[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Change with Time of the Surface Tension of Sodium Laurate Solutions

BY G. C. NUTTING AND F. A. LONG

Attainment of the equilibrium surface tension of dilute aqueous solutions of long chain capillary active strong electrolytes is slow.[1,2,2a] To transport to the surface region sufficient solute to saturate the surface by an unhindered process of diffusion from the bulk of the solution should require only a small fraction of the time actually necessary for surface saturation.[3] The rate of transport may be drastically reduced, however, by a potential barrier to ions set up by the ions themselves as they diffuse into the surface region. A second retarding factor that may possibly be of importance is the time required for stable orientation of the long, highly unsymmetrical ions in the surface film and the accompanying diffuse double layer.

A significant time effect may thus be expected among solutions of sodium salts of higher fatty acids (the soaps), with added complexities arising from the influence of hydrolysis on the surface active species.

It has been found that the surface tension of dilute solutions of sodium laurate and nonylate increases markedly with *p*H.[4,5] When the *p*H is so low that there is incipient precipitation of fatty acid the surface film over the solution doubtless contains an appreciable fraction of non-ionized fatty acid molecules—possibly present as an "acid soap." The fraction of fatty acid increases very greatly with the length of the hydrocarbon chain and in a stearate solution is probably predominant.[6] As the *p*H is raised the composition of the surface films changes and the proportion of fatty acid ions becomes dominant.

At equal surface concentrations the surface free energy of the ion-covered solution would probably be somewhat smaller than that of a solution whose surface consists of neutral molecules containing the same paraffin chain, owing to electrostatic repulsion between the paraffin chain ions.[7] However, for similar bulk concentrations, the solute concentration in the surface of the ion-covered solution would undoubtedly be the smaller, again due to mutual repulsion of the ions. Since experimentally the surface tension for an ionic layer is usually larger, the second effect seems to be dominant.

In reporting the increase in surface tension with *p*H it has been tacitly assumed that the surfaces at the time of measurement were in all cases saturated. The recent work on the slow fall of surface tension of paraffin chain salt solutions makes questionable the correctness of this assumption. At low *p*H it seems reasonable that adsorption of fatty acid molecules or of micellar particles for which there is no special hindrance to diffusion into the surface is so rapid that a surface only a few minutes old is indeed practically saturated.[8] At higher *p*H adsorption of the fatty acid ions may be expected to be a slow process, requiring several hours for completion. The surface tension of such a solution if measured, as it well might be, two minutes after the surface is formed will be higher than the equilibrium value, corresponding to the only partial saturation of the surface with fatty acid ions.

The present study is of the rate of attainment of the equilibrium surface tension of saturated surfaces over the *p*H range 7 to 11 and at several concentrations of sodium laurate.

Experimental Part

Surface tensions were measured by the method of sessile bubbles. The laurate solutions were contained in a vessel 6 × 6 × 4 cm. made of Pyrex glass to minimize spurious effects due to contamination of the solutions by polyvalent metal ions. A glass plate was cemented to the Pyrex cell with paraffin, ensuring against evaporation of the solutions or entry of carbon dioxide. Bubbles of purified nitrogen were blown under the slightly concave surface of a Pyrex lens placed near the center of the cell. The equatorial diameter and the height from the equator to the apex of the bubble were measured by means of a low power microscope mounted on two accurate screws, the one permitting motion in the vertical, the other in a horizontal direction. The entire apparatus was mounted on an extremely rigid support in a constant temperature room

---

(1) Adam and Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).

(2) Nutting, Long and Harkins, THIS JOURNAL, **62**, 1496 (1940).

(2a) McBain and Wood, *Proc. Roy. Soc.* (London), **A174**, 295 (1940).

(3) Doss, *Kolloid. Z.*, **86**, 205 (1939).

(4) Long, Nutting and Harkins, THIS JOURNAL, **59**, 2197 (1937).

(5) Powney and Addison, *Trans. Faraday Soc.*, **34**, 372 (1938).

(6) Powney and Jordan, *ibid.*, **34**, 363 (1938).

