

these values, along with values obtained by other methods.

TABLE IV

## DISSOCIATION CONSTANT OF METHYL YELLOW

Solvent	$pK_1$	$pK_1$ (lit.)
Methanol	3.3	3.4 <sup>1</sup>
Ethanol	3.1	3.1 <sup>a</sup>
Butanol	3.1	2.8 <sup>b</sup>

<sup>a</sup> The value reported by us in a previous paper (ref. 5) was erroneously given as 3.55 instead of 3.1. <sup>b</sup> R. B. Mason and M. Kilpatrick, *THIS JOURNAL*, **59**, 372 (1937).

There is a satisfactory check in the case of methanol and ethanol. The lack of agreement in butanol might be due to the presence of water in the butanol used by Mason and Kilpatrick. The amount of water can be estimated from these data. From equation (6) we find

$$K_1' = K_1 \left[ \frac{c_{H_2O}}{K_p} + 1 \right]$$

where  $K_1'$  is the apparent dissociation constant. So

$$pK_1 - pK_1' = \log \left( \frac{c_{H_2O}}{K_p} + 1 \right)$$

Setting  $pK_1 - pK_1' = 0.3$ , and  $K_p = 0.033$ , we

get  $c_{H_2O} = 0.033$  mole per liter, corresponding to 0.075% water in the butanol used by the above authors.

The colorimetric method could be used for the determination of traces of water in ethanol and butanol. From equation (6) it follows that

$$C_{H_2O} = K_p \left( \frac{rc}{K_1} - 1 \right)$$

It is seen from Table II that the ratio  $r$  increases about 2.5 times when 0.18% water is added to pure ethanol.

## Summary

1. The effect of traces of water on the color equilibrium of methyl yellow in dilute solutions of hydrogen chloride in methanol, ethanol and butanol, has been studied.
2. The relative basicities of these solvents have been determined and were found to decrease in the order: methanol, ethanol, butanol.
3. The dissociation constant of methyl yellow in these solvents has been calculated.

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## The Change with Time of the Surface Tension of Solutions of Sodium Cetyl Sulfate and Sodium Lauryl Sulfate

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

### Introduction

The static value of the surface tension of a pure liquid is attained within a very minute time after the surface is formed, for in order to reduce the surface free energy to its minimum value only a reorientation of molecules already present is necessary. With solutions, however, there is in general at equilibrium an excess or deficiency of solute in the surface layer and an appreciable time interval may be required for the transport of solute molecules from the bulk of the solution into the surface or *vice versa*.

Bond and Puls<sup>1</sup> have measured the surface tension of surfaces whose age is about 0.003 sec. and find that for a variety of aqueous solutions, including solutions of inorganic salts and the lower aliphatic alcohols, the surface tension even in so short a time changes to approximately the static value. They have been able to show that their

experimental values of the surface tension change agree reasonably well with predicted values if diffusion alone is responsible for the time effect.

In the case of certain other solutions the final surface tension is not reached until days or weeks have passed. Examples are solutions of paraffin chain salts and of other molecules which are in part strongly hydrophobic, yet which dissociate into ions in water.<sup>2</sup> Doss<sup>3</sup> has presented evidence that unhindered diffusion would lead to establishment of equilibrium in the surface in a far shorter time than is observed, and that the rate of diffusion of the ions is slowed up enormously near the surface by the electrostatic repulsion of the ions already present in the surface layer.

In the present paper data are presented on the change with time of the surface tension of solutions of sodium cetyl sulfate and sodium lauryl

(2) N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).

(3) K. S. G. Doss, *Kolloid-Z.*, **86**, 205 (1939).

(1) W. N. Bond and H. O. Puls, *Phil. Mag.*, **24**, 864 (1937).

sulfate. The time effect has been studied over the interval between two minutes and about six hours, over a wide range of concentrations, and at particular concentrations in the presence of various inorganic salts.

### Experimental Methods

Sodium lauryl sulfate and sodium cetyl sulfate are salts of strong acids and are thus much better suited for a study of time effects than are the soaps since with the latter a small change in  $pH$ , induced perhaps by atmospheric carbon dioxide, has a large effect on the surface tension. Samples of these two salts were generously supplied by E. I. du Pont de Nemours and Co. and were supposedly of high purity. In addition a partial analysis was carried out and the amount of barium sulfate and alcohol formed indicated a purity of 99% or better.

Surface tensions were measured by the ring method, with the apparatus used by Harkins and Jordan.<sup>4</sup> The apparatus was immersed in a thermostat kept at  $40.00 \pm 0.05^\circ$ . A slow current of water-pumped nitrogen, saturated with water vapor at the temperature of the thermostat, was passed through the apparatus. That this eliminated evaporation was shown by the fact that the volume of the liquid in the cup did not change measurably in two weeks. The ring used in the measurements was of platinum iridium and its mean radius was 0.6378 cm. After precautions had been taken to prevent condensation of water on the suspension wire, it was found that the weight of the wire and ring remained constant to within 0.1 mg. over a two-day period.

Since it was found that electrolytes in small amounts affected considerably the rate of change of surface tension, much care was taken in preparing the solutions. The water used was conductivity water, redistilled in a quartz still. Solutions were made up in very clean soft glass volumetric flasks by diluting stock solutions of 0.01  $M$  alkyl sulfate. The solutions were used shortly after they were prepared since experiments showed that solutions kept for a long time in glass vessels gave results different from either fresh solutions or solutions kept in quartz vessels.

