CLXXIX.—*Surface Tensions of Salts of the Fatty Acids and their Mixtures.*

By ERIC EVERARD WALKER.

THOSE salts of the fatty acids which are useful soaps lower the surface tension of water to an altogether abnormal extent; a study of the surface tension of soap solutions is therefore of very special interest. The object of the present paper is to examine this property under a variety of conditions and thereby to learn something of the changes which take place in solution when the temperature or concentration is varied or when one soap is wholly or partly replaced by another of the same or a nearly related series.

It was believed that the information so gained would lead to a better understanding of the manner in which different soaps interact in solution to produce an effect on the surface tension which is either greater or less than would be expected from the proportions in which the constituents are present.

The results have to a large extent justified expectations, in that a theory primarily advanced in order to explain the manner in which surface tension varies with temperature, concentration, and the number of carbon atoms, has been found capable of explaining the behaviour of mixed soaps in solution.

Measurement of Surface Tension.

The surface tension was measured with a simple form of dropping pipette. It is not claimed that the results obtained are of absolute value, and in fact it was found that different pipettes gave different results. It is, however, well known that the apparent surface tension of soap solutions depends to a very marked extent on the exact conditions under which it is determined. All that can be claimed is that the conditions were carefully standardised so that the results might be of comparative value. The pipette and receiver were completely immersed in a constant-temperature bath, necessitating a simple device outside the water-bath for regulating the rate of flow. This consisted of a U-tube connected with the upper end of the pipette and fitted with a tap on the longer arm. Water was allowed to flow from the longer arm into the shorter at a regulated speed, thus allowing the soap solution to flow out of the pipette at a similar rate.

The required quantity of acid was weighed out, dissolved in alcohol, and neutralised with an alcoholic solution of sodium

hydroxide. This was evaporated, the residue dissolved in water and the solution made up to the required weight. The water used was redistilled and the first and last thirds were rejected. The alcoholic sodium hydroxide solution was made up by dissolving sodium in alcohol redistilled over lime. All concentrations were expressed in terms of the number of grams of *acid* per 100 grams of solution.

Solutions made up in this way could be kept unchanged for a day or so. If the alcoholic sodium hydroxide solution is made up with ordinary stick sodium hydroxide, progressive rise in the surface tension takes place, noticeable after an hour or so. The effect of keeping solutions made as described is shown in the following table.

Surface Tension in dynes per cm.

	Laurate.	Myristate.	Palmitate.
Fresh solution	29.2	19.8	19.8
After four hours at 60°	29.2	19.7	19.8
After twenty-four hours at 60°	29.1	19.5	19.9
After eight days at room temperature ...	29.9	19.7	20.2

The soap solution, which had been kept at the required temperature for fifteen minutes or longer, was drawn up into the pipette, taking care to avoid air bubbles. The regulating U-tube and the receiver were then attached and the apparatus was placed in the water-bath. Five minutes were allowed to elapse before the determination was made, in order that the temperature might become uniform.

The soap solution was then adjusted to the top mark on the pipette, approximately 2 c.c. were run out drop by drop at a rate of 20 drops every minute, the flow being stopped at the first complete drop after the 2 c.c. mark had been passed. The pipette was calibrated to read to 0.01 c.c. between 2.0 c.c. and 2.1 c.c. The volume was then reduced to grams for the purpose of calculation.

Twenty drops every minute was chosen as the rate of flow. A much slower rate has its advantages, especially in the case of soap solutions, but it was considered unsatisfactory in the present instance on account of the tendency of moisture to condense on the jet and drop at high temperatures, and of the probability that unsaturated soaps would interact with the atmosphere.

All surface tensions were calculated with reference to the drop number of water determined with the same pipette, at the same temperature as that used for the determination of the soap solution.

Effect of Concentration.

In this manner the surface tensions of several salts of the fatty acids were determined at concentrations varying from 0.005 per

TABLE I.

