CCLXXX.—*The Rates of Saponification of Various Commercial Oils, Fats, and Waxes and Pure Triglycerides by Aqueous Alkali.*

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The only published accounts of actual measurement of the rate of saponification of commercial oils and fats and of pure triglycerides by aqueous alkali are those of Norris and McBain (J., 1922, **121**, 1362), Finch and Karim (*J. Soc. Chem. Ind.*, 1926, **45**, 35T, 469T), and McBain, Howes, and Thorburn (*J. Physical Chem.*, 1927, **31**, 131). These studies have been concerned with four pure triglycerides and only a few commercial oils. The rates of saponification in these heterogeneous systems bear but little relation to the many studies, experimental and theoretical, made in homogeneous solutions. The purpose of the present study is to measure the rate of saponification of a large number (*viz.*, 23) of the available commercial oils and fats, as well as two of the pure triglycerides, under strictly comparable conditions. The data for other triglycerides will be presented in another communication.

The experiments of Norris and McBain, like the later ones of Finch and Karim, were carried out essentially as follows. Equivalent amounts of oil and alkali were boiled out and stirred together for a definite time; a sample was then taken for analysis, the reaction being stopped by the addition of a known volume (excess) of hydrochloric acid. By analysis, the weight of oil saponified was determined and expressed as a percentage of the amount of oil taken. The results obtained from these preliminary surveys showed that the reaction takes place at the surface of contact between the oil phase and the aqueous phase, and that the rate of saponification is dependent upon the area of the interface as well as the rate at which the alkali is brought to the surface and the products of the reaction removed from it. However, measurements using the above method all have the disadvantage that, as the reaction proceeds from beginning to end, several different sets of phases may successively be present and also that the concentrations of all the different constituents are varying. It is thus impossible to determine accurately the effect of varying any one factor.

For this reason the new method used in the work of McBain, Howes, and Thorburn (*loc. cit.*) was developed. The principle of this method is to keep all of the reagents except the hydroxide in such large excess as to be approximately constant throughout any one experiment, thus keeping all the physical as well as chemical factors constant. The rate of disappearance of the dilute hydroxide, as followed by means of the hydrogen electrode, was found to be unimolecular in so far as the hydroxyl ion is concerned. There was thus developed a rapid, quantitative method for the measurement of the rate of saponification by aqueous alkali in which any one factor can be varied singly and its influence thereby determined; and this we have now used for the determination of the rate of saponification of various oils, fats, and pure triglycerides in the presence of the same soap with a view to determine whether the rate varies with different oils, and, if so, to find the extent of variation and the factors involved.

Materials and Apparatus.—The standard sodium hydroxide solutions were prepared by dissolving sodium drippings in freshly boiled-out distilled water. The commercial oils used, with the exception of one sample of coco-nut oil and the tallow, lard, and butter, were obtained from Messrs. Curtis and Tompkins, of San Francisco. The tallow was extracted from beef suet by heating, and the free fatty acid removed before use by treating it with sodium hydroxide. The castor oil, Chinese vegetable tallow, sesame, hemp-seed, linseed, perilla, soya, and rape-seed oils were from Manchuria, the tung oil from China, the palm oil from Sumatra, the peanut and cotton-seed oils from Texas, the coco-nut oil from the Philippine Islands, and the rest from California. The second sample of coco-nut oil was the neutralised sample used in the work of McBain, Howes, and Thorburn (*loc. cit.*) in England, as obtained through the kindness of Messrs. Christopher Thomas Bros., of Bristol. The pure triglycerides, trilaurin and tristearin, and the sodium and potassium laurates, sodium palmitate, and sodium and potassium oleates were obtained from Kahlbaum. The soap used as a constant emulsifying agent was a potassium coco-nut oil soap obtained through the courtesy of the Davies–Young Soap Co., Dayton, Ohio. They stated that only Cochin coco-nut oil, potassium hydroxide, and distilled water were used in making it. It contained 62·5% of anhydrous soap.