The solutions were brought to  $40^\circ$  and then introduced into the surface tension apparatus. The level of the liquid was adjusted to that of the rim of the cup and at the same time the surface was swept free from bubbles. Initial time was taken as the instant when the surface was swept

level and free of bubbles. The first measurement was taken within two to three minutes and then measurements were taken at intervals thereafter. The maximum pull on the ring was determined to 0.1 mg., equivalent to 0.013 dyne per cm.

The suitability of the ring method for measuring surface tensions changing with time has been questioned<sup>8</sup> because of the inevitable disturbance of the surface by the (small) motion of the ring. Tests were made by agitating the surface with the ring as violently as possible and in no case was a change in the surface tension of over 1% observed. It appears from this evidence that solute particles once in the surface film are averse to reentering the solution. However, it is still true that a small error is involved in the expansion of the closed surface inside the ring as this is pulled from the surface.

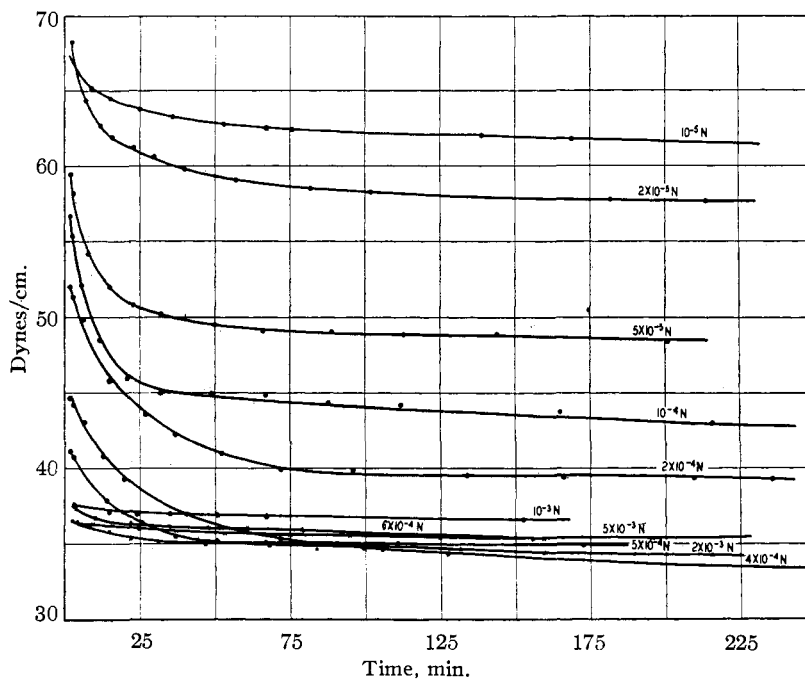


Fig. 1a.—Sodium cetyl sulfate solutions at  $40^\circ$ : surface tension *versus* time curves for various concentrations. At ten minutes time the concentrations of the solutions are, in order of increasing surface tensions:  $2 \times 10^{-3}$ ,  $5 \times 10^{-3}$ ,  $6 \times 10^{-4}$ ,  $10^{-3}$ ,  $5 \times 10^{-4}$ ,  $4 \times 10^{-4}$ ,  $2 \times 10^{-4}$ ,  $10^{-4}$ ,  $5 \times 10^{-5}$ ,  $2 \times 10^{-5}$ ,  $10^{-5}$  mole per liter.

### Decrease of Surface Tension with Time

**Sodium Cetyl Sulfate.**—Surface tension *versus* time curves for sodium cetyl sulfate,  $Na(Cet)SO_4$ , have been obtained at 19 concentrations between  $10^{-5}$  and  $10^{-2} N$ . Most of the curves are shown in Figs. 1a and 1b. It is to be noted that at concentrations below 0.0006  $N$  there is a considerable decrease in the surface tension in the first few minutes, while at higher concentrations the tension measured after two minutes is about the same as that measured after several hours. After the initial, more or less rapid, decrease in surface tension a much slower decline sets in which is linear

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

with time and nearly the same for all the solutions. The work of Adam and Shute<sup>2</sup> on cetylpyridinium bromide and cetyltrimethylammonium bromide suggests that the linear decrease may continue for weeks in the case of the more dilute solutions. Figure 1b shows clearly that the form of the surface tension curve at times below fifty minutes changes entirely from a very rapidly decreasing slope at 0.0002 *M* to an almost flat curve at 0.0007

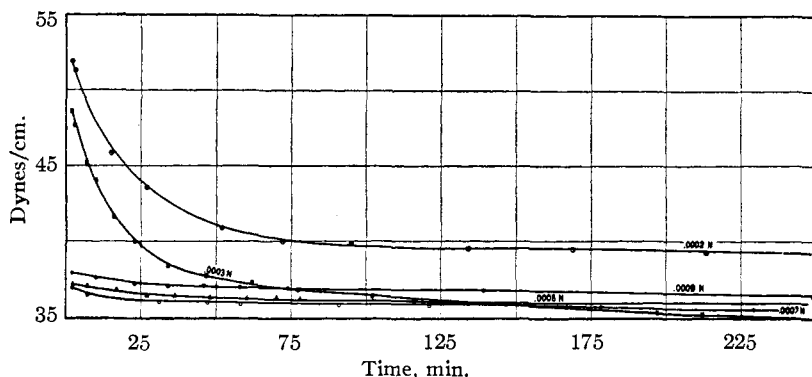


Fig. 1b.—Sodium cetyl sulfate solutions at 40°: surface tension *versus* time curves for various concentrations. At ten minutes the concentrations of the solutions are, in order of increasing surface tension:  $7 \times 10^{-4}$ ,  $8 \times 10^{-4}$ ,  $9 \times 10^{-4}$ ,  $3 \times 10^{-4}$ ,  $2 \times 10^{-4}$  mole per liter.