(7) Abramson, "Electrokinetic Phenomena," p. 130; Adams, "The Physics and Chemistry of Surfaces," 2d ed., p. 336.

(8) Powney and Jordan (ref. 6) show that under certain conditions the concentration of fatty acid in the solution, as measured by the hydrolysis, is many times greater than the concentration of a saturated solution of the acid, owing to formation of micelles of "acid soap."

maintained at 25°. In calculating the surface tension the corrections given by Porter[9] were applied. The apparatus was tested and found to give accurate results over the range of surface and interfacial tensions 72 to 2, using bubbles of air in water, nitrobenzene, benzene and ethyl alcohol; and drops of methyl hexyl ketone, undecylenic acid and isobutyl alcohol in water.

Most of the soap solutions used were prepared from a quantity of Eastman Kodak Co. lauric acid (Sample II) of freezing point 43.2° or from sodium laurate made from this acid by the method of Harkins and Clark.[10] A few runs were made with lauric acid (Sample I) of extreme purity (freezing point 43.22°) kindly given us by Professor E. E. Reid.[11] Time–surface tension curves of laurate solutions from the two sources at concentrations of 0.001 *N*, 0.0025 *N*, and 0.005 *N* at *p*H 11 were closely similar, indicating that the purity of the Eastman lauric acid was sufficiently high to permit its use in the remainder of the work. Conductivity water was used in preparing all the solutions.

Solutions made up from lauric acid were prepared by adding the calculated amount of standardized sodium hydroxide solution to weighed amounts of the acid and then adding the buffer solutions and conductivity water to give the proper volume. Solutions of *p*H 11 were 0.001 *N* in sodium hydroxide, and the concentration of the phosphate and carbonate buffers used to maintain other *p*H's was in all cases 0.001 *N*. The carbonate buffers were prepared from sodium carbonate and sodium bicarbonate. For the phosphate buffers, potassium mono-hydrogen and potassium di-hydrogen phosphates were used. Solutions of the same *p*H and of the same soap concentration but prepared with different buffers gave similar results, indicating the lack of specific buffer-mixture effects.

It is well known that the surface tension of solutions of soaps and soap-like substances is affected by added salts. However, the effects of sodium and potassium salts usually are significant only for comparatively large salt concentrations. For the present work, salt effects are probably quite unimportant because of the low salt concentration and also because the concentration of added electrolyte was similar for all the solutions.

The *p*H of the various solutions was measured with a glass electrode calibrated with standard buffers for the *p*H range involved.

Results and Discussion

The curves of Fig. 1 show that at *p*H 11 and concentrations between 0.001 *N* and 0.02 *N* there is actually a pronounced time effect in the surface tension of laurate solutions. After the first measurement, made at a surface age of about four to six minutes, the surface tension falls gradually over a period of several hours, ultimately attaining a static value five to ten dynes lower than the initially measured tension.

At concentrations higher than about 0.02 *N* the time effect largely disappears. The fall after the initial measurement is only a fraction of a dyne and occurs within a few minutes. Powney and Addison[5] indicate that the critical concentration for micelle formation in sodium laurate solutions under conditions of suppressed hydrolysis is about 0.02 *N*. Such a disappearance of the time effect just past the concentration at which micelle formation begins has been noted previously in experiments on solutions of the alkyl sulfates.[1,2]

