to be lubricated but does not cohere to itself. In the use of oil as a lubricant, it is also true that the oil adheres to the lubricated surfaces and soon forms two layers of oil which glide over one another. We have then strong adhesion on the part of lubricant and a weak cohesion. The same is true of soap solutions and will explain their slipperiness and lubricating power. The slipperiness we feel when alkali is used on the hands is probably due to its action on the skin or on the material which keeps in place the epithelial cells. The actual removal of these cells with the impurities attached to them and covered by them would account for the cleansing action of alkali and alkali carbonate on the skin.

The position here taken is then: that the cleansing power of soap is largely or entirely to be explained by the power which it has of emulsifying oily substances; of wetting and penetrating into oily textures; and of lubricating texture and impurities so that they may be removed easily. It is thought that all of these properties may be explained by taking into account the low cohesion of the soap solutions and their strong attraction, adhesion or affinity to oily matter, which together cause the low surface-tension between soap solution and oil.

A STUDY OF SOAP SOLUTIONS.

By H. W. Hillyer.

Received March 20, 1903.

It was noted in the preceding article that while toward air the surface-tensions of soap solutions vary but little as the concentration is changed, the surface-tension between soap solutions and oils is rapidly diminished as the concentration is increased. To ascertain the law connecting concentration and surface-tension, the following experiments were made. They not only show this relation but serve to confirm the idea that the diminution of surface-tension is dependent solely on the amount of undecomposed soap present in the solution. Unfortunately in this pioneer work it was not realized how desirable it was to have the same kerosene for all experiments, and consequently the results are not strictly and numerically comparable except in the cases which are plotted together. But it is thought best at this time to publish these results, as their general tendency is quite clear and as they serve to indicate the basis on which rests the method for evaluating soaps which will soon be published.

A decinormal solution of sodium oleate was prepared by dissolving 14.1 grams of oleic acid in 500 cc. decinormal sodium hydroxide solution. The solution was almost completely clear. It was then filtered. The solution was diluted successively to lower concentrations and the number of drops formed when these various solutions were passed through kerosene was noted. Duplicate counts were made and the number of drops found in the separate counts are indicated.

SODIUM OLEATE.

Concentration.	N/10.	N/20.	N/40.	N/80.	N/160.	N/320.	N/640.	Water.
No. drops	464 460	269 270	184 181	116 116	80 78	51 54	35	20
Another set of solutions...	..	292	184	118 124	74 77	49 47	32 31	.. ..

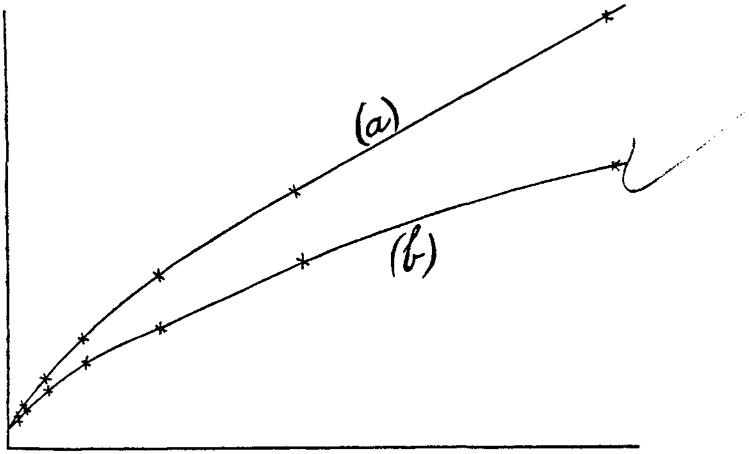

Fig. 1.

In the diagram (Fig. 1, *a*) the ordinates show the number of drops formed and the abscissas show the concentrations. The number of drops is not proportional to the concentration but falls below proportionality as the concentration increases. In another experiment, the solutions were very carefully made and after preparation were placed in stoppered flasks in a large tank of water that they might be kept as nearly as possible at an average room temperature. The special object of this experiment was to ascertain whether any change took place on standing which would indicate that a hydrolysis of the soap was gradually going on. In this case the kerosene was the same throughout the experiment, but different from that used in the last. For each count the kerosene was changed except where the solutions were very dilute. The solutions of various concentration were prepared as rapidly as possible and then the counts made. After this the solutions were kept at the temperature of the tank of water and the counts repeated from day to day.

