

CLXII.—*A Study of the Rate of Saponification of Oils and Fats by Aqueous Alkali under Various Conditions.*

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It is a strange fact that there appears to be no published account of the kinetics of saponification by aqueous alkali. Various papers have reported studies of rate of reaction in homogeneous alcoholic solution, but, even in these, attention is directed more to the possibility of enunciating a theory of the mechanism of the reaction than to an investigation of the actual rate.

Experiments in homogeneous solution have very little bearing on the industrial process, for it is obvious that the former rate of reaction must be very different from the rate in the heterogeneous system of oil and aqueous alkali, where many physical factors exert considerable influence. The latter is the actual system with which the soap boiler is concerned, and so far he has worked on purely empirical tradition.

This paper records an attempt to study the rate of reaction of the process by observing the effect of alteration of conditions likely to affect it. The results, in conjunction with others from extensive work on phase-rule diagrams of systems such as sodium palmitate, sodium chloride, and water, have thrown some light on the various complicated processes taking place in the soap boiler's pan.

In the study of a heterogeneous system such as this, it is probable that physical considerations will outweigh purely chemical factors. The reaction can only take place at the surface of the two mutually insoluble liquids, oil and aqueous alkali. The rate will be affected by the area of this surface, which in turn will depend on the degree of emulsification. Rate of diffusion and convection will also be important factors, for the rate of movement of reactants to, and of resultants from this surface must considerably affect the observed rate. If diffusion is very slow the contact surface might conceivably become coated with products of the reaction to such an extent that saponification ceases.

Experimental results point to the conclusion that the physical considerations are of primary importance. The rate follows no simple formula, but is greatly affected by stirring, emulsification, and by the manner and degree of salting out of the soap.

When the concentration of electrolyte exceeds a certain definite value, two liquid, aqueous layers are produced, the more concentrated of which may be of gelatinous consistency. In soap-boiling parlance, this is termed "fitting" and "settling." The soap is

said to be "closed" when water is added for the purpose of bringing the whole into one homogeneous solution, and when this condition is nearly attained the fit is said to be "close." We shall refer to this type of salting out with moderate concentrations of electrolytes, namely, into two liquids, as "opening" the soap solution for lack of any distinctive technical or scientific term. A still higher range of concentrations salts out the soap almost quantitatively in the form of solid aggregations of curd fibres. This form of salting out is commonly referred to by the descriptive term "graining"; a term which we shall adopt here. It is evident that salting out may vary in type during the course of the reaction, or may not necessarily occur at all.

Although it may well be that saponification proceeds in stages so that diglyceride is first formed from the triglyceride and is then successively saponified to monoglyceride and glycerol, the demarcation into these stages cannot be observed in saponification with aqueous alkali. These reactions proceed with comparable velocity, and hence the outside layer of each droplet of oil will be completely decomposed, whilst the interior remains unaffected.

Further work is necessary to determine the exact influence of these factors.

#### *Experimental Method.*

*Chemicals used.*—Standard solutions of sodium hydroxide were made by dissolving sodium drippings, free from carbon dioxide, in recently boiled, distilled water. The solutions were standardised by titration against standard hydrochloric acid and kept in flasks fitted with guard tubes of potassium hydroxide. Standard hydrochloric acid was prepared by the method of Hulett and Bonner (*J. Amer. Chem. Soc.*, 1909, **31**, 390), the required concentration being obtained by diluting a weighed quantity of this standard acid with the calculated amount of recently boiled, distilled water.

Standard alcoholic solutions of sodium hydroxide (used in analysis) were made up in the same way, using recently boiled absolute alcohol. They were standardised just before use.

The oils used were of two kinds :

(1) Commercial oils—cocoa-nut oil and soja-bean oil, obtained through the kindness of Chris. Thomas and Bros., Ltd. These oils had previously been carefully neutralised, since otherwise the varying amount of free fatty acid present in commercial oils as usually employed, would have greatly influenced the rate. The mean molecular weight of the fatty acids from cocoa-nut oil was 214·1 and from soja-bean oil 284·9.

