The extremely low values for the molecular areas found in this work indicate a very tight packing of the hydrocarbon chains in the film. The lowest previously accepted value is 20 sq. Å. The value of 18.4 sq. Å. obtained here is almost the lowest which can be obtained by the close packing (as in hexagonal close packing) of hydrocarbon chains.

Summary

It is found that a film balance of great simplicity of construction and operation, and of high accuracy, is obtained by the use of the Wilhelmy method for the determination of surface tension in a proper differential form. Since the differential method thus developed makes use of the balance between a vertical pull of the surface tension directed downward, and the vertical upward force of buoyancy of the liquid, this may be considered as a vertical-pull method, as distinguished from the ordinary horizontal-pull film balance now in general use. While the method is suitable for investigations of the highest accuracy, its great simplicity makes it particularly suitable for biological and industrial work. The apparatus has the following additional advantages. (1) It can be built easily so that only quartz, or some other suitable material, comes in contact with the water. This makes it easy to investigate the effect of minute quantities of metal ions, while with the ordinary film balance this is very difficult. (2) It is suitable for a study of the effect of the rate of continuous compression of a film. (3) Its operation is very rapid, and easily may be made entirely automatic.

The effects of calcium ion on the films of stearic acid have been studied. Without the addition of this ion, the acid on 0.001 *f* sodium bicarbonate at 24.5° forms an expanded film with a limiting area of 20.5 sq. Å. per molecule, and this is converted into a condensed film at 10 dynes per cm. The extrapolated limiting area of this condensed region (19.70 ± 0.08 sq. Å. per molecule at zero pressure) is the same as the actual limiting area of the extremely condensed film which stearic acid forms on the same buffer made 0.0001 *f* in calcium chloride. Thus Ca^{++} ion compresses the fatty acid ions of the film, and eliminates the expanded region obtained without it.

The mathematical theory of the ordinary "horizontal-pull" film balance is developed, and data are presented which show that the two types of film balance give essentially the same values of the surface pressure with either liquid or solid films, even if the latter are extremely rigid.

CHICAGO, ILL. RECEIVED AUGUST 11, 1937

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO AND BAKER CHEMICAL LABORATORY OF CORNELL UNIVERSITY]

The Surface Tension of Aqueous Soap Solutions as a Function of Hydrogen Ion (*p*H) and Salt Concentration. I. Sodium Laurate and Sodium Nonylate

BY F. A. LONG, G. C. NUTTING AND WILLIAM D. HARKINS

1. Introduction

This investigation was undertaken as a preliminary to a study of the effects of hydrogen ion and salt concentration upon the surface tension of biological liquids. These effects are extremely great in soap solutions, as was shown for solutions of sodium oleate by Harkins and Clark and by Powney.[1] Solutions of soaps alone have been found to exhibit very low surface tensions at very small concentrations[2] and this was explained by Harkins and Clark as due to the fact that the acid formed by the hydrolysis of the soap is very much more highly adsorbed than the soap itself: that is, than the negative paraffin chain ion plus electrostatically held positive metal ion.

Soap solutions are of particular interest on account of the presence in them of a considerable number of paraffin ion micelles above a certain critical concentration, which is low if the paraffin chain is long.[3] Since this critical concentration seems to lie in the region of rapid change of surface tension with soap concentration, an

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(1) William D. Harkins and G. L. Clark, THIS JOURNAL, **47**, 1854 (1925); J. Powney, *Trans. Faraday Soc.*, **31**, 1510 (1935).

(2) William D. Harkins, G. L. Clark, E. C. H. Davies, THIS JOURNAL, **39**, 541 (1917); E. E. Walker, *J. Chem. Soc.*, **119**, 1521 (1921); L. Lascaray, *Kolloid-Z.*, **34**, 73 (1924); A. Lottermoser and W. Tesch, *Kolloid-Beihefte*, **34**, 339 (1931).