SODIUM OLEATE, TIME AND DILUTION.

Concentration.	N/10.	N/20.	N/40.	N/80.	N/160.	N/320.	N/640.	Water.
December 2nd	297	196	125	88	63	41	26¼	14
December 3rd	296	200	126	87	61	40½	26½	14
December 5th	..	194	123	85	62	40½	26½	..
December 8th	301	..	132	..	59½	..	26½	..

From this it seems that in the course of six days no change takes place in the surface-tension. There is no evidence of any decomposition of the soap by a diminution of the number of drops in either strong or dilute solutions. The curve (Fig. 1, *b*) showing the relation of concentration to number of drops is here shown in connection with that given above that it may be seen that the two have the same shape. They should not, however, be compared numerically except to enforce the fact that the effects are quite different with different samples of kerosene. When sodium oleate solutions stand in uncorked flasks, the carbon dioxide of the air decomposes the soap and the number of drops formed by a given solution gradually diminishes. This is especially marked in case of dilute solutions.

SODIUM PALMITATE AND STEARATE.

Pure sodium palmitate and stearate are very little soluble in cold water, so little in fact that it is difficult by shaking them with cold water to produce a foam. Palmitate and stearate, when rubbed on the hands with cold distilled water, do not give the effect of soap but seem more nearly like paraffin or tallow. On account of this small solubility in cold water, it was necessary to devise a method of working at a higher temperature. The apparatus finally used is very simple. It consists of a beaker of about 700 cc. capacity provided with a cover of zinc with its edges turned down. In the cover are three holes one for the thermometer and two large enough to receive short wide test-tubes. One of the test-tubes serves as a reservoir to hold the hot soap solution to be used, while the other is the working part of the apparatus. After the water in the beaker has been heated to boiling, a supply of the solution to be tested, which has been heated to bring the soap into solution, is placed in the reservoir tube. Then 15 cc. of kerosene are placed in the working tube and the pipette put in. When all is thoroughly heated to the boiling temperature, the pipette is filled with the solution, placed with its end below the oil and the number of drops counted. At first, great difficulty was encountered in getting concordant results but it was learned that when the lower end of the pipette was *ground* off the numerous minor capillary tubes in the glass of the lower part of the pipette continually gave out small amounts of air and when this formed into bubbles on the end of the pipette it caused an increase in the number and decrease in the size of the drops which were forming. As this exudation of air was irregular and introduced a new factor in the surface-tension problem a means was necessary to prevent it. The remedy was to so shape the pipette that the lower end after grinding could be heated to the point of fusion until all the small capillaries were closed without closing the main capillary or narrowing too much the surface on which the drops were to form. The form finally worked out is shown in the accompanying sketch (Fig. 2).

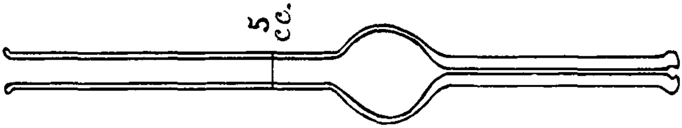

Fig 2.

Twentieth-normal sodium palmitate was made by treating 12.8 grams palmitic acid with 500 cc. decinormal sodium hydroxide and 500 cc. water, and heating all on the water-bath. The solution was quite clear. Small quantities of palmitic acid were added until oil droplets were plainly visible and the solution was filtered. This solution was then diluted with hot water to make the concentrations used below and these were kept on the steam-bath at 60°-70°. None of them were more than slightly cloudy at 60°-70°. They were tested in the apparatus just described, and gave the number of drops here set down.

SODIUM PALMITATE.

Concentration.	N/20.	N/40.	N/80.	N/160.	N/320.	N/640.	N/1280.
No. drops	424	315	223	94	49	32	23
	..	..	226	88	49	33	23½

On plotting these data, the curve (Fig. 3, *a*) results. The sag in the curve near its origin was thought so remarkable that a second set of solutions was prepared and tested.

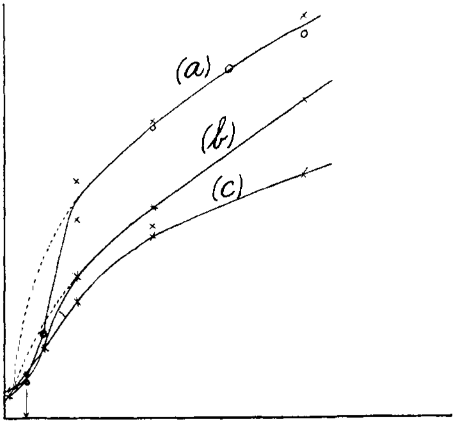

Fig. 3.