(2) Pure triglycerides—triolein and tripalmitin were obtained

from Kahlbaum. The purest chemicals obtainable were used throughout.

*Apparatus employed.*—The apparatus used simply consisted of a three-necked, round-bottomed flask resting on a sand-bath. A reflux condenser was fitted to one neck; through the other two necks passed a thermometer and a stirrer. The stirrer was a small silver propeller, made from a silver disk, bound to the roughened end of a glass rod with silver wire. When in use, the stirrer was run directly by an electric motor. The rate of stirring was kept constant (about 2,400 revs./min.) and recorded in each case.

In some experiments, where "bunching" occurred,\* it was found necessary to replace the sand-bath by a water-bath to which some glycerol had been added. By immersing the flask in this bath, it was possible to keep the contents at the required temperature (100—105°) without involving the risk of cracking the flask, due to the extreme local heating which occurred when scarcely any liquid was present.

*Experimental Procedure.*—The method of experiment is to measure 50 c.c of standard alkali into the flask and heat it to boiling. A weighed quantity of oil (usually an equivalent amount) is then added and stirring commenced. Boiling and stirring are continued for a definite time, whereupon a sample is removed for analysis and the reaction in it stopped by the addition of acid. Usually a separate experiment was set up for each measurement, and measurements were made in duplicate at least.

*Method of Analysis.*—(1) A sample is taken and acidified with a known volume (excess) of hydrochloric acid. This throws the soap out of solution in the form of fatty acids.

(2) The oil phase and aqueous phase are now separated by filtration, the filter-paper first being wetted with water. The oils are washed with water until free from hydrochloric acid.

(3) Titration of the filtrate gives the quantity of hydrochloric acid in excess, and therefore *the total weight of sodium* in the sample as soap and free alkali.

(4) The oils are dissolved in absolute alcohol and titrated with

\* "Bunching," "balling," "gumming" (?), "going stringy" (?), refer to the unmanageable condition of the contents of the soap pan when the soap is all in homogeneous solution and the viscous mass is filled with fine bubbles of air or steam. It is avoided by maintaining sufficient concentration of alkali or salt to ensure salting out either as two liquids or as curd and lye. Even where the contents of the soap pan appear to be homogeneous in normal working, closer examination would probably prove in every case that salting out had actually occurred, as can be seen by the separation into two liquid layers when a specimen is removed and allowed to stand, without stirring, in a closed glass vessel for several days at 100°.

standard alcoholic sodium hydroxide (water is added just before the titration is complete so that the end-point occurs in 60—80 per cent. alcohol). This gives the amount of free fatty acid, from which follows directly *the weight of sodium which was combined in soap*.

(5) The last result together with the saponification value\* of the oil gives the weight of oil saponified, which can then be expressed as a percentage of the amount of oil taken. The saponification values of the oils used were 255 for cocoa-nut oil and 190 for soja-bean oil.

### *Experimental Results.*

(a) *Effect of Stirring.*—The first experiments were necessarily of a semi-qualitative nature. Cocoa-nut oil was used and *N*-sodium hydroxide in approximately equivalent amounts. These constituents were vigorously boiled together for an hour in the apparatus previously described, but without mechanical stirring. It was found that under these conditions the rate was extremely slow, only 2.5 per cent. of the oil taken being saponified in an hour. On pouring the reaction mixture into a measuring cylinder, it separated into two layers almost at once, practically all the oil collecting in the top layer. This showed that very little of the oil had been emulsified, but this portion was in the form of droplets a fraction of a millimetre in diameter.

This rate was obviously too slow to be convenient for experimental purposes. With the hope of increasing the emulsification, and therefore the rate, the stirrer was introduced. The desired effect was obtained, for in an hour (still using *N*-sodium hydroxide) 45—50 per cent. of the oil taken was saponified. That is, the stirring had increased the initial rate about twenty-fold.