(3) G. S. Hartley, "Aqueous Solutions of Paraffin Chain Salts," "Actualites Scientifiques et Industrielles, "Paris, 1936. See also papers by McBain.

accurate study of the effect of *p*H on the surface tension seemed to be of interest. Unfortunately earlier investigations of this problem have been affected by one of two serious errors. One of these is a failure to use the correct theory in the calculation of the surface tension from the data. For example the ring method has been used in the most extensive investigations of this type, but the results published are not surface tensions, since the method of calculation is incorrect. In general the results not affected by this error *have* been obtained under non-equilibrium conditions, the most important cause of which is the presence of atmospheric carbon dioxide as has been shown by Bulkley and Bitner[4] and by Lottermoser and Baumguertel.[5] From the work of the latter authors it appears that only by using carbon dioxide-free water and by carefully shielding the solutions from contamination by the air can reproducible results be obtained.

2. Preparation of Materials.—Pure sodium laurate and sodium nonylate were prepared from Eastman lauric and nonylic acids by the method of Harkins and Clark.[1] By titration of absolute alcohol solutions of the soaps it was shown that excess free fatty acid or alkali was present in amount less than 0.5% of the weight of the soap. The purity of the soaps was also tested by adding excess standard acid to weighed samples, removing the resulting fatty acid by ether extraction, and back-titrating with standard alkali. For both soaps the observed amount of fatty acid was within 0.5% of that calculated.

The carbon dioxide-free water which was used for all solutions was produced by subjecting ordinary distilled water to an additional distillation and then boiling this water for some time to remove residual carbon dioxide. The water was protected from subsequent contamination by soda-lime tubes.

Only phosphate, borate and carbonate buffers were used. The buffer solutions were prepared from the doubly distilled water and reagent quality chemicals. The surface tension of all the buffers was measured in the absence of soap and in no case did the value obtained differ sensibly from that for pure water.

Experimental Methods.—The surface tension of the majority of the solutions was measured by the ring method using an apparatus of the type designed by Harkins and Jordan[6] and the corrections given by them were employed in the calculations. A few measurements were made by the drop weight method making use of the apparatus and procedure developed by Harkins and Brown.[7]

In the experiments by the ring method the flask which contained the liquids whose surface tensions were to be determined was immersed in a constant temperature bath. The construction of the flask was such that contact of its contents with atmospheric gases was prevented easily. The mean diameter of the platinum-iridium ring was 1.2756 cm. and that of the wire, 0.0314 cm. It is important to emphasize that the values of the surface tension obtained by the ring method have been subjected to the Harkins and Jordan corrections since, without these corrections, even though the apparatus had been calibrated for pure water, some of the results would have been in error by five or ten per cent. from this source alone.

In the surface tension determinations by the drop weight method the solutions were again carefully shielded from contamination by carbon dioxide. The diameter of the glass dropping tip was 0.3552 cm.

It is interesting to note that, for identical soap solutions, the drop weight method gives slightly higher values for the surface tension than the ring method, while both methods give identical values for pure liquids. The precision of each method is better than 0.5% but the surface tension values from the drop weight method are consistently higher by one or two per cent. Since the ring method values are lower, which indicates that more complete surface adsorption has taken place, it is probable that they are the more accurate. The absolute accuracy of the determinations may not be better than 3 or 4%.

The solutions to be measured were made up either by placing a weighed amount of the dry soap in a volumetric flask and adding water and solutions of buffer and neutral salt, or by diluting more concentrated solutions of the soap. One portion of a solution was used for the surface tension measurement and another portion for the determination of its *p*H. The measurements of surface tension were ordinarily made in an atmosphere of water-pumped nitrogen which had been passed through a purifying train for the removal of any possible dust, grease and carbon dioxide. All measurements were made at 25 ± 0.05°. The hydrogen ion concentration of the solutions was measured by means of a glass electrode whose accuracy and constancy was checked frequently with the aid of a standard phthalate buffer. The values given for the *p*H of the solutions are accurate to within one-tenth *p*H unit.

3. Effects of *p*H and Salts on the Surface Tension of Aqueous Sodium Laurate Solutions (Tables I and II).—Both hydrogen ion and salt concentration have a remarkably great effect upon the surface tension of solutions of soaps and in particular of sodium laurate. For example at a *p*H of 10.4 to 11.2 the clear solution at 0.005 molar exhibits the high tension of 60.85 dynes per cm. with a 0.001 N buffer, but the very low tension of 23.2 dynes per cm. at a *p*H of 7.46 and 0.01 N buffer. The surface tension of the solution with 0.001 N buffer is found to rise rapidly from a *p*H of 7.5 to about 10 and then to remain almost constant (Fig. 1, curve 3). If a more concentrated buffer is used the surface tension at a *p*H of 7.5 is almost the same, but is much lower at a higher *p*H.

