DETERGENT ACTION OF SOAPS.

PART I. INTERFACIAL TENSIONS OF PURE SOAP SOLUTIONS.

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INTRODUCTION.

A good deal of attention is lately being paid to the study of surface activity of the solutions of soaps of fatty acids, and of sulphates and sulphonates of the higher fatty alcohols. Although a large amount of data has by now accumulated, the subject still does not admit of rigid conclusions being drawn. While *surface tension* measurements with many soaps have been carried out, a consistent study of the influence of carbon atoms in homologous series has not yet been attempted. With regard to *interfacial tension* studies, *i.e.*, the study of surface activity when air is replaced by a liquid phase of a non-polar compound, investigations have not gone beyond myristate, and the study of any parallelism or divergence between the surface and interfacial activity has still to be done, especially at different concentrations of the soap solutions.

The work of Harkins and collaborators (*Jour. Amer. Chem. Soc.*, 1917, **39**, 541) postulates in general terms what probably happens at an interface, the underlying idea being that, the surface tension is dependent on the orientation and packing of the molecules in the surface layer, and that, the forces involved in this action, are related to those involved in solution and adsorption. In a system with a polar-nonpolar solute at the interface, there will be a polar setting and packing of the solute molecules brought about by the differential 'solubilities' of the two parts of the molecule due to the adsorption at the surface, which in virtue of the same cause, will be quite out of proportion to that calculated from the Gibb's law of adsorption. Thus Harkins has found that the surface film of a sodium oleate solution becomes entirely saturated at concentrations as low as 0.001 N and that, as the length of the polar end of the molecule increases, adsorption at the surface also increases. Considering the interface between solution and air, or between any two liquids, towards which the two parts of the molecules of the solute show reverse solubilities, the effect of this polar setting is to make the transition to the adjacent phase less abrupt, by reducing the surface energy, *i.e.*, the interfacial tension.

This simple conception of the reduction of interfacial tension, when applied to aqueous soap solutions, is beset with considerable difficulties which have been the subject of investigations by numerous workers. Donnan (*Kolloid Z.*, 1910, **4**, 208) investigated the effect of different concentrations of solutions of *the sodium soaps* of various fatty acids of the homologous series up to myristate, on the *interfacial tensions* against a high grade hydrocarbon oil. The results indicated that, for the same molal concentration, myristate showed the maximum lowering of the interfacial tension, the latter tending to become constant as the concentration was increased. Experiments on similar lines with regard to *surface tension* are reported by various workers. Walker (*Jour. Chem. Soc.*, 1921, **119**, 1521) has investigated the effect of concentration, the length of the carbon chain and the temperature, on *surface tensions* of solutions of sodium soaps up to behenate in the homologous series. His conclusions are in general agreement with those of Donnan, in so far as they both show that the surface activity increases with carbon atoms up to myristate. Further, it is shown that molecular weight, temperature and concentration all exert an effect on capillary activity, which rises to a maximum and then decreases as the value of any one of these three variables is increased while those of the other two are kept constant. Considering the effect of temperature, it is found that above 60°, sodium palmitate shows maximum lowering, while at 45°, maximum lowering is shown by myristate, and at lower temperatures, by oleate. Sodium stearate, arachidate and behenate show lower activity than myristate and palmitate, even at 90° C.

Lascaray (*Kolloid Z.*, 1924, **34**, 73) has studied *surface tensions* over a very wide range of concentrations from 0.0002 N to 0.4 N at 18° C. and finds that, when lowering is plotted against number of carbon atoms, the curves show a reversal at myristate for all concentrations below 0.005 N. He has discussed the influence exerted on the surface activity by the several constituents of the soap solution and concludes that colloidal particles have but little influence on surface tension.

Godbole and Sadgopal (*Kolloid Z.*, 1936, **75**, 193) studied the *surface tensions* of the 0.1% solutions of both sodium and potassium soaps, which decreased with increase in molecular weight, reached a minimum at myristate, and again increased. Sodium soaps showed higher capillary activity than potassium soaps up to laurates, above which, potassium soaps were found to be more active.