Experiments with (1) no stirring, (2) reduced rate of stirring, and (3) part-time stirring, were performed. Results showed that with no stirring, even with vigorous boiling, initial reaction was always slower than with stirring. Cocoa-nut oil, however, stirred for the first half-hour only, reacted as far in an hour as when stirred for the whole time. These few experiments would appear to indicate that it is the initial stirring which matters; once the oil is emulsified, and sufficient soap has been formed to aid this process by stabilising the emulsion, the reaction proceeds quite as quickly without stirring. However, we have repeatedly observed that it is not until the

\* The saponification value of an oil is the number of milligrams of potassium hydroxide required to saponify 1 gram of oil completely. It can be obtained by totally saponifying a known weight of the oil with excess of alcoholic potassium hydroxide and determining the amount of potassium hydroxide used (For practical details, see "Oils, Fats, and Waxes," by Fryer and Weston, Part II).

reaction between cocoa-nut oil and *N*-sodium hydroxide has gone to the extent of 90 per cent. that all the oil is permanently emulsified.

Experiments in duplicate with reduced rate of stirring showed that reduction from 2,400 revolutions per minute to 980 revolutions per minute reduced the rate from 45 and 50 per cent. saponification in one hour, to only 19 and 22 per cent. This result shows that the amount of saponification in one hour was proportional to the rate of stirring, even when stirring was already extremely vigorous. The saponification is very roughly proportional to the rate of stirring raised to the power  $\frac{2}{3}$ . This shows clearly the essentially physical basis of the rate observed. The general results are contained in Table I.

TABLE I.\*

*Comparison of percentage saponification of oils boiled with aqueous alkali under various conditions of stirring.*

Oil.	Concn. of NaOH.	Time (hours).	Initial stirring.		Oil saponified per cent.	Percentage of oil saponified with standard stirring (2,400 revs./min.) during the whole time.	
			Dura- tion (hour).	Rate (revs. per min.).			
Cocoa-nut	1 <i>N</i>	1	$\frac{1}{2}$	2,400	32	45—50	
	"	1	$\frac{1}{2}$	"	56	45—50	
	"	4	1	"	92	91	
	"	1		none	2.5	45—50	
	"	2		"	12—20	74—80	
	"	4		"	31—52	91	
	"	2 <i>N</i>	1		"	75	96
	"	1 <i>N</i>	1	1	980	19—22	45—50
Soja-bean	1 <i>N</i>	1		none	28—36	67—70	

\* The large differences in the results of the duplicate experiments with no stirring can be explained by the fact that boiling is very uneven. The higher figures were obtained when boiling was good; the lower ones, when violent bumping occurred. The kind of boiling naturally affects the size and number of oil droplets present.

(b) *Standard Experiments.*—Having established a definite method of attack, a series of standard experiments was carried out with the four typical oils.

A complete set of experiments was made of duration of half-hour, one hour, and four hours with each oil in turn, using successively *N*-, 2*N*-, and 4*N*-sodium hydroxide solution. Equivalent quantities of oil and alkali were used in each case, and stirring was uniform except where bunching made the mixture so viscous that stirring was impossible.

In most cases the results were reproducible within a few units per cent.; in other cases, they varied by several units per cent., but

these discrepancies were usually due to the occurrence of frothing or bumping, causing difficulty in manipulation, or salting out increased the difficulty of taking a sample for analysis (see Table II).

TABLE II.

*Percentage saponification when oils are vigorously stirred with an equivalent amount of boiling solution of sodium hydroxide.*

Oil.	Time.	Percentage saponification with		
		<i>N</i> -NaOH.*	2 <i>N</i> -NaOH.*	4 <i>N</i> -NaOH.*
Cocoa-nut	20 minutes	4	—	—
	$\frac{1}{2}$ hour	18	95—96	93—94 †
	1 " "	45—50	95	95—97 †
	2 hours	74—80	—	—
	4 " "	91	96—98	96—98 †
	1 day	95	99·8	—
Soja-bean	2 days	97	—	—
	$\frac{1}{2}$ hour	12 ††	17—18 †	36—38 †
	1 " "	67—70 ††	92—93 ††	97—98 ††
Triolein	4 hours	97—98 ††	94—98 ††	96—98 ††
	$\frac{1}{2}$ hour	65	37—47 †	80 ††
	1 " "	77—84	85 ††	88 ††
Tripalmitin	4 hours	89—90	91—93 ††	92 ††
	$\frac{1}{2}$ hour	70—72	100 †	95 †
	1 " "	84—86	—	—
Tristearin	$\frac{1}{2}$ hour	13	—	—
	1 " "	18—32	—	—
	4 hours	—	90 ††	—

\* These normalities refer to the mols. per litre of the initial alkali taken at room temperature.