*M*. Figure 1a shows that at 4 and  $5 \times 10^{-4}$  *M* the curve has the same general form as at  $2 \times 10^{-4}$  *M*. Thus the abrupt change in the time relation occurs very close to  $6 \times 10^{-4}$  *M*.

The abruptness with which the large initial drop in surface tension ceases at 0.0006 *M* is exhibited in Fig. 2 where the ratio of the surface tension after five minutes to that after two hundred minutes,  $\sigma_5/\sigma_{200}$ , is plotted against the logarithm of the concentration. The true value of the surface tension of all the solutions at zero

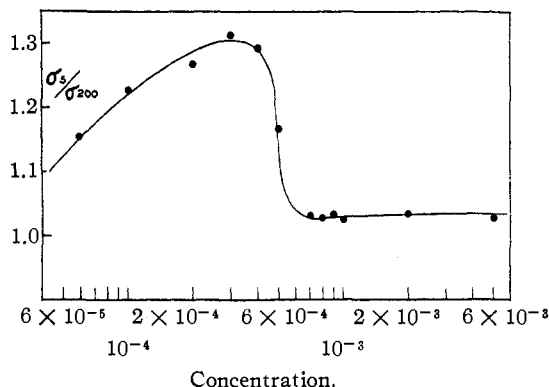


Fig. 2.—Sodium cetyl sulfate solutions at 40°: the ratio of the surface tension at a surface age of 5 min. to the surface tension at 200 min. for various concentrations.

time is doubtless the surface tension of water at 40° (69.6 dynes) and the final value of the surface tension for all concentrations is not far from 35 dynes. The course of the attainment of this final value is very different for different concentrations. Our experiments do not show the true final value of the surface tension but the ratio of  $\sigma$  at five minutes to  $\sigma$  at two hundred minutes serves to show clearly the sharp change in the time decrease of the surface tension which occurs at about 0.0006 *M*, since it is in the first fifty-minute period that the great differences are manifest.

Figures 3a and 3b exhibit the influence of added electrolytes on the rate of change of the surface tension of 0.0004 *N* Na(Cetyl)SO<sub>4</sub>. It is seen from Fig. 2 that there is a large difference between the "initial" and "final" surface tensions of solutions of this concentration, and the primary effect of added electrolytes is to diminish this difference, producing *S. T. vs. time* curves similar to solutions  $6 \times 10^{-4}$  *N* and stronger. Thus 0.01 *N* sodium chloride, hydrochloric acid, sulfuric acid and sodium hydroxide give almost identical curves, while the curve of 0.01 *N* lithium nitrate is similar in shape, but lies above even the curve of the cetyl sulfate solution alone and thus resembles the 0.001 *N* solution without added electrolyte. Increasing the concentration of the electrolyte lowers and further flattens the curves.

Silver ions are much more effective in lowering the surface tension than the alkali metal ions and  $H^+$ , but the greatest effect is shown by  $Mg^{++}$  at  $10^{-4}$  and  $10^{-3}$  *N*. These solutions which contained  $Mg^{++}$  were extremely viscous, but clear throughout the experiments, and had surface tensions of about 30 dynes which scarcely changed with time.  $10^{-3}$  *N*  $Ca^{++}$  lowered the surface tension slightly, but  $10^{-6}$  *N* and higher concentrations raised it considerably. At the highest concentration,  $10^{-4}$  *N*  $Ca^{++}$ , there was visible precipitation during the measurements, and the obvious removal of the alkyl sulfate ions from the solution accounts for the increased surface tension. In other solutions containing polyvalent positive ions, even though permanently free from turbidity, the tight binding

of the metal and cetyl sulfate ions is expressed in the heightened surface tension.

exception is provided by the solution which contains  $1 \times 10^{-5} N$  aluminum sulfate.

**Sodium Lauryl Sulfate** ( $\text{Na}(\text{Lauryl})\text{SO}_4$ ).—Figure 4 presents curves for this salt at ten concentrations from  $5 \times 10^{-4}$  to  $5 \times 10^{-2} N$ . At concentrations below  $5 \times 10^{-4} N$  the results were very erratic and are not reported. The surface tension of the solutions decreases in a rather regular fashion with concentration. The amount of the decrease is not nearly so great at the lower concentrations as with cetyl sulfate. The most remarkable result is that, except for 0.01  $N$  and stronger solutions, whose curves are very flat anyway, the surface tension *vs.* time curves have broad minima which are followed by a rise of gentle, nearly constant upward slope. The surface tension variation of none of the solutions was followed for more than six hours, so that it is not possible to estimate either the value of the static surface tension or the time required to approach it.