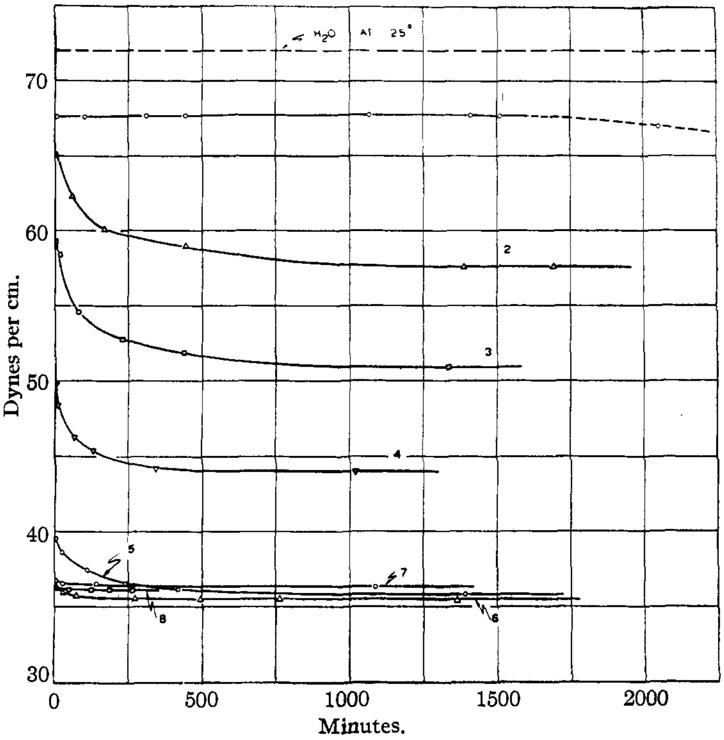

Fig. 1.—Surface tension of sodium laurate solutions at *p*H 11. Concentrations are as follows:

Curve 1	0.001 *N*	Curve 5	0.02 *N*
2	.0025	6	.03
3	.005	7	.04
4	.01	8	.07

Unlike the alkyl sulfates, however, the equilibrium surface tension of the laurate solutions in the non-micellar concentration region depends strongly upon the concentration. A characteristic value at each concentration is attained within a maximum (usually) of twelve hours and this

---

(9) Porter, *Phil. Mag.*, **15**, 163 (1933).

(10) Harkins and Clark, THIS JOURNAL, **47**, 1854 (1925).

(11) Reid and Meyer, *ibid.*, **55**, 1574 (1933).

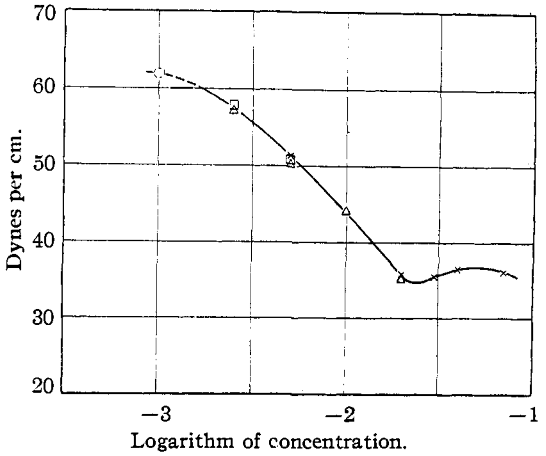

Fig. 2.—Equilibrium surface tension of sodium laurate solutions at *p*H 11 and 25°. Squares indicate measurements made with lauric acid Sample I; triangles, lauric acid Sample II; crosses, sodium laurate. The dotted circle for 0.001 *N* was obtained by extrapolation of curve 1 in Fig. 5.

value has been found repeatedly to remain perfectly constant for periods up to forty-eight hours.

A minimum in the curve of equilibrium surface tension *versus* concentration occurs near 0.025 *N* and 35.5 dynes per cm. The slow rise at higher concentrations leads to a broad maximum at 0.05 *N* and 36.5 dynes, and then the curve falls slightly once more as is shown in Fig. 2.

Figure 3 represents data on 0.005 *N* laurate at five *p*H's from 7.7 to 11.0. On lowering the *p*H from 11 the time effect diminishes at an increasing rate and finally vanishes almost completely. A 0.005 *N* solution at *p*H 7.7 is slightly supersaturated, for during the observation period of twenty-hour hours a noticeable turbidity developed. Partial removal of solute accounts for the very slight rise of surface tension with time. In the fresh solution most of the soap was doubtless bound up in micelles, since the critical concentration for micelle formation is probably much less than 0.02 *M* when hydrolysis is not suppressed. It is to be noted that the equilibrium surface tension (22.5 dynes) characteristic of a micellar solution of *p*H 7.7 is much lower than the tension (about 35 dynes) displayed by micellar solutions of *p*H 11. This is probably due to the large proportion of fatty acid molecules in the micelles formed at *p*H 7.7. In the surface film formed by dissociation of such micelles fatty acid ions are widely enough separated from one another by neutral acid molecules to minimize the tendency of electrostatic repulsion to disperse the surface active particles. Hence the density of oriented paraffin chains in the surface film is high and the surface tension of the solution correspondingly low.