† = Salting out (curdling, graining) occurred.

‡ = Bunching finally occurred.

§ = Sample taken just as salted-out soap was redissolving.

The results for the separate oils are as follow :

*Cocoa-nut Oil.*—This oil shows a slow initial period with *N*-alkali, and very great slowing off in the last stages of the reaction. With 2*N*-alkali there is no salting out; the rate is therefore greatly increased and the reaction goes to the extent of 95 per cent. in the first half-hour. With 4*N*-alkali salting out occurs at first, but the salted-out soap redissolves before the end of the first half-hour, so that the rate (except perhaps in the very initial stages, which have not been investigated) runs almost parallel to that with 2*N*-alkali.

*Soja-bean Oil.*—With *N*-alkali the rate is slower, in the initial stages, than with cocoa-nut oil. This is probably due to the slight salting out which occurs even at this low concentration. The maximum rate comes somewhat earlier than with cocoa-nut oil, the reaction now going to the extent of 70 per cent. in an hour as compared with 50 per cent. After four hours, the reaction has gone

to the extent of 97 per cent.  $2N$ -Alkali causes salting out, but the rate is slightly increased during the initial periods.  $4N$ -Alkali again increases the rate, especially during the initial period, but in no case does the reaction go further than 98 per cent. in four hours.

*Triolein.*—With  $N$ -alkali the slow initial period must be very short, for the reaction goes to the extent of 65 per cent. in the first half-hour. On the other hand, the slowing off at the end of the reaction is very pronounced, for after four hours only 90 per cent. of the oil is saponified.  $2N$ -Alkali causes salting out and almost halves the initial rate. After the first half-hour, the salted-out soap dissolves and the rate is increased, so that in an hour the reaction has gone as far as with  $N$ -alkali in one hour (85 per cent.), and in four hours, slightly further (92 per cent.).  $4N$ -Alkali causes salting out, but also increases the rate, so that the reaction proceeds to the extent of 80 per cent. in the first half-hour. After four hours, however, only 92 per cent. of the oil is saponified, again showing the very great decrease in rate during the later stages of the reaction with this oil. Although there is no direct experimental evidence, these results suggest very forcibly that here, at any rate, the whole of the reactive surface between the two phases, aqueous alkali and oil, has become coated (in the later stages) with a layer of soap through which diffusion is difficult, and therefore the reaction is extremely slow.

*Tripalmitin.*—This fat seems to be more easily saponified than either of the previous ones. With  $N$ -alkali in half an hour, 71 per cent. of the amount of fat taken is saponified. There is no salting out. With  $2N$ -alkali, salting out occurs, but the salted-out soap very soon redissolves and the reaction is complete in less than half an hour.  $4N$ -Alkali also causes salting out; the rate is slightly diminished, 95 per cent. of the fat being saponified in half an hour.

(c) *Effect of Added Sodium Chloride.*—A series of experiments was carried out similar to the previous ones except that the initial solution of sodium hydroxide contained also a known amount of sodium chloride. The results are collected in Table III.

(d) *Effect of Soap Initially Present.*—To find the effect of having soap present at the beginning of the reaction, an alkaline soap solution was made by adding 0.5—1 gram of the fatty acids obtained from cocoa-nut oil to 50 c.c. of boiling  $N$ -sodium hydroxide solution and stirring for a few minutes. This converted the fatty acids into soap. Oil was then added, equivalent in quantity to the calculated amount of remaining alkali, and the mixture boiled and stirred for a definite time, as in previous experiments.