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[4] R. Bulkley and F. G. Bitner, *Bur. Standards J. Research*, **5**, 951 (1930).

[5] A. Lottermoser and B. Baumguertel, *Kolloid-Beihefte*, **41**, 73 (1935).

[6] W. D. Harkins and H. F. Jordan, THIS JOURNAL, **52**, 1751 (1930).

[7] W. D. Harkins and F. E. Brown, *ibid.*, **41**, 499 (1919).

The lowering of the surface tension as the concentration of the buffer increases is an effect due to the concentration of the salt. For example if at a given *p*H a 0.001 *N* buffer is used, then the addition of enough sodium chloride to make the total salt concentration 0.1 is found to lower the surface tension to a value almost exactly that found when a 0.1 *N* buffer is used. Such values are represented in Fig. 1 by triangles.

TABLE I

VARIATION OF THE SURFACE TENSION OF 0.005 MOLAR SODIUM LAURATE SOLUTION WITH *p*H AT 25°

Buffer	*p*H	Appearance of solution	Surface tension dynes/cm.	Method
A. Buffer concentration 0.1 normal				
NaOH	12.05	Clear	44.14	Ring
Carbonate	11.22	Clear	43.22	Ring
Carbonate	10.75	Clear	42.97	Ring
Carbonate	10.24	Clear	41.53	Ring
Borate	10.05	Clear	41.10	Ring
Carbonate	9.76	Clear	39.63	Ring
Borate	9.40	Clear	38.65	Ring
Borate	9.03	Clear	36.00	Ring
Borate	8.61	Clear	30.87	Ring
Borate	8.21	Clear	27.07	Ring
Phosphate	8.10	Clear	25.82	Ring
Borate	7.95	Very sl. cloudy	25.76	Ring
Phosphate	7.68	Cloudy	23.60	Ring
B. Buffer concentration 0.01 normal				
Na_3PO_4	11.71	Clear	56.77	Ring
Carbonate	11.00	Clear	57.37	Drop wt.
Carbonate	10.93	Clear	56.41	Ring
Carbonate	9.77	Clear	54.23	Ring
Phosphate	8.91	Clear	49.20	Ring
Bicarbonate	8.49	Clear	44.49	Ring
Phosphate	7.96	Clear	31.38	Ring
Phosphate	7.65	Sl. cloudy	25.18	Ring
Phosphate	7.46	Cloudy	23.18	Ring
C. Buffer concentration 0.001 normal				
NaOH	11.21	Clear	60.89	Ring
Carbonate	10.38	Clear	60.84	Ring
Bicarbonate	8.80	Clear	53.20	Ring
Phosphate	8.15	Clear	43.59	Ring
Phosphate	7.58	Clear	27.73	Ring
Phosphate	6.95	Turbid	30.90	Ring
Phosphate	6.00	Very turbid	31.34	Ring

TABLE II

EFFECT OF ADDED SALTS ON THE SURFACE TENSION OF BUFFERED 0.005 MOLAR SOLUTIONS OF SODIUM LAURATE (25°)

*p*H	Buffer concn. *N*	Added salt, *M*	Surface tension, dynes/cm.
A. Buffers made from sodium salts			
8.96	0.001	0.009 NaCl	49.26
10.05	.001	.009 NaCl	54.15
8.93	.001	.1 NaCl	34.85
8.56	.01	.09 NaCl	31.25
9.03	.01	.09 NaCl	34.99
10.60	.01	.09 NaCl	42.43
10.85	.01	.03 Na_2SO_4	45.36
10.85	.01	.09 KCl	44.38
B. Buffers made from potassium salts. These data are not shown in the figures			
8.35	0.01	... KCl	42.67
11.00	.01	... KCl	57.48
10.4	.001	0.009 KCl	55.58
10.2	.001	.099 KCl	43.08
8.22	.001	.009 KCl	41.31
8.27	.001	.099 KCl	28.60
8.33	.01	.09 KCl	31.58

Since curve 3 of Fig. 1 represents the surface tension when only a very dilute buffer is used, it may be considered to give most exactly the dependence of the surface tension upon *p*H, while curves 2 and 1 exhibit the very pronounced salt effect. Thus the presence of the salt increases the adsorption of the surface active constituent from the solution. This effect is greatest at the higher values of the *p*H where the presence of the extremely surface active acid is most improbable, and where the surface active component would seem to be the soap.

