·0818	0·00915	5·16
0·1388	5·3660	0·00687	7·9261	0·00979	4·94
0·1388	7·4565	0·00793	8·3362	0·00855	5·58
0·1388	6·4728	0·00834	7·7412	0·00857	5·97
0·1118	6·844	0·0109	8·82	0·00821	9·78 §
0·1118	9·396	0·0095	8·82	0·00982	8·50 §
0·1118	7·665	0·0116	8·80	0·00984	10·42 §
0·1096	4·917	0·0144	8·80	0·007877	13·13 §
0·1096	4·501	0·0177	17·60	0·004895	16·15 §
0·1096	4·501	0·0182	17·60	0·004512	16·58 §
0·1096	4·389	0·0177	17·56	0·004295	16·5 §

* Specimen A.   † See corresponding footnote in Table I.

‡ A saturated solution would be $2·93N_w$-palmitic acid.

§ Measurements by Miss King, in which the solutions were allowed to stand from 3 to 12 days, thus confirming that time does not appreciably affect the equilibrium at 90°.

TABLE III.

Experiments in which $0·100N_w$-*solutions of sodium palmitate (Specimen B) and water were shaken at 90° with xylene to which various amounts of palmitic acid had been added in advance.*

| Soap soln. (g.).	Xylene soln. (g.).	HP in xylene.		Excess in H₂O layer after.	
		Before, N_w.	After,* N_w.	NaOH, N_w.	Acid soap, N_w.
5·1691	7·0673	0·1170	0·1217	0·0058	—
4·1934	8·4574	0·1386	0·1385	0·00067	—
6·0092	5·2940	0·1464	0·1452	—	0·0002
4·6990	6·3900	0·1686	0·1655	—	0·0033
6·7521	5·7714	0·1758	0·1704	—	0·0038
5·0572	5·6892	0·1840	0·1790	—	0·0044
5·5903	8·1763	0·1954	0·1909	—	0·0053
5·1498	5·1032	0·2384	0·2310	—	0·0076
4·9988	6·7175	0·9545	0·9371	—	0·0207

* A saturated solution of palmitic acid would have been $2·93N_w$.

usual amount of solution was used; hence, the solutions were evaporated at 80° under 20 mm. Hg.   There is also a strong tendency to emulsification when the xylene contains between 10% and 20% of palmitic acid, but this diminishes again at higher concentrations.   The formation of acid soap is indicated by the soap layer becoming absolutely opaque.   An experiment with 25% palmitic acid ($0·9545N_w$) is given in Table III and is also included in Fig. 1.

Effect of Electrolytes upon the Extractability.—Table IV and Fig. 2 record experiments in which various pure salts were dissolved in

the $0.1N_w$-sodium palmitate solution at 90° before it was shaken with xylene. The salts increased the tendency to frothing, and as the concentration of salt required for salting into two aqueous layers was approached, emulsification became so prominent that the xylene layer finally could not be analysed. The salts made the

FIG. 1.

←——Excess NaOH (N_w)——   ——Excess HP (N_w)——→
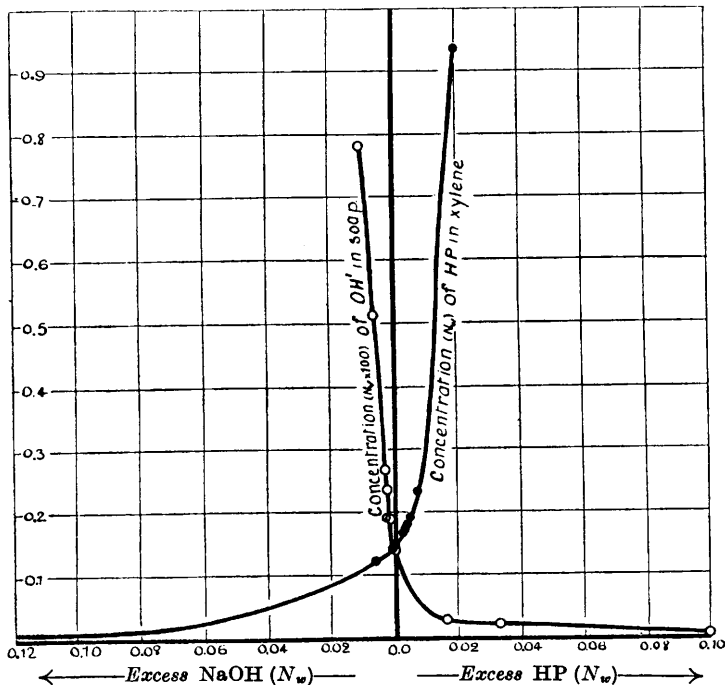
Hydrolysis equilibria in aqueous sodium palmitate containing excess or deficiency of either sodium hydroxide or palmitic acid. The curve for hydrolysis alkalinity is that obtained by McBain and Martin by the E.M.F. method. The other curve shows the concentrations of palmitic acid in xylene when the xylene layer is in equilibrium with the soap solution of the final concentration indicated (one experimental point lies off the left of the diagram). Were the palmitate ion constant throughout, the concentrations of hydroxyl ion and of free palmitic acid in the aqueous phase would be inversely proportional to each other.

originally clear soap solution cloudy. All the experiments were carried out with Specimen B of sodium palmitate.