Surface Tension at 60° in dynes per cm.

Concentration.	Laurate.	Myristate.	Palmitate.	Stearate (impure).	Arachidate.	Oleate.
0.005	64.0	64.0	64.2	65.7	—	65.7
0.01	61.3	54.7	42.2	52.0	—	46.9
0.025	54.9	39.2	26.6	32.5	—	28.0
0.05	45.9	26.9	21.85	26.7	65.3	23.75
0.075	41.1	22.5	20.95	24.4	—	22.95
0.1	38.0	21.2	20.5	23.9	61.0	22.55
0.15	—	20.3	19.95	—	—	—
0.2	29.2	20.6	19.85	22.4	56.9	—
0.25	—	21.2	—	—	—	—
0.3	24.5	—	20.7	22.5	—	—
0.4	—	23.9	22.3	—	56.7	—
0.5	21.2	—	—	23.1	—	—
0.75	26.5	—	—	23.1	—	—
1.0	28.3	26.4	23.65	23.6	—	—
1.5	29.3	—	—	—	—	—
2.0	29.4	—	—	—	—	—

cent. to 1.0 per cent. The standard temperature chosen was 60°. The results (mean values) are given in Table I. In Fig. 1 these results are represented graphically. The concentration is represented by the abscissæ and the *lowering of the surface tension* (water = 66.0 dynes/cm. at 60°) by the ordinates.

The palmitic acid was impure. It had the correct equivalent, but contained about 7 per cent. of oleic acid and melted at 58—59°. The stearic acid was a commercial sample. It contained only 1.5 per cent. of oleic acid, but about 40 per cent. of palmitic acid. It was, however, suited to the present purpose, since the pure soap is only soluble to the extent of 0.2 per cent. at 60°. The remaining acids were practically pure. With the exception of "stearic acid," however, they all give a good idea of the general trend of the curve. It is interesting to note that this impure soap follows closely the contour of the palmitate curve, although it contains a preponderating proportion of stearate. This will be referred to later in the section on mixtures. The interesting point about these curves is that they tend to rise to a maximum and that this maximum is almost the same for all soaps the solubility of which is great enough to allow the maximum to be reached. This is very suggestive, and indicates that at this point the surface layer of all soaps is similar. Probably it consists of a stable emulsion containing a high percentage of soap.

Using carefully purified materials, the initial part of the curve was redetermined. Special care was taken over these determinations, since it is at these low concentrations that different soaps can best be compared with one another. For instance, it is scarcely

fair to compare a 0.2 per cent. palmitate solution with a 0.2 per cent. laurate solution, since the former has reached its maximum while the latter has not. At a concentration of 0.5 per cent., sodium laurate would appear to be more effective than either myristate or palmitate. As the tip of the pipette had been damaged, it was necessary to use a new one, and as this gave different results from the old one, the results are not directly comparable. Two completely

FIG. 1.

independent series of measurements were made, except in the case of sodium arachidate, and the mean values are given in Table II.

TABLE II.

Lowering of Surface Tension at 60° in dynes per cm.

Concentration.	Water—66.0.			Pipette No. 3.				
	<i>n</i> -Octo-ate.	<i>n</i> -Deco-ate.	Laurate.	Myrist-ate.	Palmit-ate.	Stear-ate.	Arachid-ate.*	Behen-ate.
0.005	—	—	4.7	5.4	2.5	0.6	—	—
0.01	—	—	9.1	16.3	26.1	1.3	—	—
0.025	—	—	19.3	34.3	44.8	22.0	2.3	—
0.05	—	—	26.7	44.6	48.4	34.4	3.6	—
0.075	—	—	32.8	47.5	49.3	36.9	4.6	—
0.1	1.55	6.4	36.2	48.9	50.0	37.7	8.1	1.6

* Single series of determinations only.