Salt effects were observed with 0.004  $N$  solutions. The results are in Figs. 5a and 5b. In none of the solutions, even those containing 0.6  $N$   $\text{Na}^+$ , 0.006  $N$   $\text{Mg}^{++}$  or 0.001  $N$   $\text{Al}^{+++}$ , was there ever any trace of turbidity. The unvarying effect of addition of electrolytes was to decrease the surface tension, sometimes to values nearly 4 dynes lower than observed in even the most concentrated lauryl sulfate solutions. The minimum was displaced both to shorter and longer times and was most often broadened or rendered nonexistent, but a conspicuous

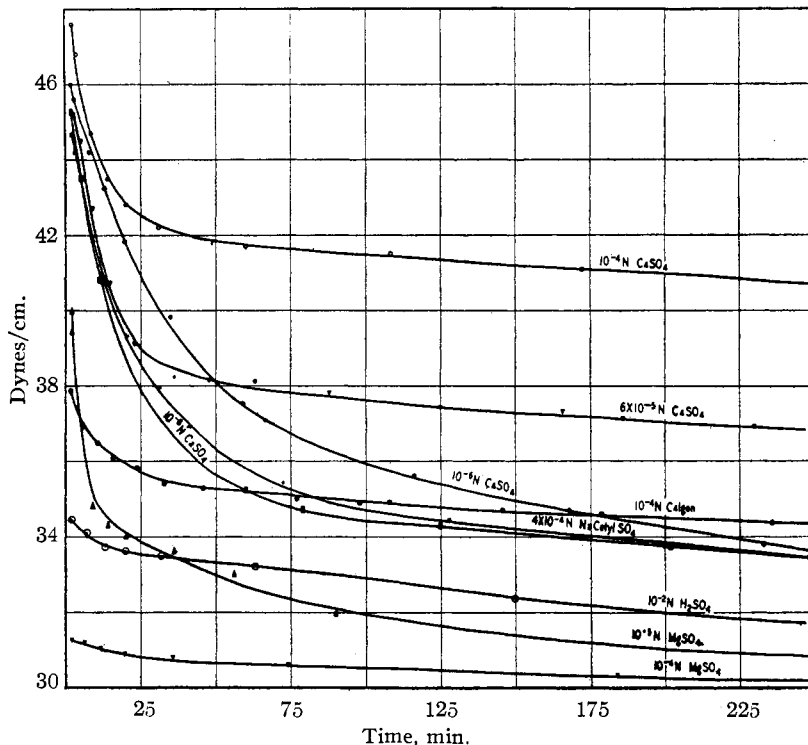


Fig. 3a.—0.0004  $N$  sodium cetyl sulfate solutions at  $40^\circ$ : the effect of added salts on the lowering of the surface tension with time.

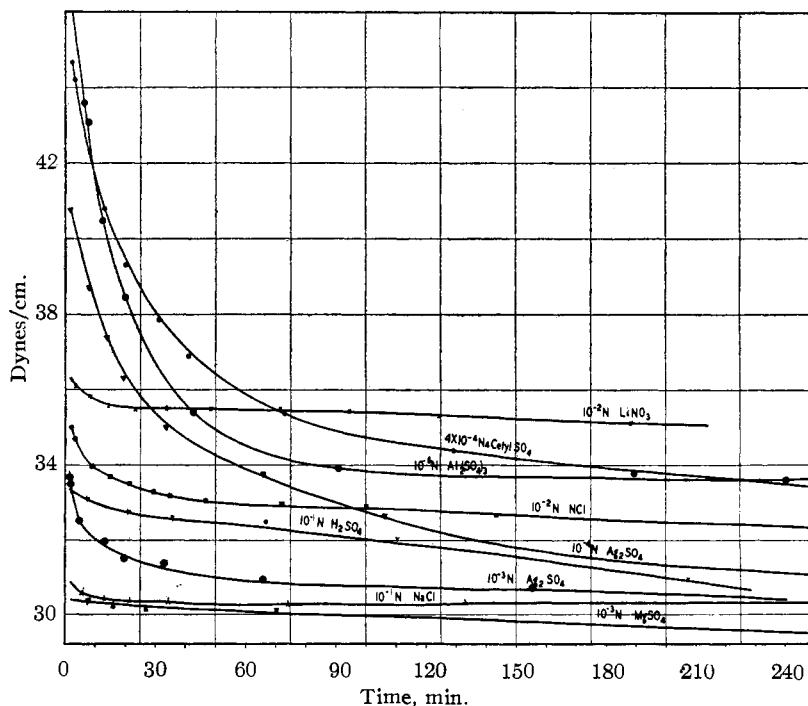


Fig. 3b.—0.0004  $N$  sodium cetyl sulfate solutions at  $40^\circ$ : the effect of added salts on the lowering of the surface tension with time.

### Discussion

At the instant of its formation the surface of the strongest alkyl sulfate solution employed contains about five thousand and the most dilute about five million water molecules to each molecule of solute, so that the initial surface tension approximates that of pure water. At all surface concentrations the solute particles adsorbed from the solution presumably behave like a two-dimensional gas in the sense that their cohesive forces are too feeble to produce permanent agglomeration and that they cover uniformly the entire surface area of the solution. Except in the very first stages of adsorption, however, the surface film cannot approach the behavior of an ideal gaseous film, and when the surface is nearly saturated and the film pressure is around 40 dynes per cm. the gas must be highly imperfect.