Discussion and Interpretation of Results.

The outstanding result of these measurements is that there is scarcely any free fatty acid in a soap solution even when it is appreciably hydrolysed. There is practically quantitative conversion of the fatty acid formed into insoluble acid soap. For

example, a $0.1N_w$-solution of exactly neutral sodium palmitate is in equilibrium with the xylene layer containing $0.143N_w$-palmitic acid. The saturation concentration or solubility of palmitic acid in xylene is $2.93N_w$; hence the xylene layer, and therefore likewise

FIG. 2.
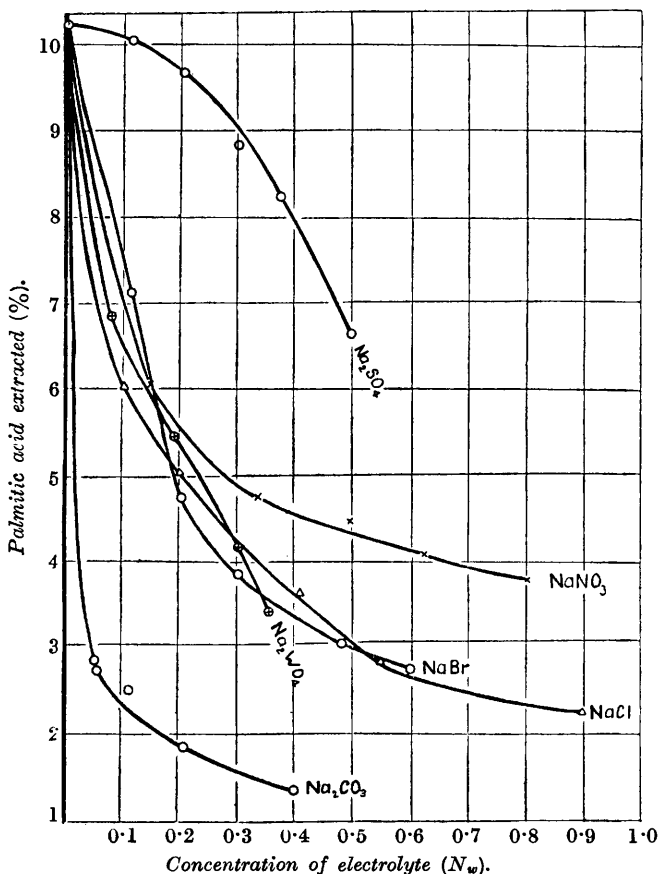
The effect of the addition of salts to aqueous sodium palmitate at $90°$ upon the amounts of palmitic acid passing into the non-aqueous layer when the soap solution is shaken with an approximately equal volume of p-xylene.

the aqueous layer, is not more than 5% saturated with palmitic acid. McBain and Taylor (loc. cit.) found the solubility of the undissociated palmitic acid in water at $90°$ to be $0.6 \times 10^{-5}N_w$, and therefore, if the distribution ratio between water and xylene is a constant, the concentration of free palmitic acid in the aqueous layer is only $3 \times 10^{-7}N_w$, whereas the hydroxyl-ion concentration

TABLE IV.

Effect of added salts upon the extractability of $0.1N_w$-sodium palmitate at $90°$.

NaP soln. (g.).	Xylene (g.).	N_w-salt.	N_w-HP in xylene.	% HP extracted.	N_w-NaOH formed.
		Sodium chloride.			
5·3619	5·8108	0	0·00942	10·48	0·0105
5·9920	4·4946	0·1000	0·0112	8·68	0·0086
5·3282	5·0708	0·2000	0·0051	4·96	0·0050
4·7650	6·1778	0·4110	0·0027	3·61	0·0036
4·7140	6·2668	0·5534	0·0020	2·84	0·0028
5·5412	5·1768	0·8970	0·0024	2·30	0·0023
		Sodium bromide.			
5·3619	5·8108	0	0·0094	10·48	0·0105
4·0070	4·8030	0·115	0·0058	7·1	0·0071
6·6604	8·4060	0·204	0·0041	4·4	0·0053
4·5606	6·3834	0·300	0·0034	3·83	0·0048
4·6928	6·1300	0·478	0·0023	3·0	0·0038
4·2768	8·4032	0·600	0·0013	2·67	0·0027
		Sodium sulphate.			
5·3619	5·8108	0·0	0·00942	10·48	0·0105
4·8294	6·3338	0·1145	0·00745	10·05	0·0105
6·3770	5·0828	0·206	0·01204	9·837	0·0098
4·9878	5·4478	0·30	0·00813	8·8	0·00913
5·6500	5·7562	0·376	0·0079	8·34	0·0083
5·7488	6·3568	0·50	0·0058	6·62	0·0066
		Sodium carbonate.			
5·3619	5·8108	0·0	0·00942	10·48	0·0105
6·2130	5·3842	0·100	0·0031	2·8	0·0028
5·8700	6·6298	0·109	0·0023	2·7	0·0027
6·2370	7·4788	0·231	0·0021	2·47	0·00248
5·3062	7·6776	0·417	0·0012	1·80	0·0019
5·4568	7·7641	0·811	0·00086	1·27	0·0012
		Sodium nitrate.			
5·3619	5·8108	0	0·009423	10·48	0·0105
5·5170	5·1642	0·1622	0·0062	5·98	0·0060
5·2456	6·5292	0·337	0·0037	4·70	0·0047
5·5046	6·642	0·475	0·0061	4·4	0·0042
4·606	8·2568	0·634	0·0022	4·0	0·0026
4·8728	6·945	0·809	0·0025	3·72	0·0037
		Sodium tungstate.			
5·3619	5·8108	0	0·00942	10·48	0·0105
5·5227	5·4125	0·1590	0·0067	6·8	0·0068
5·6696	5·2544	0·3828	0·0057	5·4	0·0054
4·2324	5·5602	0·6018	0·0052	4·1	0·0070
5·0958	7·4986	0·7152	0·0022	3·36	0·0034