Curves are plotted in Fig. 2. The interesting part about these curves is the first inflection in the early part of the curve, and the significance of this will be considered in the section on theory. It should be pointed out that sodium stearate does not form a clear 0.1 per cent. solution like sodium myristate and laurate; the solution has at 60° a curious opalescent appearance, due, no doubt, to the presence of colloidal particles. Bearing in mind McBain's work

FIG. 2.

on the proportions in which colloidal soap is present in solution, it seems probable that this phenomenon may be due to partial hydrolysis.

Effect of Temperature.

The temperature coefficients of the surface tensions of pure liquids have led to results of great theoretical significance. In the case of solutions and mixtures, however, conditions are much more complex and theory has not made much headway.

Fig. 3 illustrates forcibly the effect of temperature in the case of sodium arachidate. At 60°, it lowers the surface tension only

to a very small extent; at 90°, however, the whole contour of the curve is altered and becomes similar to that of sodium stearate at 60°.

The full line in the 60° curve represents the behaviour of a perfectly fresh solution. The dotted line indicates the surface tension of a solution which has been kept at a temperature of 60° for some time and has partly gelatinised.

FIG. 3.

TABLE III.

Temperature Curves.—Pipette No. 3.

Temp.	Oleate.	Laurate.	Laurate.	Myrist- ate.	Palmit- ate.	Stear- ate.	Arachid- ate.	Behen- ate.
	0.1%	0.5%	0.1%	0.1%	0.1%	0.1%	0.1%	0.1%
15°	51.1	51.8	22.0	—	—	—	—	—
30	50.58	51.55	32.75	41.0	—	—	0.5	—
45	49.4	49.65	35.15	50.0	41.3	25.2	—	—
60	47.7	48.0	36.45	48.5	49.3	38.7	8.6	1.6
75	45.15	45.75	32.75	46.25	(43.25) 47.0	47.2	31.6	3.15
90	42.1	41.9	21.9	40.2	(38.2) 44.4	44.6	36.3	28.2
T=82.7° 35.1								

In Table III data obtained at various temperatures are recorded, and curves are plotted in Fig. 4. In general, the extent to which the surface tension is lowered increases to a maximum with the temperature, and then decreases. Sodium oleate either shows no

maximum or more probably it is below 15° . In most cases, the temperature at which the maximum occurs rises with the molecular weight, but the behaviour of sodium laurate is exceptional. At a higher concentration (0.5 per cent.), however, the laurate curve becomes almost identical with the 0.1 per cent. oleate curve, and thus falls more or less into its place. Sodium oleate itself is interest-

FIG. 4.

ing, and differs from all the other soaps at 0.1 per cent. concentration in that its efficiency in lowering the surface tension remains high over a wide range of temperature.

Effect of Molecular Weight.

The manner in which the effect of the salts of the fatty acids on the surface tension of water changes from member to member

TABLE IV.