As previously stated, the hydrogen electrode was used to follow the disappearance of the hydroxyl ion. The *E.M.F.* measured was that of the hydrogen electrode coupled with a decinormal calomel electrode, the potential of the calomel electrode remaining constant, and the change in *E.M.F.* being due to the changing potential of the hydrogen electrode. The cell whose potential was measured was as follows :

(Pt) H_2	$0{\cdot}1N_w$-NaOH $1{\cdot}0N_w$-Soap $1{\cdot}0N_w$-Oil	KCl ½ satd.	KCl ½ satd.	$0{\cdot}1N_v$-KCl, Hg_2Cl_2 (solid)	Hg
90°	90°	90°	Room temperature		

The reaction was carried on in a three-necked, round-bottomed, 500 c.c. Pyrex flask, which was about three-quarters immersed in a thermostat at 90° ± 0·1°. The mixture was stirred by a small silver propeller bound on the end of a glass rod and driven at a speed of 2900 r.p.m. The actual arrangement of the apparatus is shown diagrammatically in Fig. 1 of the paper of McBain, Howes, and Thorburn (*loc. cit.*). The hydrogen electrodes used were of the Hildebrand type. Three electrodes, prepared at the start, were used as checks on one another and also to replace an electrode in case it became " poisoned " during the course of an experiment. A pyknometer, calibrated to contain at room temperature the required amount of $0{\cdot}3N_w$-sodium hydroxide, was used to measure the alkali added to the reaction mixture. The *E.M.F.* was measured by means of a Leeds and Northrup students' potentiometer.

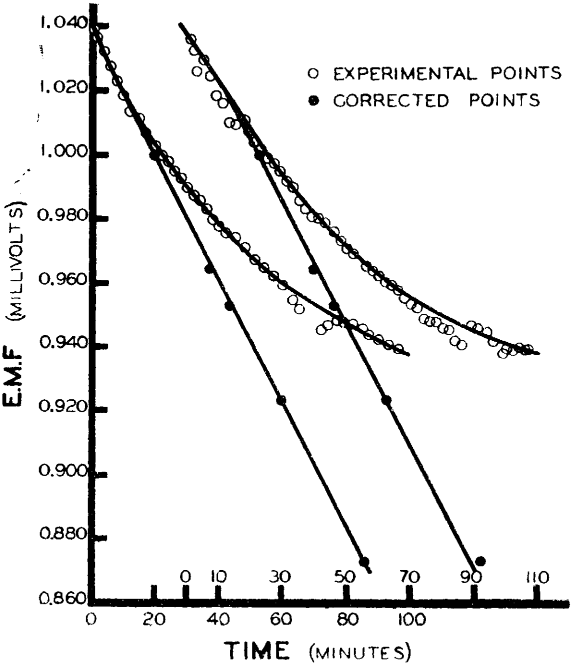
Procedure.—Each experiment was carried out using a total of 50 g. of water. The initial concentration of the soap was $1N_w$, and that of the alkali $0{\cdot}1N_w$. With each of the commercial oils, 11 g. of oil were added at the start : this was about $1N_w$ for coconut oil (based on one-third of the molecular weight) and a little less for the others. Possibly for strict comparison a constant volume of oil should have been used, but, as the commercial oils vary only slightly in specific gravity, constant weight closely approximates to constant volume, and the necessity of determining specific gravity for each oil is avoided. Furthermore, McBain, Howes, and Thorburn (*loc. cit.*) showed that, where the oil is already in excess, variation of its amount changes the rate only slightly, because usually only a portion is truly emulsified. With the pure triglycerides the exact theoretical quantity to make them $1N_w$ with respect to the fatty radical (*i.e.*, one-third of the molecular weight) was added at the start. Glycerol was not added at the beginning because of its small influence on the rate. The data of McBain, Howes, and Thorburn indicate that, if the total amount of glycerol produced by complete saponification of the $0{\cdot}1N_w$-sodium hydroxide were present throughout the reaction, the velocity coefficient would be lowered only by about 2%, and as the later stages of the reaction were not used in calculating the coefficient, the influence of the glycerol produced was negligible. Two-thirds of the water was added with the soap and the other one-third with the sodium hydroxide, these two constituents being prepared in solutions of $1{\cdot}5N_w$- and $0{\cdot}3N_w$-concentration, respectively.