If the soap is sodium laurate and a potassium salt is added the lowering of surface tension is almost, but not quite, as great as if sodium chloride is added. Thus at a *p*H of 10.4 a 0.005 *N* sodium laurate solution with a 0.001 *N* buffer exhibits a surface tension of 60.9 dynes per cm. The addition of 0.009 *M* sodium chloride lowers this to 54.15 (*p*H = 10.05); of potassium chloride to 55.58 (*p*H 10.4). At a *p*H of 10.05 the value for potassium chloride would be about 54.6, so the lowering produced by this salt is only slightly less than that by the sodium salt with its common ion. In this connection it should be noted that potassium laurate is more soluble than the sodium salt.

This salt effect was found by Harkins and Clark, who, however, obtained it only with sodium hydroxide. They attributed the nearly linear decrease in surface tension, above a sodium concentration of about 0.01 *N*, to an increase in the activity of the soap in solution, due to the presence of the base, and this increased activity was supposed to give an increased adsorption.

In Fig. 1, where the *p*H dependence is plotted, the dotted portions of the several curves indicate the regions in which the solutions are not homogeneous. Since lauric acid is very insoluble, it is impossible to reduce the *p*H of laurate solutions even to seven without precipitating the acid, or, in the more alkaline solutions, possibly an acid soap. For curve 3 this figure, which gives the results for 0.005 molar sodium laurate solutions in 0.001 normal buffers, the measurements were continued into the acid region even though there was a considerable amount of precipitate present.

4. Sodium Nonylate Solutions (Table III and Fig. 2).—Since sodium nonylate has a much shorter hydrocarbon chain than the laurate, its thermodynamic activity in the surface at a given surface concentration is much greater, and so it is much less adsorbed at low concentrations. Thus all of the effects found in sodium laurate solutions may be expected to repeat themselves in those of the nonylate, but only at much higher concentrations.

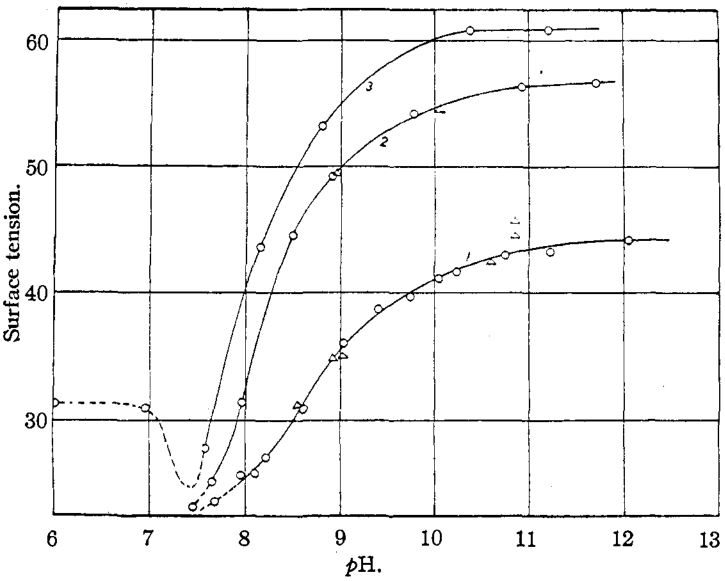

Fig. 1.—Surface tension of 0.005 M sodium laurate solutions as a function of *p*H. Curve 1 is for 0.1 N buffers; curve 2 for 0.01 N and curve 3 for 0.001 N buffers. Triangles indicate addition of neutral salt. The lowering of surface tension from 3 to 2 to 1 is due to the increase in salt concentration.

With a 0.005 M solution of sodium nonylate and 0.01 N buffers the curve which represents the effect of *p*H upon the surface tension is not very different from that for the same concentrations for laurate except that it is (1) displaced to a smaller *p*H by about two units, and (2) displaced to much higher values of the surface tension.