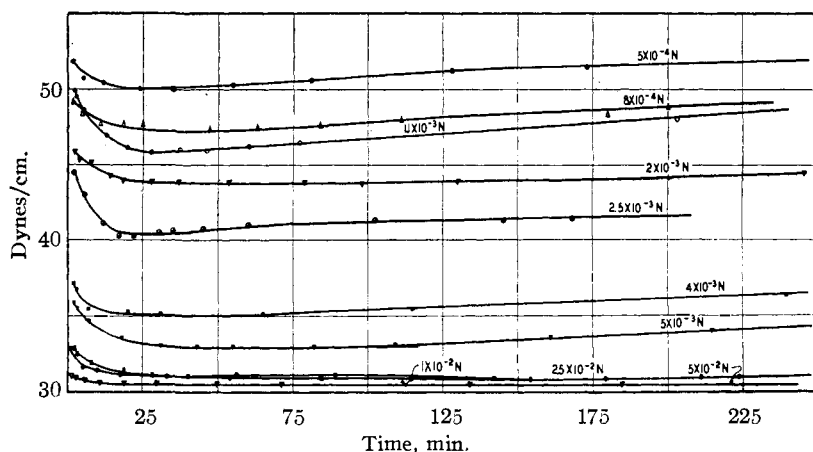


Fig. 4.—Sodium lauryl sulfate solutions at 40°: surface tension *versus* time curves for various concentrations.

The great amount of work which has been done on films of materials which contain long, unbranched paraffin chains, indicates that the area per molecule of films of sodium cetyl and lauryl sulfate under pressures of 40 dynes may fall as low as 20 sq. Å. The number of molecules per sq. cm. is then  $5 \times 10^{14}$ . The depth from which *all* solute would have to be removed in order to thus saturate the surface is inversely proportional to the bulk concentration of the solution and for a  $10^{-6}$  *N* solution the depth is 0.8 cm.; for a  $10^{-3}$  solution, 0.008 cm. Transfer of solute from such depths to the surface will be by no means instantaneous and attainment of the ultimate surface tension is correspondingly delayed.

Bond and Puls<sup>1</sup> and Doss<sup>3</sup> have given expressions for the order of magnitude of the time neces-

sary for the attainment of the static value of the surface tension of solutions, assuming that the time is determined principally by the rate of diffusion of the surface-active material. The methods of Bond and Puls are not applicable to the present work since they involve a knowledge of the change of the static surface tension with concentration. An application of Doss' equation indicates that the time necessary to half saturate the surface with solute would be of the order of one second for the concentrations employed in this work. The actual times, both from the present investigation on sodium cetyl sulfate and from Adam and Shute's work on cetylpyridinium bromide and cetyltrimethylammonium bromide, are of the order of one thousand times the predicted values. While the assumptions made by Doss are probably not strictly valid no plausible

variations could account for this *extreme* disagreement. It should be mentioned that the work of Harkins and King shows that a period of half an hour is required to give equilibrium with the surface in the case of a 0.000067 *M* solution of decylic acid. Consequently it is quite improbable that the rate of simple diffusion alone can account for the excessively slow accumulation of the solute in the surface layer which was found in our work.

The capillary active material in solutions of the alkyl sulfates is doubtless a collection of alkyl sulfate ions, each with a single negative charge. At a solution-air interface the adsorbed ions are firmly joined to water molecules through the sulfate groups, while the hydrocarbon "tails" above may assume practically any orientation with respect to the surface. At high surface concentrations the tails are closely packed and inclined steeply to the surface, and thus constitute an upper layer of liquid hydrocarbon, and a lower negative ionic layer. Sodium ions must then concentrate below this negative sheet in a diffuse positive layer. The electrical double layer thus set up provides a potential barrier to the entrance of additional alkyl sulfate ions into the surface. The height of the barrier increases with the density of ions in the surface and initially is zero,

An accurate calculation of the effect of this double layer on the speed with which ions diffuse into the surface would undoubtedly be difficult. In a rough calculation Doss, however, has shown that the hindering potential, even when the surface density of ions is small, is probably much larger than  $kT$ , the energy magnitude which determines the speed of diffusion of the ions. Thus the first ions could diffuse into the surface with rapidity but the electrical double layer caused by these ions would repel other negative ions and the rate of attainment of the equilibrium surface tension would be considerably delayed.

Evidence which qualitatively confirms this picture of the time effect can be obtained from the work of Schulman and Rideal<sup>5</sup> on mixed films. These investigators worked with partially compressed films of various insoluble substances, cetyl alcohol for example, on an approximately neutral substrate into which they injected very small amounts of sodium cetyl sulfate. The sodium cetyl sulfate was at a concentration (approximately  $10^{-5} M$ ) such as to cause the surface tension of water alone to be lowered only slowly, about 5 dynes in the first hour. But this same concentration of sodium cetyl sulfate causes a film of cetyl alcohol, initially present at a film pressure of 10–12 dynes and thus rather highly compressed, to show a surface tension lowering of nearly 50 dynes in a few minutes.

By the use of a different technique Harkins and Florence<sup>6</sup> have obtained an increase in the pressure of the cetyl alcohol film by a much greater factor. A  $10^{-5} M$  sodium cetyl sulfate solution was found to increase its film pressure to about 6 dynes in four hours. The film of this material was then

(5) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc. (London)*, **B122**, 29 (1937).