Palmitate and Myristate 60°.			Palmitate and Oleate 60°.			Oleate and Myristate 60°.			Stearate and Laurate 60°.		
% Palmitate.	$\Delta\sigma$.	Deviation.	% Palmitate.	$\Delta\sigma$.	Deviation.	% Oleate.	$\Delta\sigma$.	Deviation.	% Stearate.	$\Delta\sigma$.	Deviation.
0	48.95	—	0	47.75	—	0	48.7	—	0	34.6	—
25	49.15	-0.1	25	48.25	+0.1	25	47.75	-0.3	25	29.3	-7.2
50	49.5	+0.1	50	49.1	0.15	50	47.6	-0.6	50	30.3	-5.8
75	49.6	-0.05	75	49.55	± 0.0	75	47.65	-0.3	75	35.0	-1.8
100	49.9	—	100	50.15	—	100	47.7	—	100	37.55	—
Palmitate and Stearate 60°.			Myristate and Laurate 60°.			Stearate and Arachidate 60°.			Oleate and Laurate 60°.		
% Palmitate.	$\Delta\sigma$.	Deviation.	% Myristate.	$\Delta\sigma$.	Deviation.	% Stearate.	$\Delta\sigma$.	Deviation.	% Oleate.	$\Delta\sigma$.	Deviation.
0	39.15	—	0	33.4	—	0	7.4	—	0	37.0	—
25	43.75	+1.9	25	43.9	+5.7	25	25.4	+10.0	25	45.55	+5.85
50	46.0	+1.5	50	46.35	+5.3	50	34.2	+10.8	50	46.75	+4.35
75	48.25	+1.05	75	47.85	+3.05	75	38.15	+6.7	75	47.4	+2.35
100	49.9	—	100	48.6	—	100	39.45	—	100	47.75	—
Oleate and Stearate 60°.			Arachidate and Laurate 60°.			Palmitate and Myristate 45°.			<i>n</i> -Decoate and <i>n</i> -Octoate 60°.		
% Oleate.	$\Delta\sigma$.	Deviation.	% Arachidate.	$\Delta\sigma$.	Deviation.	% Palmitate.	$\Delta\sigma$.	Deviation.	% Decoate.	$\Delta\sigma$.	Deviation.
0	38.35	—	0	34.3	—	0	50.3	—	0	1.55	—
25	46.9	+6.2	25	9.6	-18.3	25	44.75	-2.75	25	2.2	-0.6
50	48.05	+5.05	50	9.3	-12.15	50	42.25	-2.55	50	4.7	+0.7
75	48.3	+3.0	75	9.0	-6.0	75	40.85	-1.3	75	13.6	+8.4
100	47.65	—	100	8.6	—	100	39.35	—	100	6.4	—

of the series is remarkable when we consider the gradual way in which most properties change as an homologous series is ascended. Just as in the case of temperature and concentration, the activity of the soap rises to a maximum, after which an increase in the molecular weight is associated with a decrease in the activity of the soap. The curves in Fig. 5 show how the effect on the surface tension varies with the number of carbon atoms under various conditions.

Mixed Soaps.

Solutions of 0.1 per cent. strength were made up as usual and the surface tension of these was determined. The solutions were then mixed in various proportions and the surface tension of the mixtures

FIG. 5.

determined. The results are recorded in Table IV. In Fig. 6 the results are represented diagrammatically by plotting the deviations from the "mixture law" against the composition of the solution. If a series of mixtures follows the "mixture law," that is, the surface tension of all mixtures is equal to the weighted mean of that of the constituents, the curve then becomes a horizontal straight line as in the case of palmitate and myristate or palmitate and oleate. The majority of mixtures are, however, represented by curves falling either above or below this hypothetical line.

Theoretical.

It has been shown that molecular weight, temperature, and concentration all exert an effect on capillary activity which rises to a maximum and then decreases. From this it would appear that there must be some condition of equilibrium between two forms of soap present in solution, and that if this equilibrium is disturbed, either *in one direction or the other*, by changes in temperature or

FIG. 6.

concentration (or by substituting another soap of greater or smaller molecular weight), the property of lowering the surface tension (or interfacial tension) will be greatly diminished or will disappear.

These facts can be explained and a foundation for the theory of soap mixtures laid if we regard soap in aqueous solution as containing colloidal aggregates or "micelle" in equilibrium with simpler molecules. This view has long been advocated by McBain, who arrived at this conclusion in order to explain the osmotic behaviour of soap solutions in relation to their electrical conductivity.

It may be assumed with reason that the equilibrium between these colloidal aggregates and the simpler molecules is affected by temperature and concentration in much the same manner as is the equilibrium between complex and simple molecules.

Thus dissociation is promoted by :—

increase in temperature,
decrease in molecular weight,
decrease in concentration ;

and association is promoted by :—

decrease in temperature,
increase in molecular weight,
increase in concentration.