N/20.	N/30.	N/40.	N/80.	N/160.	N/320.	N/640.	N/1280.
403	368	308	208	90	40	31	24

When these data are plotted, a curve is obtained in shape like that obtained before and practically indentical with it. If the same law connected concentration with the number of drops at low as at high concentration, the curve would be a smooth one extending to the point showing the number of drops made by water, as indicated by the dotted line. That the curve falls below this line may be explained by supposing that in the dilute solutions a marked hydrolysis takes place. Krafft and Stern found that it was necessary to dilute a solution of sodium palmitate till it contained only about 1 part in 1000 before the precipitate formed on cooling had the composition of the true acid salt, $C_{16}H_{31}O_2Na$, $C_{16}H_{32}O_2$. It is to be noted that the greatest depression in the curve above is in the region where the concentration is near to 1 part in 1000 of water. This point is marked by the arrow. If this is a true explanation, it is an interesting confirmation of the supposition that the number of drops is a function of the amount of undecomposed soap present. The hydrolysis lessens the amount of soap, and farther, the acid salt may in this case, as in the case of sodium oleate, actually diminish the number of drops which would be formed if the soap were alone. It would seem that we have here a proof that actual hydrolysis takes place while all of the substances are in solution. At the temperature at which the work was done the solutions are quite clear and show no sign of a precipitate.

SODIUM STEARATE.

Sodium stearate solution (one-twentieth normal) was made by dissolving 2.84 grams chemically pure stearic acid in 100 cc. hot decinormal sodium hydroxide solution and diluting to 200 cc. with hot water. The dilute solutions were made as before and the number of drops made by each determined at 100°. None of the solutions at 100° show more than a very slight opalescence. The number of drops formed are shown in the table:

SODIUM STEARATE.

N/20.	N/40.	N/80.	N/160.	N/320.	N/640.	N/1280.
328	213	143	72	38	31	29
340	228	149		40	28	33

The curve (Fig. 6, *b*) showing these numbers in a graphic way has very much the same shape as that for sodium palmitate and here also the greatest hydrolysis is apparently at a point where there is present about 1 part of the salt to 1000 of water. By comparing the shape of these curves with that of sodium oleate at 100° it becomes evident that their peculiar form is not due to the action of the higher temperature. As a passing observation it may be noted that when the solutions stand in the cold, the precipitates formed in the N/160 solution and those of greater concentration, float in the solutions, while the precipitates formed in the N/320 solution and those of less concentration sink in the solutions, this change of relative density also taking place when the solution contains about 1 part of sodium stearate in 1000 of water.

SODIUM OLEATE AT 100°.

Sodium oleate solutions when tested at 100° show no special change in the form of the curve connecting concentration and number of drops from that belonging to the oleate in the cold. Since the data were obtained using the same apparatus and same kerosene as that used for the palmitate and stearate they are plotted in the same diagram at *c* (Fig. 3).

ROSIN SOAP.

The soap made by action of alkalies on colophony is so common a constituent of yellow soaps that a study of its solutions is of some interest, especially if we may gain knowledge of the reason of the disfavor with which the soap is regarded. A solution of rosin soap approximately decinormal was prepared by digesting in the cold powdered rosin in excess with decinormal sodium hydroxide solution as long as any rosin was dissolved. This solution was diluted with freshly boiled cold water to give the concentrations indicated below and each tested in the cold to learn the number of drops made by each.

ROSIN SOAP IN THE COLD.

Concentration.	N/10.	N/20.	N/30.	N/40.	N/60.	N/80.	N/160.	N/320.	N/640.
No. drops	361	236	201	151	118	78	47	32	26
	353	243	207	155	123	79	46	34	25

These results are plotted in curve *a* (Fig. 4). The same solutions were tested at 100°, using the same pipette and same kerosene.

ROSIN SOAP AT 100°.