(6) W. D. Harkins and R. T. Florence, unpublished work.

swept off quickly by the use of barriers. Then a few drops of a solution of cetyl alcohol in a low boiling ligroin were put on the surface. The solution spreads rapidly and pushes off any trace of the sodium cetyl sulfate. Even although the amount of cetyl alcohol used on the area gives by itself a pressure of only about 0.2 dyne/cm. the sodium cetyl sulfate diffused into the surface so rapidly that the pressure had risen to

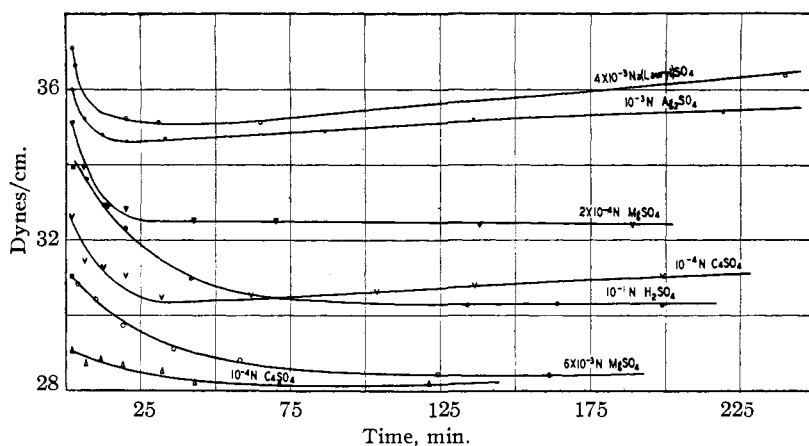


Fig. 5a.—0.004 N sodium lauryl sulfate solutions at 40°: salt effects.

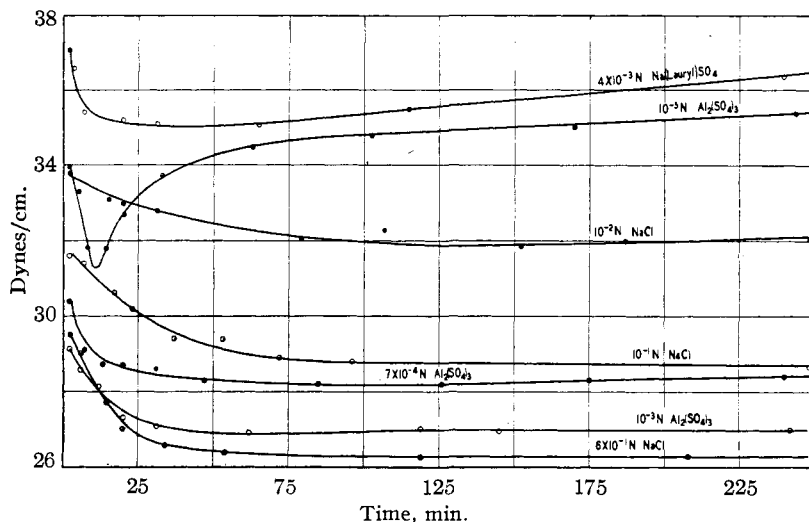


Fig. 5b.—0.004 N sodium lauryl sulfate solutions at 40°: salt effects.

over 50 dynes per cm. in less than three minutes.

Although in the last experiment described the pressure of the alcohol film alone is very low, nevertheless the surface was almost completely covered by the alcohol since its molecular area was only slightly above that found for a completely condensed liquid film (21.85 sq. Å. for cetyl alcohol at 20°).

Thus in either of the cases cited above the sur-

face was so completely covered by the alcohol that the sodium cetyl sulfate molecules in general moved into holes; in the film, completely surrounded by alcohol molecules. Thus no potential barrier was present to slow down their entrance and the diffusion into the surface was rapid. Also, since very few molecules of the solute were required to fill these holes, the adjacent solution was only very slightly depleted. In such a case both of these factors cooperate to make the rise of film pressure a very rapid one.

In the case of films of the sodium cetyl sulfate by itself a phenomenon appears which is even more spectacular than the time effect itself. This is its sudden cessation at a definite concentration. As is shown in Figs. 1 and 2, the time effect for sodium cetyl sulfate at 40° stops abruptly at about  $6 \times 10^{-4} M$ . For sodium lauryl sulfate the similar change comes at about  $7 \times 10^{-3} M$ . A very similar result has been reported by Adam and Shute for the salts investigated by them. Although the explanation of the time effect as being due to the electrostatic repulsion of the surface layer of ions seems fairly straightforward, the problem as to just why this effect should almost disappear at a definite concentration needs further consideration.

There is a close correlation for a given salt between the concentration at which the time effect stops and that at which the conductivity of the solution of the salt shows an abrupt break. Thus for sodium cetyl sulfate at 40° an abrupt decrease in the conductivity sets in at a concentration of about  $5 \times 10^{-4} M$  and for sodium lauryl sulfate at  $6 \times 10^{-3} M$ .<sup>7</sup>

The concentrations above which the time effect disappears are almost the same, that is, respectively,  $6 \times 10^{-4}$  and  $7 \times 10^{-3} M$ . Other properties of these solutions also show abrupt changes in the same concentration regions.<sup>8</sup>

These sharp changes have been explained by Hartley as due to a formation of ionic micelles, spherical aggregates of around 60 paraffin-chain ions with about half this number of "gegenions" attached more or less firmly to the aggregate. The concentration at which this abrupt change enters has been called the "critical concentration for micelles." And it is clear, not only from our results but from results of other workers on essen-

tially "fresh" solutions,<sup>9</sup> that the surface properties of these solutions also show sharp changes at concentrations close to the critical concentration for micelles. The difference when surface tension is the phenomenon involved is, however, that it is not so much the final value which shows a change but the rate of attainment of the final, equilibrium value.