Figure 4 shows the time effect in 0.001 *N* laurate solutions from *p*H 6.9 to 11.0. The findings on 0.005 *N* laurate are repeated qualitatively. With decreasing *p*H the equilibrium surface tension and the time required to attain it diminish markedly. At *p*H 10 the equilibrium value, 60.3, is attained only after three days, while at *p*H 6.9 the static surface tension of 30.8 is reached within about an hour. No directly measured equilibrium surface tension for *p*H 11 can be reported. Observations on several solutions of *p*H 11 gave a surface tension close to 67.8 dynes at a surface age of about five minutes. The initially measured value was maintained for almost a day and then the surface tension began to drop slowly. By

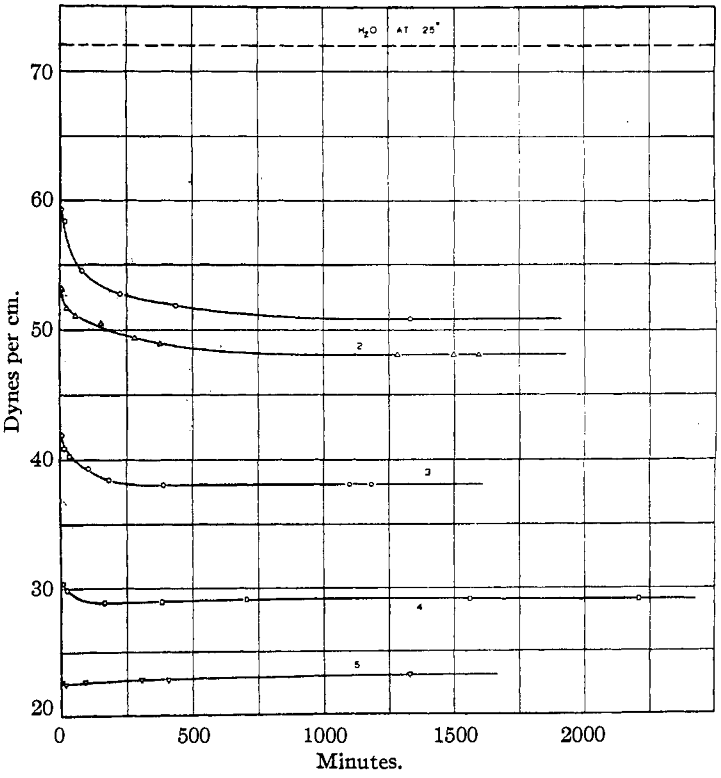

Fig. 3.—Time effect in 0.005 *N* laurate solutions.

Curve	1	2	3	4	5
*p*H	11.0	9.4	8.5	8.0	7.7

extrapolating the upper curve in Fig. 5 it appears that the equilibrium surface tension at *p*H 11 is about 60.8 dynes. To reach this a week or more would doubtless be required. In so long a time appreciable interference with the natural rate of fall by contamination or by jarring is quite probable and the significance of measured surface tensions is therefore questionable.

In our earlier experiments[4] the surface tension of newly formed surfaces of laurate solutions was measured by the ring method. The only results that are strictly comparable with the present work are for 0.005 *N* solutions in 0.001 *N* buffers. The initially measured surface tension using the method of sessile bubbles is consistently lower than with the ring method—about 1 dyne per cm. at *p*H 11, 5 dynes at *p*H 9 and 9 dynes at *p*H 8. The discrepant results are ascribable to the different surface ages at which initial measurements by the two methods were made. The first measurement of a sessile bubble was completed usually five to six minutes after its formation, while the ring measurement was made when the surface age was two to three minutes. The time–surface tension curves show that the change of surface tension in the initial minutes is greatest when the *p*H is low and that the tension of a surface five minutes old may well be 10 dynes less than that of a surface three minutes old. Drop weight measurements involve even fresher surfaces and it is found that the surface tension is still higher than when determined by the ring method.[4]