It should be remembered that on account of the lowering of the surface tension the solution is more concentrated in the surface layer. In the case of those soaps lowering the surface tension to a large extent, there must be some circumstance which facilitates the concentration of the soap in the surface layer. This is to be found in the readiness with which they form complex colloidal molecules. According to McBain, there are only immeasurably small quantities of colloidal soap in dilute solutions. At the surface, however, under the influence of high concentration and high pressure, conditions are suitable for the formation of large colloidal aggregates. The lowering of the surface tension tends to hold these at the surface against their osmotic pressure. This osmotic pressure is, however, small and the surface concentration is therefore abnormally great.

To bring this theory into line with facts, we must assume that very large micelle are not so active, weight for weight, in lowering the surface tension of soap solutions as those of moderate size. Therefore, if the size of the colloidal aggregates is increased beyond a certain limit, there is a falling off of efficiency, even although the surface concentration may remain high. Such an assumption is reasonable in view of the fact that the special forces active in the surface layer only penetrate beneath the surface to an extent depending on the range of molecular action (see Parks, *Phil. Mag.*, 1903, [vi], 5, 517). Therefore, when the colloidal particles reach

dimensions which are large in comparison with molecular magnitudes, a falling off in efficiency must necessarily be expected (Lewis claims that emulsions of paraffin in aqueous solution have little or no effect on the interfacial tension. *Phil. Mag.*, 1908, [vi], **15**, 499). Hence we have the following system :—

Small micelle efficient in lowering the surface ten- sion, but difficult to chain to the surface on account of their relatively high osmotic pressure.	$\rightleftharpoons$	Large micelle inefficient in lowering the surface ten- sion, but easy to chain to the surface on account of their relatively low osmotic pressure.
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It may be assumed that the highly efficient soaps, such as palmitate and myristate, are those in which surface concentration and specific activity are so combined as to give a maximum value. Those of lower molecular weight are less efficient because the relatively high osmotic pressure of the small micelle hinders the formation of a high surface concentration. The higher homologues readily form large micelle, which, having a low osmotic pressure, are easily adsorbed in the surface layer. Nevertheless, one would expect that the surface concentration of stearate, arachidate, and behenate would be progressively less than that of palmitate on account of the decreased activity of the larger micelle. There is, however, every reason to suppose that the surface concentration of these soaps is much greater than that of the "nut oil" soaps, which lower the surface tension to a corresponding extent (see p. 1522).

Milner (*Phil. Mag.*, 1907, [vi], **13**, 96) and Lewis (*Phil. Mag.*, 1908, [vi], **15**, 499; 1909, [vi], **17**, 466) examined the relationship between surface tension and surface concentration for a variety of solutions in the light of Gibb's theory. Both authors grafted on to this theory the assumption that the solutions with which they were dealing followed the gas laws, and found that the majority of substances were very much more concentrated in the surface layer than the theory thus modified would lead them to expect. Lewis found that Congo-red was about thirty times and sodium oleate about one hundred times more concentrated in the surface layer than the theory required. McBain's work has proved that the gas laws cannot be applied to such substances in concentrated solution, and their theory was not therefore applicable to these cases, for the concentration is high in the surface layer, even although small in the body of the solution. Lewis explained the apparent discrepancy by assuming that gelatinisation takes place in the surface layer. No special hypothesis is required, however, if McBain's theory of colloidal electrolytes is accepted.

(a) Relationship between Surface Tension and Concentration.

When the soap solution is extremely dilute, the concentration in the surface layer will be sufficiently small for the soap to consist mainly of simple molecules. As the concentration is increased, complexes will increase in the surface layer, slowly at first and then with increasing rapidity. The more complexes are formed the smaller will be the work required to be done by surface tension against the osmotic pressure in order to concentrate the soap in the surface layer.

McBain's work has shown that the osmotic pressure rises fairly rapidly with the concentration until a maximum is reached, and that it then falls slightly, thereafter rising much more slowly. As soon as the point is reached at which an increase in concentration is associated with an actual decrease in osmotic pressure, followed by a region in which the osmotic pressure rises slowly with the concentration, a very rapid increase in the surface concentration must necessarily follow. One would therefore expect that the surface concentration would at first increase slowly with the volume concentration and then with increasing rapidity.