The object of the present investigations was to study the effect of the length of the carbon chain on the *interfacial tension* of soap solutions, with a view to determine the detergent action of the soaps.

EXPERIMENTAL.

Pure soaps were prepared by careful neutralisation of pure fatty acids by standard alcoholic alkali, the mixture being refluxed for 30 to 50 minutes on a water-bath, and after the reaction was complete, the alcohol was removed by evaporation in partial vacuum and prolonged desiccation over sulphuric acid.

The method adopted for comparative measurement of the surface tension was that of measuring the drop numbers of pure benzene in soap solutions, through a specially constructed inverted pipette (Fig. 1). The bulb *e* of about 5 c.c. capacity was blown in the middle of a graduated (0.01 c.c.) capillary pipette. A piece of broken thermometer tubing *a* attached by a rubber tubing regulated the flow. The pipette was thoroughly cleaned with chromic acid, dried and filled with pure benzene. 50 c.c. of soap solution were taken in a wide-mouth bottle of 100 c.c. capacity, and the pipette was fixed by a split of rubber cork on the bottle in such a way that, the curved end of it reached the bottom of the bottle. The drop-numbers from a definite volume of benzene were then measured and calculations made in the usual manner, the whole apparatus being kept in a vertical position in a glass thermostat at 25°.

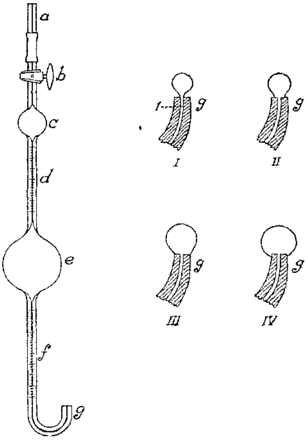

Fig. 1.

It was found that slight variation in the experimental conditions had a great influence on the accuracy and reproducibility of the results. For instance, a change in the length of the capillary piece *a*, and also the manner in which the benzene drop was formed and escaped from the pipette, influenced the drop numbers considerably. It was found that for reproducibility, the whole outer surface of the end *g*, and also a few mm. of the capillary at *g*, should be wetted by the soap solution. This happens only when the surface at *g*, is scrupulously clean. Otherwise partial wetting as shown in Fig. 2 (II, III and IV) results, and the drop number becomes uncertain. (I) shows the

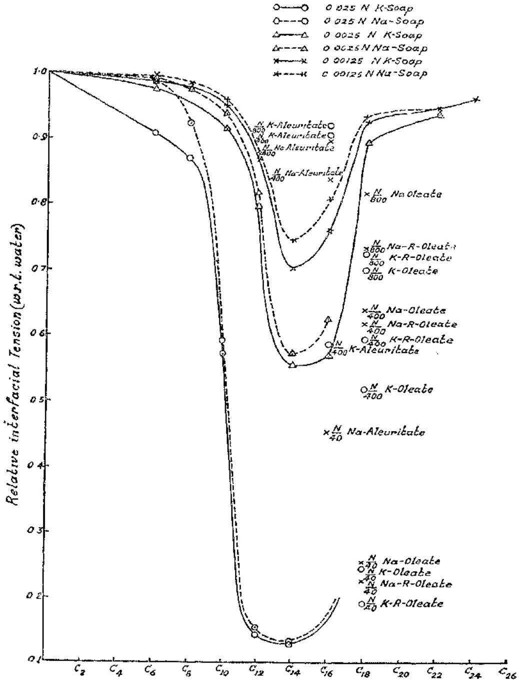

FIG. 2.

desired drop formation. If the capillary surface is clean, the drop formed as in (I) will always break at a level *l* somewhere inside the capillary, depending on the size of the drop. It will also be seen that the flat ground end of *g* need not be very wide as its width has no part in the drop formation.

The concentrations of the soap solutions used were, 0.025 N, 0.0025 N and 0.00125 N. The densities of solution of these dilutions are not very much different from each other and from that of water (Lascaray, *Kolloid Z.*, 1924, 34, 73). The results are tabulated in the following tables in which drop-numbers and the interfacial tensions relative to water for each soap are given, and shown graphically in Fig. 2.

INTERFACIAL TENSIONS OF SOAP SOLUTIONS.