or hydrolysis alkalinity is $0.0013N_w$, as found by several independent methods. Hence, all the palmitic acid representing the difference between these two numbers is removed from solution in the form of acid soap.

It is possible from the data of McBain and Taylor to predict

what concentration of palmitic acid should have been found in $0.1N_w$-aqueous sodium palmitate at 90°. Taking the dissociation constant of palmitic acid as 1×10^{-5}, that of water as 33×10^{-14}, the concentration of simple palmitate ion in the solution as $0.035N_w$, and the concentration of hydroxyl ion as $0.0013N_w$, one can predict the concentration of palmitic acid as $9 \times 10^{-7}N_w$. The $3 \times 10^{-7}N_w$ was estimated above on the assumption that palmitic acid has the same solubility in pure water as it has in $0.1N_w$-sodium palmitate saturated with xylene; this is probably not quite correct and may account for the small discrepancy.

The possible influence of salts upon the distribution coefficient, and still more upon the degree of insolubility of acid soap, constitutes the chief uncertainty in interpreting the results in Table IV and Fig. 2. It is clear that the addition of salts to the soap solution diminishes the extractability and probably the hydrolysis, although this should be checked by direct measurement of hydrolysis alkalinity. All these soap solutions were rendered alkaline by the abstraction of palmitic acid, those containing most salt being least affected and yet giving up least palmitic acid. The behaviour of all salts is very similar with the exception of sodium carbonate and sodium sulphate; the difference in the case of the former is clearly due to its alkalinity, but no explanation is forthcoming as to the peculiar shape of the curve for sodium sulphate unless the salt was slightly acid, which was not tested at the time. The effect of the various salts bears no relation to their effect upon salting out of soaps, to the Donnan equilibrium, or to the Hofmeister series, and shows no influence of valency, because all the salts replace each other mol. for mol. with the exception of the carbonate and sulphate. The effect is undoubtedly due to diminution in the concentration of simple palmitate ion (the substance that hydrolyses) and its replacement by colloid. The same explanation would account for the rapid fall in the % hydrolysis with increasing concentration of soap as is illustrated in Table II; 17% of the total palmitate in $0.0774N_w$-solution was extracted by an equal amount of xylene, whereas from a solution of twice the concentration only 5% was extracted.

In conclusion, attention may be directed to the series of buffer reactions which occur within a soap solution and render its hydrolysis alkalinity less dependent upon extraneous additions than is usually the case with standard buffers. For example, large change of concentration of the soap, addition of acid or even of a small amount of alkali, and variation of the amount of any non-aqueous solvent with which the solution is shaken all effect only a small change in the concentration of hydroxyl ion. The hydrolysis is chiefly regulated by the insolubility of the acid soap, which is

greatest for the highest fatty acids and distinctly less for unsaturated fatty acids.   Further experimental work is now in progress at Stanford University.

Summary.

1. Contrary to the opinions hitherto expressed by most writers, no soap solution contains more than the merest trace of uncombined fatty acid, and even that is completely dissolved, none being in the emulsified or free condition.   Thus, in spite of the sparing solubility of the higher fatty acids, soap solutions are unsaturated with respect to them.   This is conclusively proved by the fact that any non-aqueous solution brought into equilibrium with an aqueous soap solution is very far from being saturated with fatty acid, even when a large excess of the acid has originally been added to the system.

2. Practically all of the fatty acid corresponding to the hydrolysis alkalinity is locked up in combination as (insoluble) acid soap. Soap solutions are excellent buffers.

3. Electrolytes, even up to high concentrations, diminish the extractability, and probably the hydrolysis, of dissolved soap.