Concentration.	N/10.	N/20.	N/30.	N/40.	N/60.	N/80.	N/320.	N/640.
No. drops	288	215	183	123	68	45	35	29
	289	215	187	127	67	45	35	28

These results are plotted in curve *b* (Fig. 4). The notable thing in both curves is the sag near the origin. The more dilute solutions give a smaller number of drops than might be expected if the same law held that governs with higher concentrations. If, as is indicated by the facts given in this and the preceding paper, the number of drops is a measure of the amount of undecomposed soap present in solution, it seems that with the rosin soap as with the palmitate and stearate a marked hydrolysis takes place in dilute solutions. The solutions with the exception of the decinormal and one-twentieth normal are much clouded, even in the cold, showing by this also that hydrolysis has taken place. The hot solutions, even the most concentrated, are cloudy. The hydrolysis indicated by this cloudiness is also shown by the fact that the curve for the hot solutions lies below that for the cold solutions. Elevation of temperature is favorable to diminution of surface-tension and a greater number of drops might be expected with all these solutions at the higher temperature but, as a smaller number is found, the explanation lies in the hydrolysis caused by heating the solutions.

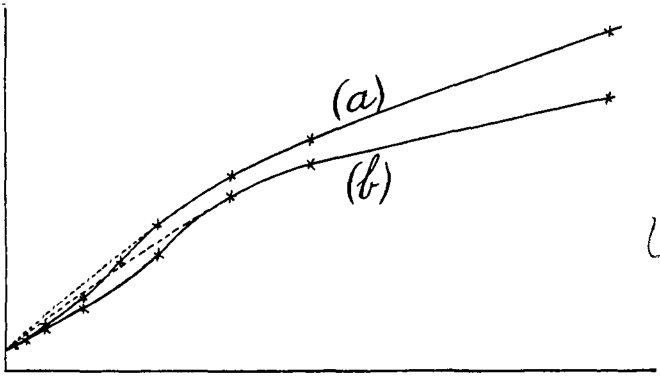

Fig. 4.

In looking over the results obtained, it is of interest to note their agreement with well-known facts in regard to the soaps. The oleate is very soluble in cold water and even in dilute solutions shows little hydrolysis. Soaps rich in oleate are useful for toilet purposes and for wool-scouring when cold water is used. Its stability in dilute solutions would make it of value as a detergent even until it is completely rinsed away and its ready solubility would make it easy to wash away.

For laundry work, dish-washing, and other work, when hot water is used, practical experience shows that the most desirable soap is a tallow soap. This is rich in palmitate and stearate with some oleate. As shown by the curves, the palmitate and stearate have a very high efficiency at a high temperature, especially when the concentration is great. When the concentration is lessened, marked hydrolysis takes place and the efficiency rapidly falls off, but with mixed soaps this low efficiency of the palmitate and stearate is supplemented by the relatively high efficiency of the oleate in dilute solutions, which will sustain the detergent effect until all impurities are washed away, including the acid palmitate and stearate which might otherwise be retained by the fabric. When the temperature is low, palmitate and stearate are so little soluble as to be of no practical value, since the only effect of water on them is to hydrolyze them and set free a small quantity of alkali which, according to the hypothesis here favored, has no detergent effect on neutral oils.

Rosin soap is usually regarded as a comparatively undesirable ingredient of soaps. By a test with decinormal solution, it is of about the same efficiency according to the dropping test in kerosene as sodium oleate. But when the dilution curves are studied, it is seen that dilute solutions, especially in the heat, show marked hydrolysis which is necessarily accompanied by separation of the rosin acids. Here the acid product of hydrolysis separates in a cloud and does not stay in solution as with the palmitate and stearate in the heat. The separated rosin acids may well settle on the fabric being washed and impart to it the odor of rosin, cause it to be yellow and make it ready to easily take up dust. This effect may be partially offset in using mixed soaps, by the other ingredients whose detergent action will tend to remove the rosin acids, but the evil effect will still, to some extent, remain.

In this work, when kerosene is used as the test substance, it is, of course, true that we are really measuring the detergent effect of the various soaps toward kerosene only. Some few observations show that toward other fats and oils the relative efficiency of the different soaps is different. It may be necessary to take this into account when judging the value of a soap for some special purpose.

LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY
OF WISCONSIN, March 17, 1902.

NOTES.

Note on the Bromination of Heptane.—Venable[1] found that the bromination of normal heptane from the *Pinus Sabiniana* yielded

---

[1] *Am. Chem. J.*, **10**, 237.