TABLE I.

Sodium Soaps.

Soaps	0·025 N		0·0025 N		0·00125 N	
	Drop number	Ratio to water	Drop number	Ratio to water	Drop number	Ratio to water
Water	180·6	1·0	180·6	1·0	180·6	1·0
NaOH solution	196·8	0·917	188·2	0·959	183·2	0·985
C_6 Caproate	182·5	0·989	182·4	0·990	182·0	0·992
C_8 Caprylate	196·9	0·921	184·3	0·980	184·6	0·978
C_{10} Caprate	305·4	0·591	192·7	0·937	188·2	0·959
C_{12} Laurate	1161·5	0·155	221·2	0·816	206·3	0·875
C_{14} Myristate	1315·7	0·137	316·2	0·571	242·8	0·743
C_{16} Palmitate	..	..	289·0	0·625	223·7	0·807
C_{18} Stearate	..	..	..	..	194·5	0·933
C_{18} Oleate	707·4	0·255	265·7	0·680	222·8	0·810
Ricenoleate	792·0	0·228	287·0	0·629	247·0	0·731
Water	186·0	1·0	186·0	1·0	186·0	1·0
C_{18} Stearate	..	..	..	..	199·5	0·932
C_{20} Arachidate	..	..	..	..	227·6	0·836
C_{22} Behenate	..	..	..	..	197·0 (171·4) ?	0·944 (1·085) ?
C_{18} $(OH)_3$ Palmitate ..	410·3	0·453	227·4	0·837	207·5	0·896

TABLE II.

Potassium Soaps.

Soaps	0·025 N		0·0025 N		0·00125 N	
	Drop number	Ratio to water	Drop number	Ratio to water	Drop number	Ratio to water
Water	180·6	1·0	180·6	1·0	180·6	1·0
C_6 Caproate	199·5	0·909	185·3	0·974	183·4	0·985
C_8 Caprylate	207·8	0·869	185·0	0·976	184·0	0·981
C_{10} Caprate	315·9	0·572	198·3	0·911	190·5	0·948
C_{12} Laurate	1252·0	0·144	227·1	0·795	208·2	0·867
C_{14} Myristate	1365·0	0·132	357·3	0·505	256·2	0·705
C_{16} Palmitate	..	..	317·7	0·568	237 8	0·859
C_{18} Stearate	..	..	202·0	0·894	195·0	0·926
C_{18} Oleate	737·3	0·245	347·4	0·520	258·0	0·700
Ricinoleate	936·4	0·193	303·9	0·594	249·8	0·723
Water	186·0	1·0	186·0	1·0	186·0	1·0
C_{22} Behenate	..	..	198·3	0·938	197·0	0·944
C_{24} Lignocerate	..	..	..	..	193·5	0·961
C_{18} $(OH)_3$ Palmitate ..	317·3	0·586	206·0	0·903	198·3	0·916

Surface and Interfacial Tensions.—In considering the above results in the light of those of the previous workers who have measured surface tensions of soap solutions, one important point appears to have been brought forth, *viz.*, that the relative lowering of the interfacial tensions between water and benzene is systematically greater than the surface tension lowering between water and air. To illustrate this, the comparative results of Lascaray for surface tension are given below:—

N	Surface tension	N	Relative interfacial tension
0·001	0·924	0·00125	0·743
0 0015	0·868	0·0025	0·571
0·005	0·688	0·025	0·137

The value of relative surface tension calculated from the data of Godbole and Sadgopal is 0.374 for sodium myristate at about 0.004 N. The fact that the interfacial lowering of soap solution is greater than the surface tension lowering, is in conformity with the conclusions of Harkins regarding the influence of polarity of the phases on the surface activity of a polar-nonpolar solute at the interface. The orientation of the soap molecules appears to be more perfect at the benzene-water interface than at the air-water interface. This difference has a direct bearing on the subject of detergency, where emulsification or degreasing is the main operation. The lowering of interfacial tension will be a more satisfactory criterion of the degreasing ability than the lowering of surface tension, which does not take into account the nature of the surface to be wetted.