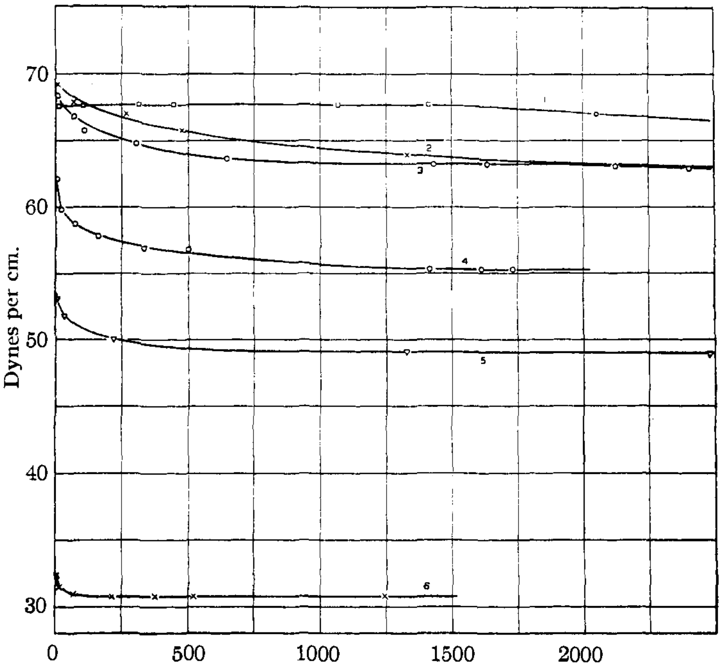

Fig. 4.—Time effect in 0.001 *N* laurate solutions.
Curve 1, *p*H 11.0. Surface tension 66.5 dynes at 2760 min.
Curve 2, *p*H 10.0. Static surface tension of 60.3 dynes attained at 4300 min.
Curve 3, *p*H 9.2. 59.0 dynes observed at 7300 min.
Curve 4, *p*H 8.3. Curve 5, *p*H 7.8. Curve 6, *p*H 6.9.

The equilibrium surface tension of 0.005 *N* sodium laurate solutions is about ten dynes lower than the previously reported ring method values throughout the *p*H range 7.7 to 11. This difference of ten dynes is 20 to almost 50% of the static surface tension. At *p*H 11 the difference at the times of initial measurement is small but ultimately approximates ten dynes because of the slow attainment of equilibrium. At *p*H 8 the initial difference is nine dynes and increases only to ten dynes because of the greatly decreased time effect in the less alkaline solutions.

Curves of equilibrium surface tension plotted against *p*H for 0.001 *N* and 0.005 *N* sodium laurate in 0.001 *N* buffers are given in Fig. 5.[12]

These results combined with similar data for other paraffin-chain strong electrolytes suggest that the phenomenon of slow attainment of the equilibrium surface tension is a general phenomenon for such compounds. In all such cases the explanation of much of the observed effect is probably that of Doss[3]—that a surface layer partially covered with paraffin-chain ions inhibits the entry of further ions into the layer. However, it has been shown recently that solutions of certain weak electrolytes such as hydrocinnamic acid also require long periods for establishment of the equilibrium surface tension.[13,14] A satisfying explanation of this observation has not yet been given. A suggestion possibly worthy of experimental test is that steric factors may sometimes

---

(12) Since this work was submitted to the Journal, Tartar, Sivertz and Reitmeier (THIS JOURNAL, **62**, 2375 (1940)) have published surface tension data for sodium laurate solutions buffered with sodium carbonate. These authors have also utilized the sessile bubble method, but the temperature at which their experiments were carried out was 40° so that their results are not strictly comparable. However, qualitatively their results are similar to our own at *p*H 11.

(13) McBain, Vinograd and Wilson, *ibid.*, **62**, 244 (1940).