The actual procedure followed in any one experiment was as follows. The required amounts of soap and oil were weighed into the reaction flask; this was put in place in the thermostat, and the potassium chloride siphon, the stirrer, and the outer jacket of the hydrogen electrode were inserted. The top of the hydrogen electrode jacket was closed with a stopper, and the soap and oil were then stirred together for 20—30 minutes, hydrogen being bubbled through the whole time to ensure saturation. At the end of this time, the sodium hydroxide was added through the hydrogen electrode jacket, the pyknometer containing it having previously been placed in the thermostat for about 5 minutes to bring the alkali to the proper temperature. The hydrogen electrode was then inserted and frequent readings of *E.M.F.* were taken.

Calculation of Results.—Since the progress of the reaction was followed by means of a hydrogen electrode, the measured *E.M.F.*

is directly proportional to the logarithm of the hydroxyl-ion concentration. The unimolecular velocity coefficient, *k*, should be equal to 1/*t* times the logarithm of the ratio of the initial hydroxyl-ion concentration to that at time *t*. Since the logarithm of the hydroxyl-ion concentration occurs both in the expression for the rate and in the value of the *E.M.F.*, the velocity coefficient is proportional to 1/*t* times the change in *E.M.F.* up to time *t*. Therefore, *E.M.F.* plotted against time should give a straight line whose slope would be the velocity coefficient in millivolts per minute.

Fig. 1.



Actually, however, the reaction is incomplete and reversible, owing to equilibrium being obtained when the hydrolysis-alkalinity is of the order of *N*/1000. Therefore, although the change in *E.M.F.* is at first nearly proportional to time, the *E.M.F.* must ultimately tend to a constant value independent of time and corresponding to the hydrolysis-alkalinity. A simple, graphical method for correcting for this reverse action and obtaining the integrated value of *k* without calculation is described in detail in the paper of McBain, Howes, and Thorburn (*loc. cit.*), where the table of correction values is given once for all.

To apply the correction, a point is found on the *E.M.F.–t* curve where the *E.M.F.* is greater than the final equilibrium *E.M.F.* by an amount corresponding to a number in the standard table. The corresponding number in the table is then the amount by which this point has to be lowered vertically to put it in its corrected position. The slope of the straight line so obtained is the velocity coefficient for the forward reaction expressed in millivolts per minute. It is seen from Fig. 1 that straight lines do result from applying this correction.

As a rule, in drawing the straight line to obtain the velocity coefficient, least weight was given to the last corrected point, because, as the reaction approaches equilibrium, the corrections increase very rapidly, and any error is unduly magnified. Although the equilibrium *E.M.F.* depends upon the kind and concentration of the soap in the equilibrium mixture, the value of E_ζ, the *E.M.F.* corresponding to equilibrium, should vary only slightly with the different experiments because the effect of the soap formed during the reaction is negligible in comparison with the effect of the large excess of soap initially present. This was found to be true, and 0·910 was taken as the nearest correct value of E_ζ and was used in all the calculations.

Experimental Results.

The data obtained are collected in Table I, which is arranged in decreasing order of velocity coefficients (*k*), the fastest being castor oil and the slowest rape-seed oil. The iodine numbers (see Hilditch, " The Industrial Chemistry of the Fats and Waxes," 1927, Chap. II) and the measured acid values of the oils are given in the second and third columns, respectively. Next follows an indication of the composition of the oils as described by Hilditch (*op. cit.*, Chap. III). Here each of the fatty acids is represented by the number of carbon atoms in the chain, and the number of double bonds is shown for the unsaturated radicals. Thus C_{12} to C_{18} represent the saturated radicals laurate to stearate; $C_{18}^{=}$ and $C_{22}^{=}$ the oleate and erucate; and $C_{18}^{2=}$ and $C_{18}^{3=}$ the linolate and linolenate, respectively. The number preceding this shorthand formula indicates the % of that glyceride in the oil; thus castor oil, $85C_{18}^{=}OH,9C_{18}^{=}$, is shown as being 85% ricinolein and 9% triolein, only the major constituents being given. Next are given the values of *k* (in millivolts/min.), one for each independent experiment, which represent the slope of the straight line as illustrated in Fig. 1, and lastly, the final mean value of *k* for saponification in millivolts per minute. Since about 144 millivolts represent the whole course of the forward reaction, the reaction has gone nearly half way in the number of minutes required for a change of 21 millivolts, and, allowing for the reverse reaction, it has gone to the extent of 99·5% in the number of minutes required for a change of about 300 millivolts. For perfect saponification infinite time would as usual be required, but in any case the final stages of this reaction are much slower than those of a unimolecular reaction owing to the reverse reaction of hydrolysis. The final stages of an ordinary saponification where both oil and alkali disappear are, of course, still more retarded. From the numbers in the table, it would take less than 10 minutes for the castor oil to use up the alkali to the extent of 99·5%, whereas rapeseed oil would require 32 hours to do the same under these conditions.