At a concentration of 0.1 for the nonylate, or 20 times as much, the curve is displaced to higher values of the *p*H and lower surface tensions (Fig. 2).

5. Salt or Electrolyte Effect on the Surface Tension of Solutions of Sodium Cetyl Sulfate (Table IV).—That the salt effect is not due to the weakness of the acid of the soap is shown by Table IV, which indicates that with sodium cetyl sulfate the surface tension of the 0.0001 M solution is 63.4 dynes per cm., but the presence of 0.02 M sodium chloride, hydrogen chloride, or sodium hydroxide, lowers the value to about 39 dynes.

6. Effect of Concentration of the Soap (Tables V and VI).—Sodium laurate is highly adsorbed from its solutions at concentrations between 0.001 and 0.01 M (Fig. 3). It is probably more strongly adsorbed if the soap alone is present or if the *p*H is 8.5, than at a *p*H of 11.1. To make it certain that this is true it would be necessary to have a knowledge of the activity of the soap in the solutions involved. The effect of concentration is not very different with the nonylate (Fig. 4), except that at a given concentration the surface tension is higher and the adsorption lower.

7. Discussion

The data obtained in this work indicate that the principal effect of a lowering of *p*H upon the surface tension is due to increased hydrolysis and the resultant formation of the acid. For example with 0.005 M sodium nonylate with

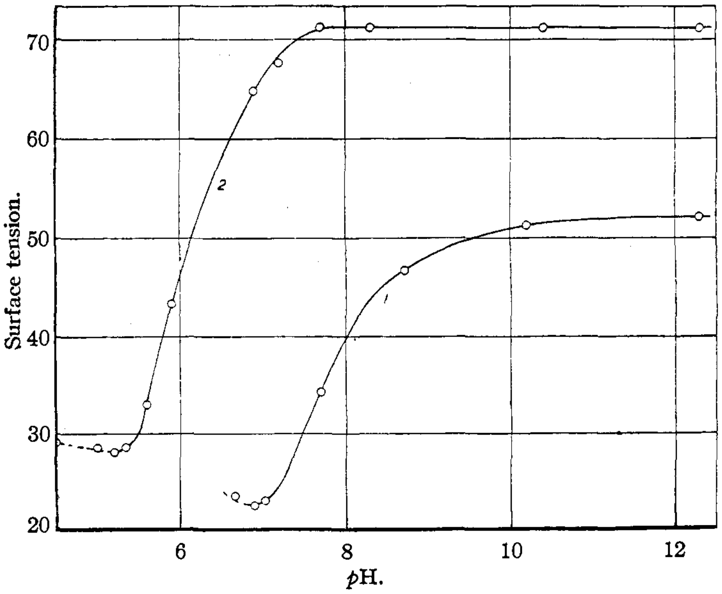

Fig. 2.—Surface tension of sodium nonylate solutions as a function of *p*H. Curve 1 gives the results for 0.1 M sodium nonylate in 0.01 N buffers; curve 2 is for 0.005 M sodium nonylate in 0.01 N buffers.

TABLE III

VARIATION OF THE SURFACE TENSION OF SODIUM NONYLATE SOLUTIONS WITH pH (25°)

Buffer	pH	Appearance of solution	Surface tension
A. 0.005 M sodium nonylate in 0.01 N buffers, ring method			
NaOH	12.5	Clear	70.18
Carbonate	10.4	Clear	70.18
Borate	8.3	Clear	70.20
Borate	7.7	Clear	70.18
Phosphate	7.2	Clear	67.60
Phosphate	6.9	Clear	64.80
Phosphate	6.3	Clear	50.48
Phosphate	5.9	Clear	43.3
Phosphate	5.6	Clear	33.13
Phosphate	5.3	Clear	28.59
Phosphate	5.2	Turbid	28.04
Phosphate	5.0	Turbid	28.47
Phosphate	4.5	Very turbid	29.05
B. 0.1 M sodium nonylate in 0.01 N buffers, drop weight method			
NaOH	12.3	Clear	52.08
Borate	10.2	Clear	51.25
Borate	8.7	Clear	46.69
Borate	7.7	Clear	34.34
Phosphate	7.0	Sl. opalescent	23.01
Phosphate	6.9	Turbid	22.47
Phosphate	6.7	Turbid	23.45