The result was that the rate was increased; 75 per cent. of oil

TABLE III.

*Comparison of the rate of saponification of oils when boiled with equivalent quantities of aqueous alkali and varying amounts of common salt, with and without stirring.*

Oil.	Concn. of NaOH.	Concn. of NaCl.	Time (hour).	Time of stirring (hour).	Oil saponified per cent.	Percentage of oil saponified under the same conditions without NaCl.
Cocoa-nut	N	1N	1	1	92	45—50
"	"	3N	"	"	96	"
"	"	5N	"	"	96	"
"	"	"	$\frac{1}{2}$	$\frac{1}{2}$	17.5	4
"	"	"	1	$\frac{1}{2}$	41	32
"	"	"	"	none	18	2.5
Soja-bean	"	0.5N	"	1	57	67—70
"	"	1N	"	"	55	"
"	"	5N	"	"	20—35	"

was saponified in the first hour as compared with 45—50 per cent. when no soap was initially present.

By varying the amount of stirring, it was found that five minutes' initial stirring, when soap was present, caused the same amount of oil to be saponified in one hour as when no soap was initially present but stirring was continued during the whole of the time (49 per cent.).

TABLE IV.

*Comparison of the rate of saponification of cocoa-nut oil boiled with an equivalent amount of aqueous alkali and about 1 gram of soap, with whole-time and part-time stirring.*

Concn. of NaOH.	Wt. of fatty acid (gram).	Time.	Time of stirring.	Percentage saponification.	
				Obs.	Standard.
1N	0.756	1 hour	1 hour	75	45—50
"	0.751	1 "	5 mins.	49	"

(e) *Effect of One Constituent in Excess.*—Experiments were carried out both with alkali and with oil in excess. The results are shown in Table V.

TABLE V.

*Percentage saponification when cocoa-nut oil and aqueous alkali are boiled together with vigorous stirring, and one constituent is in excess.*

Concn. of NaOH.	Time (hours).	Propn. of oil to NaOH.	Saponification.	Percentage saponification when oil and NaOH are present in equivalent amount.
1N	4	3 : 4	97% of oil	91
"	4	5 : 4	98.5% of NaOH	91
"	2	11 : 10	87% of NaOH	74—80
2N	1	1 : 2	95—99% of NaOH	95—97



In both cases the amount saponified, of the constituent present in less amount, was greater than where the reactants were equivalent. The explanations for these results are two :

(1) When the alkali is in excess the concentration is not so low at the end of the reaction.

(2) When the oil is in excess the surface exposed must be greater throughout.

(f) *Effect of Temperature.*—Experiments were carried out by vigorously stirring together amounts of the neutral soja-bean oil and alkali at room temperature, and also by grinding in a mortar at room temperature. In both cases, the reaction did not start. An observation was also made that directly the stirring or grinding ceased, the mixture separated completely into two layers, showing that no emulsion had been formed. This was probably the reason that scarcely any reaction took place.

It is somewhat difficult to obtain a well-defined value for the temperature coefficient of a reaction the rate of which is of so complicated a form. It was decided to make use of the observation in standard experiments with cocoa-nut oil and *N*-alkali, that the rate after the first and up to the fourth hour may be represented by a unimolecular formula. The materials in two such experiments, which were carried out under standard conditions at 100° for one hour, were then allowed to cool to about 60°, and the stirring was continued for three hours longer. The first experiment indicated that the reaction goes 1.3 times faster for each rise in temperature of 10°. The second experiment, in which the reaction had proceeded much further before cooling, gave a value 1.6. It is well known that the temperature coefficient of typical chemical reactions is such that a rise of temperature of 10° doubles or trebles the rate, whereas the temperature coefficient of physical processes such as diffusion lies between 1.2 and 1.3 where the conditions are kept constant. Enhanced convection, through the greatly diminished viscosity, fully accounts for the slightly higher value of the temperature coefficient in the present case.