(14) McBain, Ford and Mills, *ibid.*, **62**, 1319 (1940).

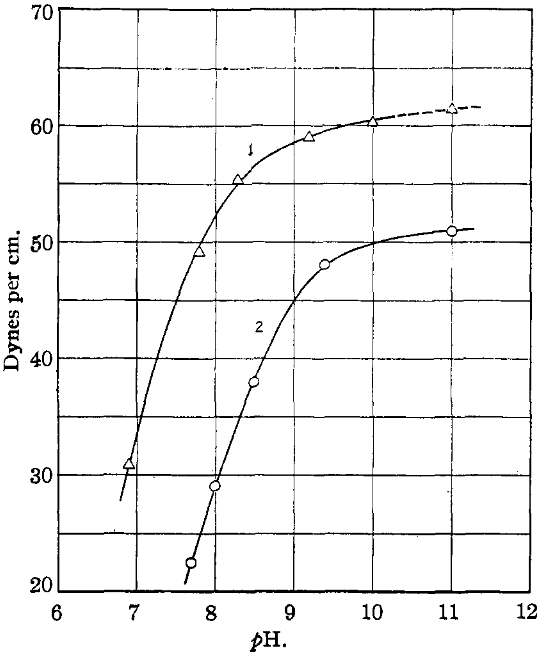

Fig. 5.—Equilibrium surface tension of sodium laurate solutions in 0.001 *N* buffers. Curve 1 is for 0.001 *N* laurate. Curve 2 is for 0.005 *N* laurate.

grossly retard the speed of stable orientation of molecules in the surface region, so that the speed of transport of solute from the bulk of the solution to the surface region is no longer the principal factor determining the time effect in the surface tension.

Summary

The fall with time of the surface tension of aqueous solutions of sodium laurate has been measured by the method of sessile bubbles at 25°. The range of soap concentration was from 0.001 *N* to 0.07 *N*, and of *p*H from 7 to 11. At *p*H 11 and concentrations less than the critical concentrations for micelle formation the surface tension falls gradually for several hours. The equilibrium surface tension depends upon the concentration. The time effect largely disappears in micellar solutions. With decreasing *p*H the equilibrium surface tension and the time required to attain it diminish markedly. This result is thought due to the possibility of closer packing of fatty acid molecules than ions in the surface film and the more rapid diffusion of non-ionized molecules into the surface region.

ITHACA, NEW YORK RECEIVED AUGUST 6, 1940

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Calorimetric Investigations of Organic Reactions. III. The Heats of Ionization of Glycine at 25°[1]

BY JULIAN M. STURTEVANT

The only data concerning the heats of ionization of amino acids at present available are those determined from the temperature coefficients of the ionization constants.[2] While it is probable that the ionization constants themselves are quite reliable, the temperature coefficients are small, so that the per cent. errors in the heats of ionization may be large. For example, in the case of the acid ionization of glycine, measured by Owen,[3] errors in the values of log K_A of ±0.5 per cent. could, in the most unfavorable case, cause an error of 25% in the temperature coefficient and the heat of ionization. The per cent. error to be expected in the heat of the basic ionization of glycine as determined by electromotive force measurements is considerably smaller, partly because the temperature coefficient of the ionization constant is larger and partly because the basic constants themselves are smaller and can therefore be determined with greater accuracy.

The present paper reports some calorimetric measurements of the heats of neutralization of glycine by hydrochloric acid and sodium hydroxide. The interpretation of the calorimetric data is complicated by various medium effects, but it is believed that reliable values for the ionization heats are obtained.

Experimental Part

The calorimetric measurements were made in the apparatus described elsewhere.[4] In the present experiments, varying amounts of hydrochloric acid or sodium hydroxide contained in the dilution cup were allowed to react with varying

---

(1) Part of the material in this paper was presented at the Cincinnati meeting of the American Chemical Society, April, 1940.

(2) See the review by Harned and Owen, *Chem. Rev.*, **25**, 31 (1939).

(3) Owen, THIS JOURNAL, **56**, 24 (1934).

(4) Sturtevant, *J. Phys. Chem.*, in press.