0.01 N buffers the surface tension remains at a constant value of 70.2 over the long range of pH from 12.5 to 7.2. Thus the lowering of the surface tension from 72.1 for water to 70.2 dynes per cm. may be attributed to the adsorption of nonylate ions plus the electrostatically held sodium ions. Below this pH the surface tension decreases more and more rapidly with decreasing pH due to the increasing hydrolysis of the soap, and finally falls to 28.0 dynes per cm. at a pH of 5.2. When the soap is 0.1 M the sodium nonylate lowers the surface tension to 47.9 dynes per cm. but at a pH of 6.7 it falls to 23.5 dynes per cm. The same low tension is found when solutions of the soap are measured in the presence of carbon dioxide. According to Laing[8] the film which forms on a neutral soap solution in the absence of carbon dioxide has the composition of an acid soap.

TABLE IV

EFFECT OF ELECTROLYTES ON THE SURFACE TENSION OF SODIUM CETYL SULFATE SOLUTIONS AT A TEMPERATURE OF 25°

Concn. of soap, M	Added electrolyte, M	Surface tension
0.001	..	37.4
.0001	..	63.4
.0001	0.02 NaCl	38.8
.0001	.02 HCl	38.2
.0001	.02 NaOH	40.0

TABLE V

SURFACE TENSION OF SODIUM LAURATE SOLUTIONS AT VARIOUS CONCENTRATIONS (25°)

Concn. of Soap, M	pH	Surface tension	Method
A. Unbuffered solutions			
0.00005	7.0	71.52	Drop wt.
.0005	7.2	70.39	Drop wt.
.005	8.1	44.97	Drop wt.
.05	9.9	32.50	Drop wt.
B. 0.01 N $NaHCO_3$ buffer			
0.0001	8.5	71.19	Ring
.0005	8.5	68.89	Ring
.0012	8.5	63.49	Ring
.005	8.5	44.49	Ring
.012	8.6	29.46	Ring
.04	9.0	25.81	Drop wt.
C. 0.01 N Na_2CO_3 buffer			
0.0001	11.1	71.26	Ring
.0005	11.1	69.50	Ring
.0012	11.1	67.22	Ring
.005	11.1	56.41	Ring
.012	11.0	45.69	Ring
.012	11.0	47.03	Drop wt.
.04	11.0	36.65	Drop wt.
.1	11.0	35.95	Drop wt.

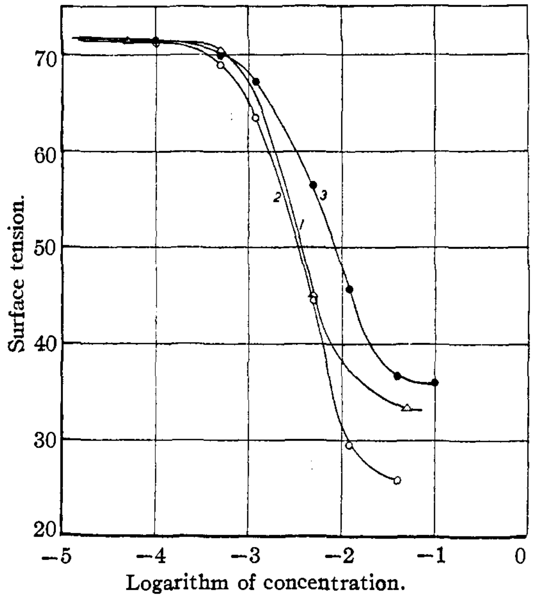

Fig. 3.—Surface tension of sodium laurate solutions as a function of concentration. Curve 1 is for solutions in water alone; curve 2 for solutions at a pH of 8.5; and curve 3 for solutions at a pH of 11.1.

In solutions of the long chain alkyl sulfates Lottermoser and Puschel[9] have found that the discontinuity in the conductivity curves, which is

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[8] M. E. Laing, *Proc. Roy. Soc.* (London), **A109**, 28 (1925).

[9] A. Lottermoser and F. Puschel, *Kolloid-Z.*, **63**, 175 (1933).