The data of Table I show that the hydrogen electrode responds surprisingly well to the dilute alkali of the aqueous phase, ignoring the presence of the high admixture of unsaturated oil. Furthermore, it measures the alkali even in the presence of the N-solution of unsaturated soaps such as oleate.

TABLE I.

Rate of Saponification of Pure and Mixed Triglycerides in Identical Environment and Conditions.

Oil.	Iodine number.	Acid value.	.Composition.	k.	Mean k.
*Castor	83—86	‡	$85C_{\overline{\overline{18}}}OH, 9C_{\overline{\overline{18}}}$	36·5 38·2 35·3 38·0 35·5	36·7
*Lard	52—77	5·50	$60C_{\overline{\overline{18}}}, 32C_{16}, 8C_{18}$	20·0	20·0
Tristearin	0	0·46	$100C_{18}$	5·8 6·3	6·05
Coco-nut (1)	8—10	4·9	$51C_{12}, 19C_{14}, 10C_{8},$ $8C_{18}, 5C_{\overline{\overline{18}}}, 5C_{10}$	4·45 4·75 4·32 4·78	4·58
Coco-nut (2)	8—10	‡	$51C_{12}, 19C_{14}, 10C_{8},$ $8C_{16}, 5C_{\overline{\overline{18}}}, 5C_{10}$	4·45 4·75* 4·65* 4·4	4·56
*Butter	26—38	‡	$45C_{\overline{\overline{18}}}, 16C_{14}, 15C_{16},$ $5C_{12}$	4·12 4·34	4·23
*Chinese vegetable tallow	28—38	0·89	$67C_{16}, 34C_{\overline{\overline{18}}}$	3·8 4·3	4·05
Trilaurin	0	1·19	$100C_{12}$	3·30 4·22 3·65	3·72
*Japan wax	5—15	§	Mostly $C_{16}, 5C_{4}$	3·1 3·5	3.3
*Fish oil	124·5	‡		2·8—3·5 2·4—3·1	2·6—3·3
*Lard	52—77	‡	$60C_{\overline{\overline{18}}}, 32C_{16}, 8C_{18}$	1·80 2·10	1·95

Oil.	Iodine number.	Acid value.	Composition.	*k*.	Mean *k*.
Palm	53—58	9·0	$48C_{18}^{=}, 36C_{16}, 9C_{18}, 7C_{18}^{2=}$	1·95 1·93	1·94
*Sesame	103—117	1·37	$70C_{18}^{=}, 18C_{18}^{2=}, 12C_{18}$	1·50 1·70	1·60
*Palm kernel	15—20	‡	$52C_{12}, 16C_{18}^{=}, 15C_{14}, 8C_{16}$	1·2—2·5 1·4—2·2	1·3—2·35
*Hemp-seed	145—160	0·7	$C_{16}, C_{18}^{2}, C_{18}^{=}, C_{18}^{3=}$	1·40 1·20	1·30
*Beef tallow	35—47	‡	$48C_{18}^{=}, 32C_{16}, 14C_{18}$	1·24 1·19	1·22
Peanut (ground nut)	85—95	2·38	$60C_{18}^{=}, 21C_{18}^{2=}, 7C_{16}$	1·05 1·04	1·05
Linseed	170—185	1·72	$62C_{18}^{2=}, 24C_{18}^{3=}, 9C_{16}, 5C_{18}^{=}$	1·00 1·10	1·05
*Whale	110—150	‡	$33C_{18}^{=}$, 15†, $12C_{16}, 9C_{18}^{2=}, 8C_{14}$	0·80 0·8	0·80
Perilla	193—206	1·88	(The most unsaturated oil.)	0·68 0·69	0·69
Cotton-seed	104—113	0·19	$54C_{18}^{2=}, 23C_{18}^{=}, 23C_{16}$	0·63 0·64	0·64
*Palm	53—58	‡	$48C_{18}^{=}, 36C_{16}, 9C_{18}, 7C_{18}^{2=}$	0·61 0·62	0·62
Soya	125—140	0·13	$57C_{18}^{2=}, 33C_{18}^{=}, 6C_{16}, 4C_{18}$	0·39 0·40	0·40
China-wood (Tung)	160—180	5·6	$93C_{18}^{2=}, 7C_{18}^{=}$	0·35 0·31	0·33
*Sunflower	125—140	0·23	$58C_{18}^{2=}, 34C_{18}^{=}, 4C_{16}$	0·21 0·27	0·24
Olive	79—86	0·75	$85C_{18}^{=}, 7C_{16}, 6C_{18}^{2=}$	0·26 0·15*	0·21
Rape-seed (Colza)	97—105	2·31	$50C_{22}^{=}, 32C_{18}^{=}, 15C_{18}^{2=}$ ($57C_{22}^{=}, 20C_{18}^{=}, 15C_{18}^{2=}$)¶	0·162 0·160	0·161