#### *Discussion of Results.*

(a) *Mechanism of the Reaction.*—For a fuller discussion, reference should be made to "The Fourth Colloid Report of the British Association for the Advancement of Science," 1922. Temperature coefficient, effect of stirring, of emulsification, and of salting out alike indicate that the reaction proceeds in the surface between the oil globules and the aqueous alkali, and that the effective rate is determined by the rate at which the alkali is brought to this surface and the resulting soap removed.

(b) *Completeness of Saponification.*—Lewkowitsch (*J. Soc. Chem. Ind.*, 1907, **26**, 590; *Z. angew. Chem.*, 1907, **20**, 951) considered that saponification without excess of alkali must be very incomplete because of the very appreciable hydrolysis of soap solutions which he assumed to occur. He adduced experiments in which oils were boiled with the exact equivalent of alkali, and in which the boiling “was continued beyond the time required on a manufacturing scale,” only 93 to 94 per cent. of oil and of alkali being saponified.

Now that we know, from the measurements of hydrolysis-alkalinity by means of *E.M.F.*, conductivity, catalysis, and ultra-filtration, carried out in this laboratory, that the hydrolysis-alkalinity of concentrated solutions is much less than  $0.001N\text{-OH}'$ , it is clear that equilibrium lies much nearer to a complete reaction than was assumed, and that the reaction must proceed to the extent of more than 99.9 per cent. before equilibrium is obtained. It would appear that insufficient time had been allowed in the soap-boiling experiments of Lewkowitsch. This is borne out by the experiment in Table II with  $2N$ -alkali and an exactly equivalent amount of coconut oil, where the reaction proceeds to the extent of 99.8 per cent. in twenty-four hours. Likewise the tripalmitin is quantitatively saponified in half an hour under these conditions.

(c) *Completion of the Reaction with Excess of Alkali or Oil.*—It is when oil and alkali are taken in exactly equivalent quantity that completion of the reaction is slow. This is illustrated by the experiments of Table V. If oil and alkali are present in equivalent quantities, the reaction must finish with extreme slowness, since towards the end both surface of contact and concentration of the alkali are rapidly decreasing. If, on the other hand, either the alkali or especially the oil is in excess, the completion of the reaction may simulate a unimolecular reaction, conditions of emulsification, etc., remaining the same.

It is perhaps necessary to point out that the excess of oil does not act through displacement of the equilibrium, since this is a heterogeneous system and the active mass of the oil is independent of the amount present, no matter how greatly this is varied. Thus the action of a large excess of oil is merely to facilitate the rate of reaction by exposing the alkali to a larger area of contact.

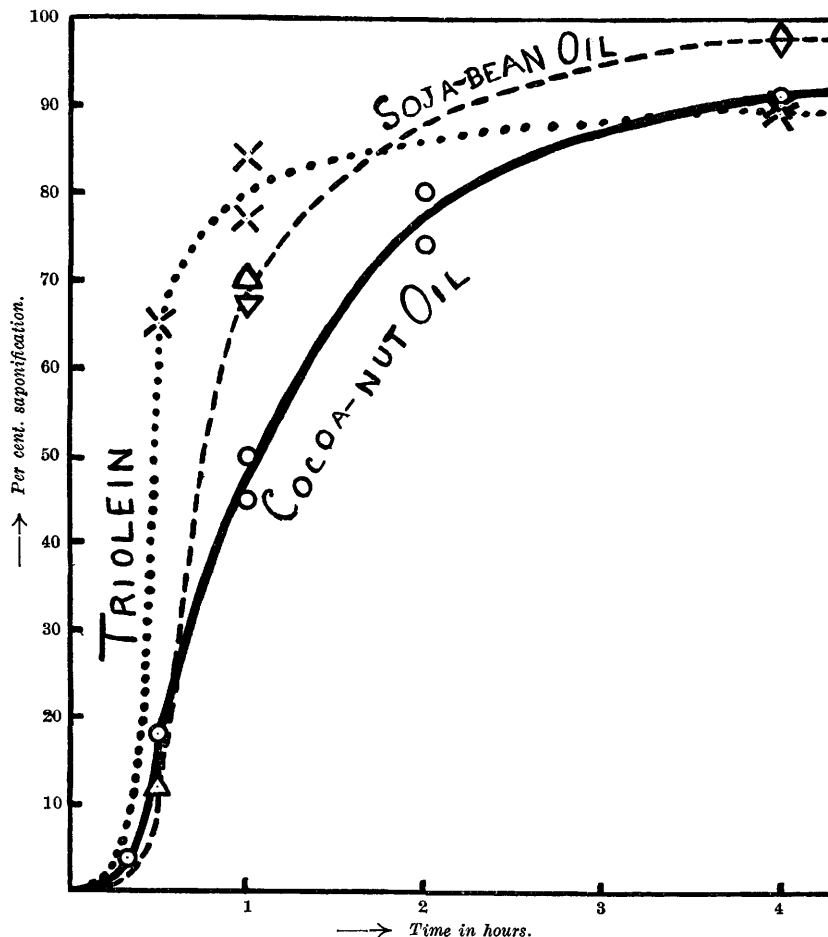
(d) *General Course of the Reaction.*—Nearly all the experiments here recorded were carried out with oil from which all free fatty acid had been removed, and with no soap initially present. The observed rate is therefore characterised by an initial incubation period, thereafter the reaction proceeds very rapidly, but there is quite unusual retardation of the very last stages of the reaction, especially when alkali and oil are taken in exactly equivalent amount.