The results which are presented here on the effect of added salts on the surface tension are just what are to be expected from a consideration of the action of added salts on the critical concentration for micelles. It has been shown<sup>8,10</sup> that the effect of added salt is to lower the critical concentration and this effect is larger for divalent than for monovalent cations. Hence it is not surprising that solutions of 0.0004 *M* sodium cetyl sulfate which contain added electrolyte show surface tensions similar to solutions of the pure salt of somewhat larger concentrations (Figs. 1 and 3). The observation that small concentrations of magnesium salts have a pronounced action offers still further evidence that divalent cations adhere more strongly to the micelles than do monovalent ones, as they should on the basis of electrostatic theory.

It is not easy to see just why the presence of micelles allows the final surface tension to be attained so much more rapidly, but the change must be due to changes in the bulk of the solution, since it is quite unlikely that there is any essential change in the surface conditions in the small concentration ranges involved. It is plausible, however, that the ease with which an ion in a micelle can get up to the surface is greater than that for the simple ion. In the first place the mobility of a micelle is such that the rate of diffusion per ion is larger for the ions in a micelle than for simple ions. Probably still more important is the condition near the surface in the region of the double layer. The double layer offers a barrier to the simple ion of many times  $kT$ . But consider the behavior of a micelle in this region, assuming for convenience a micelle of 60 simple ions with approximately half this many gegenions. As the micelle approaches the surface it will encounter the diffuse region in which gegenions are concentrated. The greater potential gradient at the surface of the micelle (compared to a simple ion) will result in a still larger number of gegenions be-

(7) Howell and Robinson, *Proc. Roy. Soc. (London)*, **A155**, 386 (1936); Lottermoser and Puschel, *Kolloid-Z.*, **63**, 175 (1933).

(8) G. S. Hartley, "Aqueous Solutions of Paraffin-chain Salts," Hermann et Cie., Paris, 1936.

(9) J. Powney and C. C. Addison, *Trans. Faraday Soc.*, **33**, 1243 (1937); A. Lottermoser and F. Stoll, *Kolloid-Z.*, **63**, 49 (1933).

(10) G. S. Hartley, *J. Chem. Soc.*, 1968 (1938).

coming attached to it. Consequently the net charge of the micelle will be reduced as it approaches the surface region. The surface will still offer an electrostatic barrier to the approach of the micelle, but the force per ion will be considerably less than for the simple ion case. As a result the rate at which ions present in micelles reach the surface may be many times that for simple ions.

In addition to these coulombic interactions which tend to hinder the formation of the surface layer, there are undoubtedly short-range non-coulombic forces between the surface layer and the ions or micelles in the solute. The non-coulombic forces will in general be attractive and thus tend to accelerate the formation of the surface layer. If these forces are greater for the micelle than for the simple ions, the result would be that, with micelles present, the height of the potential barrier for entrance into the surface would be decreased and the rate of formation of the surface accelerated. At present, however, it does not seem possible to ascertain whether these forces are of sufficient importance and sufficiently different for the micelles than for the ions to explain the observed results. It is, of course, unlikely that the micelle remains in or even enters the surface as such, since it is strongly hydrophilic and cannot decrease the surface free energy by orientation but only by dissociation. At an air-solution interface the condition essential for the existence of a small spherical micelle which is stable in the bulk of the solution is removed, the micelle dissociates and its fragments orient in the infinitely large two-dimensional micelle.

Lottermoser<sup>7</sup> and McBain<sup>11</sup> have not accepted the concept of Hartley and believe, rather, that the critical concentration for micelles represents a formation, not of ionic micelles, but of neutral colloid. This latter is considered to consist of aggregates of paraffin-chain salt molecules, each aggregate carrying only a very low net charge. This theory, although it does not seem to agree with certain other properties of solutions of paraffin chain salts,<sup>7</sup> allows an easy interpretation of the change in the time effects noted at the critical concentration. An electrical double layer would not be expected to offer any large hindering potential to a neutral or practically neutral aggregate and consequently if neutral colloid is present it could diffuse to the surface and permit

the formation of a saturated surface layer in a comparatively short time.

If, as seems likely, the surface layer of these solutions is formed from ions, a comparison of the observed surface tensions with those for neutral molecules is rather difficult. Considerable numbers of gegenions will adhere to the ionic layer, but even so the electrostatic repulsion of like ions will cause the surface layer to be less concentrated. The ionic layer will act in the opposite way to produce a lower surface tension. These two opposing effects must be approximately equal since the final surface tension is about the same as that for neutral molecules of about the same chain length.

An interesting result is obtained from an application of Gibbs' theorem to the surface tension data for paraffin-chain salts or in other cases in which the surface tension though below that of water remains constant, or even increases with concentration. Here, *if the activity is proportional to concentration*, the theorem indicates a zero, or even a negative adsorption. The apparent explanation of this is that the equation gives correctly the adsorption in the whole surface region, but that the organic solute is more concentrated in the monolayer and less just below it, than in the three-dimensional phase.