These expectations are realised in the early part of the concentration curves (see Fig. 2), and, moreover, this first inflection becomes more marked as the molecular weight (and therefore the tendency to form complexes) increases.

The occurrence of a maximum in the surface-tension curve is explained by the hypothesis that the efficiency of the colloid particles falls off as their size increases, hence the whole form of the concentration curve is in qualitative agreement with the requirements of theory.

The form of McBain's concentration-osmotic pressure curves shows that there are in certain circumstances three concentrations having one and the same osmotic pressure.

Since surface tension is so intimately connected with osmotic pressure, it would not be surprising to find that for one and the same volume concentration there could be more than one surface tension. This appears to be the case for sodium myristate at 75° and 90°. The readings were as follows :—

Drops per gram.		Drops per gram.	
75°	112	90°	84·5
	111·5		84
	94·5		101
	96·5		105
	113		103
	112		103

In another series of five readings for a temperature of 75° and using another pipette, only one high reading was obtained.

Attempts to obtain either the one reading or the other by approaching the temperature from above or below met with no success. The phenomenon is therefore different from that observed in the case of arachidic acid. Moreover, gelatinisation was not observed and would not be expected at this temperature.

(b) *Temperature.*

The theory is in harmony with the fact that there is an optimum temperature for every soap and that in general this rises as the homologous series is ascended. This optimum temperature appears to have some connexion with the melting point of the acid. It seems not unreasonable to suppose that at the melting points of the acids, the corresponding soaps exist in approximately similar molecular states so far as their tendency to form complexes is concerned.

(c) *Mixed Soaps.*

There are three ways in which mixed soaps might be expected to behave in dilute solution.

(1) The soaps might act independently, each constituent lowering the surface tension to an extent corresponding with its individual concentration. In this case, owing to the form of the concentration curves, almost any mixture would be much more efficient than a single soap, weight for weight. Mixtures would not be expected to behave in this way unless they were very dilute both in solution and *in the surface layer*. It would not, therefore, be in accordance with the theory, and is not, in fact, found to be the case.

(2) The soaps might form mixed complexes at the surface having properties intermediate between those of the constituents. If these mixed complexes in the surface layer contained the constituents in the same proportions in which they were present in solution, one might expect that the resultant lowering of the surface tension would be approximately the weighted mean of those of the constituents at the combined concentration of the mixed soaps, that is, the mixed soaps would apparently follow the so-called mixture law. There is, however, no reason to suppose that two different soaps would be adsorbed to the same extent in the surface layer either in the form of mixed complexes or otherwise. Hence it is only in the case of mixtures of soaps lowering the surface tension to approximately the same extent that one would expect the mixture law to be followed.

Thus, for instance, the three pairs :—

Myristate and palmitate at 60°.

Oleate and myristate ,, ,,

Oleate and palmitate ,, ,,

follow very closely the mixture law (see Fig. 6). At 45° , however, palmitate lowers the surface tension to a much smaller extent than myristate. Accordingly, at this temperature the mixture law is not followed. Laurate and stearate also lower the surface tension to about the same extent; they are, however, very dissimilar in other respects, the form of the concentration curves being very different. Mixtures of these two soaps do not follow the mixture law. It is, therefore, reasonable to suppose that in these circumstances the complexes formed do not possess properties intermediate between those of the two constituents.

(3) The majority of soap mixtures come under the third head, the capillary activity of the mixtures being related in no simple manner to that of the constituents. Having shown that the mixture law holds fairly closely under certain conditions, the simplest plan is to regard all mixtures not following this law as lowering the surface tension by so much more or so much less than the law would indicate. The behaviour of mixtures is therefore represented graphically on this plan in Fig. 6. From what has been said in the preceding paragraph one would expect that that soap which is most readily absorbed in the surface layer would have the predominant effect; in what follows such a soap will be called a dominant soap. As a general rule this soap will be the one which lowers the surface tension to the largest extent. This is not, however, necessarily the case, since the lowering of the surface tension depends on *two* factors :—

(1) Concentration in the surface layer.