* Data obtained by Mr. Kawakami. The standard sodium hydroxide solutions were prepared by dissolving Merck's C.P. analysed sodium hydroxide in freshly boiled-out distilled water. The surface of the sticks was first washed off with distilled water to remove as much carbonate as possible. Of course, there were probably small amounts of carbonate remaining, but comparison with other experiments in which sodium drippings were employed in preparing the hydroxide solutions shows that the small amounts of carbonate present as impurities had no appreciable effect upon the rate of saponification.

† Fifteen per cent. palmitoleate.

‡ The oil in these cases had been neutralised with alkali.

§ The oil in this case had been neutralised with absolute alcohol.

¶ J. J. Sudborough, H. E. Watson, and P. R. Ayyar, *J. Indian Inst. Sci.*, 1926, **9A**, 25.

Values are listed in Table I for two separate samples of coco-nut oil : as mentioned above, the first of these samples came from the Philippine Islands. The value of the velocity coefficient reported by McBain, Howes, and Thorburn for the second sample of coco-nut oil is 6·0 millivolts/min. That value need not equal numerically the value obtained in the present work, because a different soap was used as emulsifying agent, a somewhat different rate of stirring was used, and the blades on the stirrer may have been of a different size or shape. A difference in any one of these factors could vary the coefficient.

In Table I are included results for two fairly pure triglycerides, which enable comparison to be made with future work here or elsewhere. For the same reason, in Table II there are given the velocity coefficients which resulted when the coco-nut oil soap used in Table I was replaced by pure sodium and potassium soaps. This fully standardises our results. With the more insoluble higher soaps, which tend to cover up the electrode, it was necessary from time to time during the reaction to clean the electrode or replace it.

TABLE II.

Rates of Saponification of Pure and Mixed Triglycerides when Pure Sodium or Potassium Soaps are used in Place of the Potassium Soap of Coco-nut Oil.

Triglyceride.	Soap.	k (mv./min.).	Mean k.
Trilaurin	$1N_w$-Sodium laurate	6·15, 6·35	6·3
,,	$1N_w$-Potassium laurate	5·6	5·6
,,	K Soap of coco-nut oil	3·30, 4·22, 3·65	3·7
Soya bean	$1N_w$-Sodium palmitate	(1·4), 1·2	1·2
,,	$1N_w$-Potassium oleate	1·0, (0·9)	1·0
,,	$1N_w$-Sodium oleate	(3·4)	(3·4)
,,	K Soap of coco-nut oil	0·39, 0·40	0·40
Coco-nut (1)	,, ,, ,,	4·45, 4·75, 4·32, 4·78	4·6
,,	Na Soap of castor oil	Initial 2·5, 3·2, 2 to	2·6*
		Final 7·4, 6, 5·6	6·3
,,	Na Soap of rape-seed oil	5·1, 4·8, (4·0) †	5·0

* See last two paragraphs of this paper.

† In this experiment $0{\cdot}2N_w$-alkali was used instead of $0{\cdot}1N_w$.

Discussion of Results.