TABLE VI

SURFACE TENSION OF SODIUM NONYLATE SOLUTIONS AT VARIOUS CONCENTRATIONS (25°)

Concn. of soap, *M*	*p*H	Surface tension	Method
A. Unbuffered solutions			
0.0001	7.0	71.47	Drop wt.
.001	7.2	70.30	Drop wt.
.01	8.0	55.47	Drop wt.
.1	8.6	47.90	Drop wt.
B. 0.01 *N* Carbonate buffer			
0.0001	10.4	72.00	Ring
.001	10.4	71.60	Ring
.005	10.4	70.36	Ring
.01	10.4	69.30	Ring
.05	10.4	59.93	Drop wt.
.1	10.4	51.57	Drop wt.
.3	10.6	39.85	Drop wt.

presumed to represent the critical concentration for the appearance of micelles, comes at very nearly the same concentration as that at which the surface tension falls to its low value. The writers, in work with sodium cetyl sulfate, have found that there is a certain critical concentration below which the surface film is adsorbed very slowly, but above which it is adsorbed rapidly, which seems to indicate that at this concentration there is a change in the molecular species which is adsorbed.

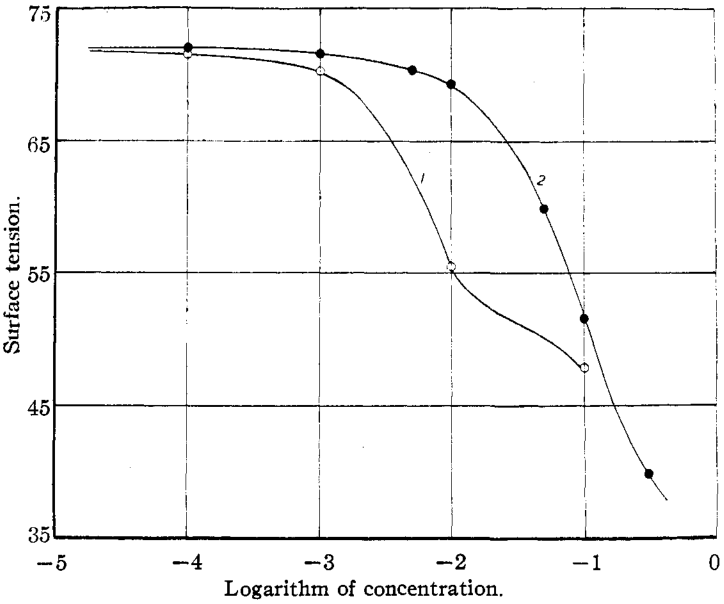

Fig. 4.—Surface tensions of sodium nonylate solutions at varying concentrations. Curve 1 is for solutions in water alone; curve 2 is for solutions in 0.01 *N* sodium carbonate at a *p*H of 11.0.

The conductivity of solutions of the long chain fatty acid soaps has been investigated by Ekwall.[10] At 21° he has noted that there is a break in the conductivity–concentration curves of sodium laurate solutions at about 0.005 molar, which corresponds in the present work to a surface tension of about 45 dynes per cm., which is well above the minimum surface tension (Fig. 2). However the effect of hydrolysis is so great as largely to obscure the effects of the micelles upon the surface tension.

It has been found by Harkins and Fischer[11] that the adsorbed film of sodium oleate in an emulsion is monomolecular with respect to oleate ions. Such a film is itself in a certain sense a large micelle, which in a basic solution consists of a layer of negative long chain fatty acid ions at the surface with a layer of electrostatically held positive "gegen" ions just below them. It has been shown[12] that these "gegen" ions are held very tightly, so that the "diffuse ionic layer" is not very diffuse.

A laurate, rather than a longer chain fatty acid salt, was chosen for this work in order to make the micelles less prominent. If it is supposed that at a *p*H of 11.1 fatty acid ions and sodium ions alone are adsorbed then the adsorption could be calculated if the activity of the soap in solution were known. If at a concentration of 0.01 *M* the activity were to vary as the concentration then the area per molecule of soap in the solution would be about 35 sq. Å., which corresponds to a monomolecular expanded film. The molecular area calculated in the same way for 0.1 *M* sodium oleate (*p*H = 11) is about 20 sq. Å.