(2) Specific activity of the soap in the surface layer.

If the dominant soap lowers the surface tension more than the other, mixtures of the two will have a *lower* surface tension than the mixture law would indicate. If, on the other hand, the dominant soap lowers the surface tension to a smaller extent than that with which it is mixed, the reverse is to be expected. All the mixtures hitherto examined, with the exception of laurate and stearate, conform to this rule if the soaps are regarded as dominating each other in the order of the following empirical list :—

1. $\left. \begin{array}{l} \text{Palmitate-}C_{16} \\ \text{Oleate} \end{array} \right\}$
2. Stearate- C_{18}
3. Arachidate- C_{20}
4. Behenate- C_{22}
5. Myristate- C_{14}
6. Laurate- C_{12}
7. *n*-Decoate- C_{10}
8. *n*-Octoate- C_8

This list, although empirical in a sense, is nevertheless in harmony with the theory put forward in this paper, which requires that the adsorptive powers (or the tendency of the soap to concentrate at the surface) shall increase to a maximum as the homologous series is ascended and then decrease. A very interesting example of the way in which one soap can almost completely dominate another in the surface layer is the case of laurate and arachidate. Arachidate lowers the surface tension by 8.6 dynes, and laurate by 34.3 dynes, nevertheless, when 75 per cent. of the arachidate is replaced by laurate the extent to which the mixture lowers the surface tension is only increased to 9.6 dynes. With regard to the form of the curves in Fig. 6, theory indicates that the greatest deviation from the mixture law should occur when a small quantity of the dominant soap is mixed with a large quantity of the other, that is, the peak of the curve should always be displaced towards that end of the diagram corresponding with low concentrations of the dominant soap. This is so in nearly every case investigated, even in the somewhat exceptional case of laurate and stearate. Mixtures of decoate and octoate are the only exceptions in this respect.

The exceptional behaviour of mixtures of laurate and stearate indicates that the principles enunciated cannot be applied absolutely rigidly. They cover perhaps the most important aspect of the problem, but when the difference in the adsorptive power is large and the difference between the capillary activities is small, as in the case of this pair, then these effects may be masked by secondary changes. Evidence of such changes is also found in the case of mixtures of oleate and stearate, and decoate and octoate, where certain mixtures lower the surface tension to a *greater* extent than either of the constituents.

Summary of Results.

The activity of various salts of the fatty acids in lowering the surface tension of water has been examined at various concentrations and temperatures, and the manner in which this activity varies with changing conditions has been explained on the basis of McBain's theory of soap solutions.

Only one additional hypothesis has been found to be necessary, and this is to the effect that the lowering of the surface tension is not solely proportional to the concentration in the surface layer, but that it depends also on the size of the colloidal particles. McBain's theory, together with this hypothesis, suffices to explain the following facts.

(1) Soaps lower the surface tension of the water in which they are dissolved to an altogether abnormal extent.

(2) In an homologous series of soaps the power of lowering the surface tension first rises with increasing molecular weight and then falls after passing through a maximum.

(3) In general, the property of lowering the surface tension rises to a maximum as the temperature is increased and then falls off.

(4) The property of lowering the surface tension increases slowly with the concentration at extreme dilution, then rises rapidly and after passing through a maximum decreases again.

(5) When soaps are mixed in solution, the extent to which they lower the surface tension cannot be determined from the properties of the constituents. By means of the theory it is possible, as a rule, to determine whether a mixture of any two soaps will lower the surface tension more or less than the weighted mean of the constituents.

In conclusion, the author desires to acknowledge the permission of Messrs. Joseph Crosfield and Sons, Ltd., to publish this paper.

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