It will be noted, from Fig. 1, that each of the three stages is different for the various oils employed.

The initial incubation period is obviously due to lack of emulsifying agent to stabilise the oil in a state of fine subdivision and corre-

FIG. 1.

*Rate of saponification when neutral oils are boiled with 1.0 N-aqueous NaOH with intense stirring (2,400 revs. per min.).*



spondingly large exposed surface. In ordinary soap-boiling practice, emulsification is effected by the initial addition of soap as well as by the presence of often very large amounts of free fatty acid in the oils used. The same pronounced effect is shown in the experiments

of Table IV. It will be seen that salting out of the emulsifying soap retards the reaction.

(e) *The Salting-out of Soap*.—Soap solutions containing only a moderate amount of salt or alkali are homogeneous, although the homogeneous liquid is extremely viscous. A slight further addition of salt causes this homogeneous liquid to separate into two liquid layers. It is only over a narrow range of concentrations of salt that two liquid layers are formed. A higher concentration of salt “grains out” the soap as solid white curd floating on a strong brine or “lye” containing only traces of soap. Here there are two phases present; namely, solid curd fibres and liquid lye. No further effect is produced by increasing the salt or alkali up to saturation point, except that the curd fibres become less hydrated.

The comparatively narrow range of concentrations in which two liquid layers can co-exist is of great importance to the soap boiler, because it is within a part of this region that most commercial soaps are finally prepared, and the endeavour is made to carry out saponification under such conditions.

For the purposes of this paper there is a great complication in that there are three possible pairs of aqueous liquid; namely, “neat soap,” “nigre,” and “lye.” For a full discussion and the corresponding experimental evidence, reference must be made to as yet unpublished communications by Burnett and Langdon referred to in the “Fourth Colloid Report” (*loc. cit.*). A concentrated soap solution, on the addition of sufficient salt, forms two liquid layers, the upper one of which is neat soap and the lower nigre; a dilute soap solution correspondingly falls or opens into two liquid layers, the upper of which is nigre and the lower lye. In both cases a slight further addition of salt causes the nigre to disappear, resulting in both cases in a liquid layer of neat soap resting on lye. Neat soap contains 30 per cent. by weight of water and is eight to ten times weight normal with respect to soap. Nigre is about  $\frac{3}{4}N$  with respect to soap; lye is but a few hundredths normal with respect to soap.

During the experiments here recorded, the amount of alkali was steadily altering, and whereas at first the alkali might have been in such concentration that all the soap formed for some time was grained out, the diminishing alkali passed rapidly through the narrow zone involving pairs of liquid layers, and all the later stages of the reaction must have proceeded in homogeneous solution, that is, homogeneous apart from the liquid globules of oil present throughout. Hence the information in this paper refers chiefly to two sets of conditions:—(a) where the soap formed is grained out, and (b) where the aqueous phase is a homogeneous solution of soap and alkali.