Behavior like that of the alkyl sulfates might be expected from solutions of the soaps, which we have regarded as less suitable for the present work than the alkyl sulfates since the former hydrolyze. However, Bond and Puls have found that observed and predicted values of  $t_{1/2}$  for 1% and 0.25% solutions of Lux are in good agreement. Assuming that the paraffin salt in Lux is sodium stearate and that the weight of water and other electrolyte is negligible, the respective molal concentrations are approximately 0.02 and 0.008.

At these concentrations the soap is largely in micellar form and the time of half-saturation of the surface would be small. That it should be as small as predicted from diffusion theory seems to indicate that the solute in the surface film is not in the form of ions but of fatty acid molecules. These have no potential barrier hindering their entrance into the surface and would pass in preferentially from a mixture of fatty acid ions and molecules. The static surface tension would be that of a liquid hydrocarbon, 25 to 30 dynes, as is observed. The pH of the soap solutions is doubtless not far above 7 so that the concentration of

(11) M. L. McBain, *Proc. Roy. Soc. (London)*, **A170**, 415 (1939).



neutral particles in the solutions must be considerable. If the  $pH$  of the Lux solutions were raised, so that the surface active particles were fatty acid ions, it is predicted that the approach to equilibrium would be far slower and that the discrepancy between  $t_{1/2}$  as calculated and observed would be as great as in the case of the alkyl sulfates and the pyridinium compounds.

Observations made by the writers on the change of surface tension of sodium nonylate and sodium laurate solutions with  $pH$  may be reinterpreted on the basis of the time effects which have been discussed.<sup>12</sup> It was found that the surface tension of dilute soap solutions increased markedly with  $pH$ . The film at  $pH$  7 was supposed to consist principally of fatty acid molecules; at  $pH$  12 principally of fatty acid ions. It was also supposed that the observed film pressure was characteristic of the film species in the equilibrium proportion at each  $pH$ . But the surface tension lowering by an ion layer should be comparable to the lowering by a layer of molecules of the same length of hydrocarbon chain. In reporting the increase in surface tension with  $pH$  it was tacitly assumed that the surfaces at the time of measurements were in all cases saturated. It seems at present likely that at low  $pH$ , adsorption of the fatty acid molecules was so rapid that the surface at the time of measurement was indeed saturated; while at higher  $pH$  adsorption of the fatty acid ion was so slow that the measured surface tension corresponded to only a partly filled surface. If the measurements had been postponed for several hours saturation would have been approached and the surface tension probably about the same as for the less alkaline solutions.

Adam and Shute's measurements on sodium lauryl sulfate are not in very good agreement with our own. Their surface tensions are invariably *higher* by 5 or 10 dynes per cm., even though the error to be expected in the ring method used by us is such as to give a value slightly too high. Also, their curves do not have the minima which we have observed. The minima suggest a change in the nature of the adsorbed particles but the character of the change cannot yet be specified.

### Summary

The change with time of the surface tension of

(12) F. A. Long, G. C. Nutting and W. D. Harkins, *THIS JOURNAL*, **59**, 2197 (1937).

solutions of sodium cetyl sulfate has been measured in the concentration range  $10^{-5}$  to  $10^{-2}$   $N$  at  $40^{\circ}$ ; and of sodium lauryl sulfate in the range  $5 \times 10^{-4}$   $N$  to  $5 \times 10^{-2}$   $N$ . The changes were followed in the interval two minutes to from three to six hours.

The effects of various uni-, di- and trivalent ions at several concentrations have been measured on 0.0004  $N$  sodium cetyl sulfate and 0.004  $N$  sodium lauryl sulfate.

In the cetyl sulfate solutions without added electrolyte at concentrations below  $6 \times 10^{-4}$   $N$  a rapid fall in tension is found followed by a slow fall, linear with time, at the same rate for all solutions. At concentrations higher than  $6 \times 10^{-4}$   $N$  the initial fall is small and the surface tension soon reaches a value of about 35 dynes per cm. The effect of electrolytes is the same as an increase in cetyl sulfate concentration, namely, greatly to hasten attainment of static values of the surface tension near 30 dynes. The effectiveness of the positive ions increases rapidly with the valence.

In the lauryl sulfate solutions the initial fall is not so marked and is followed usually by a broad minimum surface tension. The nature of this phenomenon cannot now be specified. The effect of electrolytes is again to hasten attainment of a static tension of about 25–30 dynes, and the order of effectiveness is the same as for the cetyl sulfate.

The slow fall is considered due principally to the potential barrier set up against alkyl sulfate ions diffusing into the surface by the ions already in the surface film. No quantitative account of the effect of this electric double layer on the rate of fall of surface tension has yet been possible.

The sudden change in the time effect at a definite concentration has been correlated with the appearance of micelles in the bulk of the solution. The reasons for this change are obscure but a tentative explanation is considered. The effects of added electrolytes are shown to be related to the critical concentration for micelles.

The apparent increase of surface tension of solutions of soaps with increasing  $pH$  is accounted for on the basis of slow accumulation of fatty acid ions in the surface films at high  $pH$ , and rapid accumulation of fatty acid molecules by simple diffusion at low  $pH$ .