The most striking result demonstrated by the data of Table I is the very great range of 200-fold in the time required to saponify different oils in the same environment. The factor responsible for this is, in our opinion, the relative ease and degree of emulsification of the various oils. This is supported by the qualitative observation that in the fastest reactions the oil appeared to be wholly emulsified, whereas most of it is free in the slower reactions. It will also receive support in another communication dealing with pure glycerides. The importance of emulsification has been fully recognised by many previous writers,* although somewhat obscured

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* For references, see, *e.g.*, Langton, *J. Oil Col. Chem. Ass.*, 1922, **5**, 41, 58, where the whole of these cognate subjects is carefully described and discussed with 91 references to the literature.

by the speculations put forward by others on the basis of experiments in alcoholic and other homogeneous solutions.

This simple explanation of all our results at once makes them of general significance for all the related fields of emulsification, fat-splitting, and hydrolysis, where the same mechanism must be the dominant factor. All the reactions take place in the interface between oil and water and not in either phase. Hence the primary factor is the development of this interface, which is favoured by emulsifying agents and by the degree of readiness of the oil to be emulsified. The latter property has not heretofore been studied.

All the oils were studied just as received. This at once raises the question of the influence of acid number,* or free acid, in the oil, The answer is that where the acid number was at all large, the rate of disappearance of the alkali was unduly large. Thus the untreated castor oil reacted too fast for measurement. The effect in these extreme cases simulates a poisoning of the hydrogen electrode. With lard having an acid number of 5·5 the velocity coefficient was 20, whereas after the lard had been neutralised, like the castor oil, by treatment with alkali, the coefficient was only 2. The influence upon the rate cannot possibly be due merely to the free acid in the oil reacting rapidly with the alkali, because the total free acid in the oil is only a fraction of the alkali used, and the rate remains fast to the end. Thus, for the acid value 5·5, the 2·7% of fatty acid in the lard was only $0 \cdot 0195 N_w$ with respect to the water, whereas the alkali used is $0 \cdot 1 N_w$; *i.e.*, the free acid corresponds to only one-fifth of the alkali. Thus, even instantaneous reaction of the total free acid could not have raised the rate by more than five-fourths, whereas it actually was raised 10-fold. Clearly it is through increased readiness to emulsify that this effect is produced by free acid in the oil. In this connexion it may be recalled that McBain and Eaton (J., 1928, 2166) found that free acid added to a non-aqueous phase enormously increased the solubility of soap therein.

In order to obtain comparable results, this factor had to be studied and controlled. In the first place, known quantities of free fatty acid were added to coco-nut oil to see how the rate was affected. The fatty acid used was obtained from the coconut-oil soap. The result is striking. The original rate of the coco-nut oil was 4·6; it remained 4·6 after addition of 3·7% of acid; it rose to 8·4 when the free acid was increased to 5·6%; and the rate could not be measured in the presence of 8·4% of acid. It follows that an oil of a very low acid number gives practically the same velocity

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* The acid number, being the number of mg. of potassium hydroxide required to neutralise the free acid in 1 g. of oil, corresponds to approximately twice the % of free acid in the oil (see, *e.g.*, Hilditch, *op. cit.*, p. 37).

coefficient as the completely neutralised oil. The data in Table I illustrate these effects for palm oil and lard. A further check was obtained in several cases (*e.g.*, castor oil) by taking the reaction mixture after a reaction had been finished, adding to it a fresh portion of $0{\cdot}1N_w$-alkali, and finding that it yielded the same coefficient as before within the limits of experimental error.

Upon comparing the various oils, there is an evident relation between the nature of their constituents and the rate of saponification. For example, apart from castor oil, with its distinctive chief component, there is a real, although very rough, parallelism between unsaturation (or iodine) value and rate, the most unsaturated oils being the slowest. Multiple double bonds in the carbon chain seem to inhibit saponification more than single ones such as oleate radicals.

Bergell (*Z. deut. Oel-Fett-Ind.*, 1926, **46**, 561, *et seq.*), indeed, in studying the splitting of different neutralised oils emulsified with soap at 100°, found a direct relation between their iodine values and the number of days required for splitting, and he very clearly stresses the importance of emulsification as the vital factor in all these processes. He adduces the well-known fact that when different acids are placed in an air–water interface, there are usually several times as many molecules of saturated acids per unit area as there are of the corresponding unsaturated fatty acids. Hence he would expect a given area of oil–water interface to be less effective for saponification with unsaturated triglycerides than with the more closely packed saturated triglycerides. Lascaray (*Anal. Fís. Quím.*, 1927, **25**, 332; *Rev. gén. Colloides*, 1928, **6**, No. 52, 32) has published very similar experiments and the same argument.