The adsorption (μ) is given by the relation

$$\mu = -\frac{1}{RT}\cdot\frac{\partial\gamma}{\partial \ln (a_+ a_-)}$$

where a_+ and a_- are the activities of the ions. Obviously the correct molecular areas cannot be calculated without a knowledge of these activities. An increase in the number of micelles with concentration causes the activity of the soap to increase less rapidly than if micelles were not present.

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[10] P. Ekwall, *Acta Akad. Abo. Math. Phys.*, **4**, No. 6 (1927); *Z. physik. Chem.*, **161**, 195 (1932).

[11] W. D. Harkins and E. K. Fischer, *J. Phys. Chem.*, **36**, 98 (1932).

[12] W. D. Harkins, "Colloid Symposium Monograph," Vol. VI, Chemical Catalog Co., New York, 1928, p. 17.

Summary

1. An investigation of the effect of pH on the surface tension of solutions of sodium laurate and sodium nonylate shows that the surface tension is relatively high in basic and low in neutral solutions. This agrees with the idea that the long chain paraffin ions together with the electrostatically held positive "gegen" ions are adsorbed from the strongly basic solutions, while the much more surface active acid is adsorbed more greatly from the slightly basic or neutral solutions.

2. The presence of electrolytes, such as neutral salts, is found to lower greatly the surface tension, especially in the basic solutions. This indicates either that the adsorbed constituent is made more highly surface active, as by an effect upon the ionic atmosphere of the positive gegen ions, or there is an increase in the activity in the solution of the constituent which is adsorbed, or the nature of one of the adsorbed constituents is changed. The effect is not related in a simple way to the ionic strength, but exhibits a simple relation to the concentration of the electrolyte.

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ITHACA, N. Y.

[CONTRIBUTION FROM THE COATES LABORATORY, LOUISIANA STATE UNIVERSITY]

The Oxidation of Aqueous Sulfide Solutions by Hypochlorites

BY A. R. CHOPPIN AND L. C. FAULKENBERRY

The oxidation of hydrogen sulfide results in the formation of sulfur,[1] sulfuric acid[2,3] or a mixture of these substances. No other intermediate products have been shown to be present except in the specific instance of the reaction between hydrogen sulfide and sulfur dioxide,[4] in which case polythionic acids[5] may be shown to be intermediate products. The oxidation of the alkali sulfides[6,7] is not so simple or direct[8] and may yield as end-products, sulfur, polysulfides, sulfites,[9,10] thiosulfites, or sulfates, depending upon the temperature and alkalinity of the solution. The chief difference in the oxidation of sulfide ions in acid or alkaline solutions lies in the formation of thiosulfites or polythionates. This is due no doubt to the greater stability of thiosulfates in alkali,[10,11] and its ready conversion to the polythionates[10,12,13] in acid solutions.

The *weight of opinion* seems to indicate that sulfur is the primary oxidation product of sulfides and with weak oxidants may be the only end-product in acid solution. In basic solution the hydroxyl ion becomes an important reactant[14,15] whose importance increases with concentration.

A great many of the intermediate products appearing in the oxidation of sulfides are due to secondary reactions. This is particularly true of the reactions involving oxidants such as the hypochlorites.[16,17]

Experimental

Iodometric methods were used in standardizing the solutions of sulfide and hypochlorite and to determine the oxidizing or reducing power of the mixtures. The quantity of sulfate produced was determined by a modification of the benzidine–hydrochloride method[18] which was substantiated in turn by the usual gravimetric methods. The oxidizing–reducing character of the solutions studied rendered the use of colorimetric indicators and the quinhydrone electrode impossible for determining the hydrogen ion concentration of the reaction medium. The glass electrode, however, proved quite satisfactory for this purpose and was used throughout the investigation.

Preliminary work[19] disclosed the fact that when equivalent quantities of sulfide and hypochlorite were mixed, the resulting solution showed a qualitative test for sulfide and sulfate and reduced a considerable quantity of iodine solution. This would indicate that sulfide and hypochlorite do not react equivalent for equivalent, or in a ratio of 1:1, but there is some reaction in effect whereby more hypochlorite is required than is indicated by the simple ratio.

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