The soap boiler compensates for the decreasing alkali by adding salt from time to time as the appearance of the mixture seems to require. A further communication will include experiments in which these physical factors are kept constant. In soap boiling, it is customary to complete the saponification after several days by "boiling on strength," that is, boiling with strong alkali.

(f) *Rate of Saponification where the Aqueous Solution is Homogeneous.*—It should be pointed out at once that this heading comprises all of the experiments with initially normal alkali, except perhaps just the beginning of the experiments with soja-bean oil. Further, the experiments with cocoa-nut oil are of exceptional interest in this connexion, because  $4N$ -alkali is required to salt out the resulting soap, even as liquid layers. Finally again, this heading includes all the final stages in which a concentration of remaining alkali had fallen below  $1N$ .

Although a quantitative expression for the influence of alkali cannot here be formulated, the fact emerges very clearly that the rate of saponification is greatly increased by increase in the concentration of alkali. Naturally, increased concentration of alkali increases the rate at which it is delivered to the reaction surface of the oil globules.

The reason for the slow final stages in these saponifications is presumably the highly viscous nature of the medium towards the end, where all the soap is in homogeneous solution and the alkali in this soap solution is dependent on diffusion for reaching the reaction surface. Such a process is incomparably slower than convection with the intense stirring which it was possible to employ at the beginning of the reaction. A further effect in viscous solution is the accumulation of soap in the neighbourhood of the interface, and it is in the immediate interface that the concentration of alkali cannot fall below the hydrolysis concentration of  $0.001N$ . The effect of salt at this stage will be discussed in a further communication.

The effect of salt on homogeneous soap solutions has been shown in other communications to be similar to an increase in the concentration of soap itself. That is, salt converts crystalloidal soap into colloidal electrolyte. In Table III it is seen from the experiments with cocoa-nut oil that the addition of salt greatly increases the rate, probably by promoting emulsification up to the point where salting out occurs.

(g) *Rate of Saponification when the Soap is Grained Out.*—Graining out the soap in itself reduces the rate to a fraction of its previous value. The rate is at least halved whether the salting out is effected by salt or by alkali. This must be due to the encrustation of the reacting surface with the solid, salted-out soap. Once graining-out

occurs, further addition of alkali increases the rate of saponification almost in direct proportion to the concentration of alkali. This effect of increased alkali may therefore soon mask the initial reduction in rate. In every case here recorded saponification with  $4N$ -alkali is at least as quick as with  $N$  or  $2N$ , and in most instances it is slightly faster.

Not only is graining in itself a hindrance, but further addition of salt intensifies the effect. It is evident that any similar effect in the case of alkali must be overbalanced by the enhanced rate at which alkali is supplied to the reaction surface. Further experiments are being undertaken in order to test and extend the conclusions here recorded.

#### *Summary.*

1. When neutral oils are boiled with alkali, the rate of saponification is at first negligible, then rapid, with abnormal retardation of the final stages, especially when alkali and oil are present in equivalent amount.

2. Vigorous stirring increases the initial rate by nearly twenty-fold, since the reaction depends largely on the surface of oil exposed.

3. With insufficient alkali to cause salting out, the rate is very much increased by increase in the concentration of alkali.

4. The rate depends largely on the degree of emulsification.

5. Salting-out in itself diminishes the rate by at least one-half. Further addition of alkali increases the rate almost in direct proportion to the amount added, so that a large increase in concentration of alkali produces the fastest rate.

6. When the alkali is sufficient to cause salting-out, addition of salt retards the saponification.

7. The temperature coefficient is less than 1.5 and the rate is less than proportional to the rate of stirring, both showing that the observed saponification is largely governed by physical processes.

8. A saponification may be completed within a few hours to the extent of 99.8 per cent.

9. It may be noted that in these experiments much quicker saponification is effected than in soap-boiling practice, in spite of neutralised oils, and alkali initially free from soap, having been employed.

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