The Influence of the Length of the Carbon Chain.—The second important result brought forth is that when the relative lowering of interfacial tension for a certain temperature and concentration is plotted against the number of carbon atoms in the soap molecule (Fig. 2) a minimum is obtained at myristate, similar to the minimum obtained in the surface tension measurements at the same group of carbon atoms (C_{14}) [Lascaray, Godbole and Sadgopal (*loc. cit.*)]. A similar minimum at C_{14} has been observed in the aqueous solutions of sodium alkyl sulphates by Lottermoser and Stoll (*Kolloid Z.*, 1933, **63**, 49). The effect of temperature is to shift the minimum from C_{14} to C_{16} above 40° [Walker (*loc. cit.*) and Mikumo (*J. Soc. Chem. Ind. Japan*, 1934, **35**, 591)]. The explanation for the reversal of activity in the region of C_{14} in the aqueous solutions of all the long-chain soaps so far investigated, has been attempted by various workers. In the main, the explanations centre round the consideration of what type of particle in the solution is responsible for the capillary activity. Lascaray supposed that surface activity of an aqueous soap solution is the sum of the individual abilities of the various dissolved units obtained as a result of dissociation and hydrolysis, and that the colloidal aggregates have hardly any surface activity of their own owing to their size and hydration, and have, on the contrary, an adverse influence due to their ability to remove the active units from the solution, by adsorption.

Walker (*loc. cit.*) on the other hand, postulated the existence of two types of micells, one relatively small but very effective in lowering surface tensions and the other quite large but not so capillary active. The capillary activity according to him depends on the amounts of such small micells in the solution and this in turn, would be conditioned by temperature, concentration and molecular weight. Lottermosel and Stoll (*loc. cit.*) assumed the following equilibrium condition in the soap solution:—

$$\begin{tikzcd}
\text{Undissociated simple salt (II)} \arrow[r, shift left] \arrow[d, shift left] & \text{Undissociated aggregated salt (III)} \arrow[l, shift left] \arrow[d, shift left] \\
\text{Simple ions (I)} \arrow[u, shift left] \arrow[r, shift left] & \text{Aggregated anions + Na ions (IV)} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

and identified the capillary active micells with the units III in the above equilibrium.

Recently Murray (*Trans. Faraday Society*, 1935, 31, 207) in explaining the presence of minima in the *surface tension*-concentration curves, was led to assume that, of the three kinds of particles existing in solution, namely, ionic micells, simple metallic cations and simple long-chain anions, the simple anions are the capillary active particles and that the surface tension minima occur where the concentration of the simple anions is maximum.

Although it is impossible, in the present state of evidence on the subject, to draw definite conclusions as to which particle is mainly responsible for capillary activity, certain difficulties with regard to each of the above hypotheses can be easily pointed out. The assumption of Walker that the activity is due to small colloidal micells is hardly satisfactory, as it is not definite about the micellar size, structure and the degree of hydration. The difficulties in attributing capillary activity to colloidal particles has already been pointed out by Lascaray. The colloidal formation from the molecular units to aggregated ones is in itself indicative of the drop in the capillary efficiency caused by the removal of the active species from the field of surface forces, which as is well known, penetrate beneath the surface, only to the extent of the range of molecular dimensions (*cf.* Parks, *Phil. Mag.*, 1903, 5, 517).

Nor can we attribute surface activity wholly or chiefly to all the molecularly dispersed species in the solution as assumed by Lascaray, or selectively to any of them as suggested by Murray. With greater number of the molecularly dispersed components, there is an increase in the osmotic pressure and consequently the work required to be done by surface tension against osmotic pressure in order to concentrate the surface layer being thus great, the degree of adsorption would be very low. There is thus a falling off of the surface attraction as the particle size diminishes, and its osmotic activity increases. This is in agreement with the general finding that in the lower region of the homologous series where dissociation is large, the surface activity is very low.