To this it may be objected that it is decidedly hazardous to compare the " expanded " film of unsaturated acid or triglyceride on an air–water interface * with the surface between water and an oil in bulk, where the interior of the oil is certainly as close-packed for saturated triglycerides as for unsaturated ones. Bergell and Lascaray's explanation does not at all agree with castor oil being by far the fastest, as shown in Table I. We are convinced that all the differences in rate are essentially due to the different relative degrees of emulsification of the various oils. Bergell found that for optimum

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* Adam (*J. Physical Chem.*, 1925, **29**, 97) showed that the earlier interpretation of Langmuir, that compounds containing double bonds occupy twice as great an area as the corresponding saturated compounds, through bending so that the double bonds also touch the water, was an error due to his having compared expanded films of oleic acid with close-packed films of such substances as stearic acid. The areas taken up by saturated and corresponding unsaturated compounds are identical if they are compared under similar conditions.

rate of splitting nine parts of 50% soap solution were required to one part of oil. This, however, as we have pointed out, must vary with the oil, since some are wholly and others only very incompletely emulsified under a given condition.

The different rates in Table I show no relation to the average molecular weights of the constituents of the oils.

Another factor in determining the amount of emulsified oil, and probably also its degree of dispersion, is the soap. In Table I this was kept constant; in Table II it is varied whilst the oil is kept constant. These results give a quantitative comparison of the emulsifying power of the soaps and probably of their relative detergent efficiency towards oils.

In the first place, Table II shows that there is but little difference between potassium and sodium soaps, which is generally true when both are in solution and not curded or salted out (crystallised). Secondly, the laurates are better than the soap of coco-nut oil, although far surpassed by the palmitates and oleates, which are nearly equal to each other. Sodium palmitate and potassium oleate increase the rate about three-fold over that for the coco-nut oil soap. On the other hand, the differences between some of the oils, as exhibited in Table I, would evidently not have been quite so marked had the corresponding soap been used for each oil. This alone, however, does not account for the differences. For example, the soap of castor oil is an even better emulsifier than that of coco-nut oil, and hence the castor oil would be saponified nearly 10 times more quickly than coco-nut oil.

To show how utterly unconnected is the emulsifying power of the soap and the emulsifiability of the corresponding oil, reference may be made to the velocity coefficient in the presence of the soaps made from castor oil and rape-seed oil. These soaps, as shown in Table II, are equal as emulsifiers, although the rates for the oils themselves differ 200-fold.

In the experiments with some of the medium and slower rates of saponification, such as those with soya-bean oil and sodium palmitate, those with linseed oil, and, in exaggerated form, those with coco-nut oil and the sodium soap of castor oil, the rate increased throughout the course of the reaction. This might have been observed more often had the reaction for some of the slower rates been measured for longer periods. Inspection of the data showed that the phenomenon was real, and not merely due to the time required at the beginning of the reaction for the hydrogen electrode to adjust itself to the mixture. Autocatalysis through formation of soap is excluded because of the large excess of soap present.

Two alternative explanations for the increasing rate suggest themselves: (1) that diglycerides and monoglycerides accumulate in the partially saponified oils where the rate is slow, and that these are more quickly saponified than triglycerides—this remains to be tested by experiment, but it is rather too general an explanation for just a few curves; (2) that the varying alkali appreciably affects the emulsifying power of the soap. This would appear certain; for example, McBain, Harborne, and King (*J. Soc. Chem. Ind.*, 1923, **42**, 373T; *J. Physical Chem.*, 1924, **28**, 1) found that the "carbon number" of soaps passed through a maximum value upon slight addition of alkalis, being depressed by further small additions.

Summary.

1. The rates of saponification by aqueous alkali of 25 oils and triglycerides have been studied under strictly comparable conditions at 90°, the reaction being followed by means of the hydrogen electrode.

2. The rates differ for different oils by as much as 200-fold. The results are explained as being due to the various degrees of emulsification of the different oils, some being wholly and others only partially emulsified.

3. The results are directly applicable to all such related processes as fat-splitting, hydrolysis, and "fermentation."

4. The emulsifying power of the soaps is wholly unrelated to the ease of emulsification of the corresponding oils; nor is there any relation between molecular weight and rate of saponification. In general, the time required for saponification increases with degree of unsaturation.

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