The results so far obtained, indicate that all the units derived from a surface active substance are more or less surface active, the question being one of degree. Each of them will tend to become polarised at the interface and reduce surface energy, the total effect depending firstly, on their availability or concentration at the surface, and secondly, on their sensitivity to the orienting forces. In light of this, the surface activities of both the simple units and the aggregated micells will be less than that of the simple molecules, the reason being that in the former case osmotic activity and resistance to concentration will be greater, while in the latter, insensitivity to orientation will be more pronounced. Thus as we pass from dissolved ionic units to aggregated molecules, we should expect to find maximum surface activity to be shown by the simple molecules. To put it differently, if simple molecules were to replace the ionic units or the aggregated particles, there should be an increase in the surface activity.

In considering the effect of the length of the carbon chain alone, we have seen that the effect of polarization of a surface active molecule between two phases, is to reduce the free surface energy and make the transition from one phase to the other as gradual as possible. This transition would not be gradual if the molecule is more similar in polarity to one phase than to the other. The lower soaps in the homologous series show more affinity for water than for benzene, while the higher ones behave in just the opposite manner, so that in both cases transition from one phase to the other with these soaps at the interface, would still be abrupt. One would thus expect that as the homologous series is ascended the surface activity would pass through a maximum at the middle region of the series, while at the two ends it would fall off because of the strongly polar or non-polar nature of the molecule.

If now, in the light of what has been said, we examine the results over the whole of the homologous series we find that in the lower regions, although there is greater solubility, there is stronger dissociation, more osmotic activity and also a stronger polar character due to the smaller length of the carbon chain, than what is found in the middle of the series, while in the higher regions the colloid formation and the non-polar character of the molecule are more pronounced. The combined effect of these various factors is to increase the surface activity at C_{14}. The influence of the length of the carbon chain appears to be the most decisive, as under very diverse conditions of temperature and concentration, the maxima in activity persists at C_{14}.

Sodium and Potassium Soaps.—In interfacial tensions, the potassium soaps have been found by us to be consistently more surface active than the sodium soaps, although in surface tensions, Godbole and Sadgopal find that sodium soaps below laurate are more active than the potassium soaps. Here the main operative factor appears to be solubility; the potassium soaps being more soluble, there is a greater number of soap molecules available at the surface for polarisation and the colloidal formation is generally of a smaller dimension. Any difference of behaviour shown in the surface tensions and interfacial tensions is to be attributed to the specific influence exerted by the change of phase. With soaps of the aleuritic acid it was found that the difference between the solubility of sodium and potassium soaps is far greater than is found for soaps of any other acid. The potassium soap was very easily soluble and at 0.025 N, the solution was perfectly clear, while the sodium soap solution at the same concentration was highly colloidal. In this case the higher activity of the sodium soap is anomalous although it may be attributed to its smaller dissociation and lower osmotic activity.

Effect of Unsaturation and Presence of Hydroxyl Group in the Soap Molecule.—The effect of unsaturation appears to increase the surface activity as is found by comparing the results for stearate and oleate. The addition of a hydroxyl group as in the ricinoleate appears to further increase the activity. A systematic study of the unsaturated and hydroxy groups is still required to be done before the effect of their molecular structure on surface activity can be satisfactorily explained From what has been observed so far, the causes which control the solubility appear to be the chief operative factors in the differential activities of the various soaps.

Further work is in progress.

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SUMMARY.

1. Interfacial tensions against benzene, of aqueous solutions of sodium and potassium soaps of the homologous series are measured and the results compared with corresponding surface tension measurements by other workers.

2 The results are discussed in the light of the previous theories on the subject and explanations are given for the maximum activity shown by the myristate, and for the increased activity due to unsaturation, presence of hydroxyl group and replacement of sodium by potassium in the soap molecule.

3. The various units participating in the soap solution equilibria, appear to possess surface activity to a smaller or greater extent; the simple ions of the soaps of the lower series due to their higher osmotic activity, and the aggregated particles of the higher series of fatty acids, due to their less sensitivity to the surface forces, appear to be less surface-active than the simple molecules. As these are entirely dissociated, it would appear that the surface activity is mainly dependent upon the nature of the anions. As the latter get concentrated at the surface the cations form a double layer with oriented anions. The

difference between the surface activity of sodium, potassium and even ammonium and lithium soaps observed by different workers, thus appears to be due to the fact that the entire soap molecule gets concentrated at the interface.

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