

corrected to the same conditions, after allowing for a slight difference in pressure inside and outside the aspirator, determined with an open-arm water manometer attached to the aspirator bottle. The volume of the water vapor, divided by the volume of dry air plus the volume of the water vapor, and multiplied by the total interior pressure, yields the aqueous pressure of the salt under the conditions of the experiment. The results are given in the tables.

On the accompanying curves the aqueous pressure is plotted against the temperature, and the logarithm of the aqueous pressure is plotted against the reciprocal of the absolute temperature. In the latter case the points lie very nearly upon straight lines, almost exactly so with sodium sulfate. These lines are represented very closely by the following equations:<sup>1</sup>

$$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} \quad \log p = 18.053 - \frac{9661}{T + 250}$$

$$\text{SrCl}_2 \cdot 6\text{H}_2\text{O} \quad \log p = 15.081 - \frac{6371}{T + 152}$$

$$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \quad \log p = 10.566 - \frac{2794.1}{T + 3}$$

In Table II the observed values are compared with those calculated from the equations. The concordance is such as to inspire confidence in results obtained by extrapolation over a moderate temperature range.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE UNIVERSITY OF BRISTOL.]

## COLLOIDAL ELECTROLYTES. SOAP SOLUTIONS AND THEIR CONSTITUTION.<sup>2</sup>

BY JAMES W. MCBAIN AND C. S. SALMON.

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Colloidal electrolytes are salts in which an ion has been replaced by a heavily hydrated polyvalent micelle that carries an equivalent sum-total of electrical charges and conducts electricity just as well or even better than the simple ion it replaces. This is the conclusion to which our 6 years study of soap solutions has led us.

<sup>1</sup> Antoine, *Compt. rend.*, **110**, 632 (1890);  $\log P = A + \frac{B}{T + C}$ .

<sup>2</sup> This is the paper referred to by McBain, *Trans. Faraday Soc.*, **9**, 99 (1913); *Kolloid-Z.*, **13**, 56 (1913); and *Trans. Chem. Soc.*, **105**, 957 (1914), whose publication has been delayed owing to the outbreak of war. The work was completed in the early Summer of 1914. Previous papers from this laboratory on the constitution of soap solutions commence with McBain and Taylor, *Ber.*, **43**, 321 (1910); *Z. physik. Chem.*, **76**, 179; (1912); further papers, *Trans. Chem. Soc.*, **99**, 191 (1911); *Z. physik. Chem.*, **99**, 191 (1911); **101**, 2042 (1912); **105**, 417, 957 (1914); *Trans. Faraday Soc.*, **9**, 99 (1913); *Kolloid-Z.*, **12**, 256 (1913).

This newly recognized class will probably prove to include, under certain conditions, most organic substances containing more than 8 carbon atoms capable of splitting off an ion of any kind, such as acid and alkali proteins, dyes, indicators, sulfonic acids and sulfonates, soaps, etc. Probably our conception of such inorganic substances as certain salts of the heavy metals, for instance chromium chloride, sodium tungstate or zincate, and certainly such substances as sodium silicate, will have to be revized in the light of this new knowledge. Many non-aqueous solutions also are comprized in this category, as will be shown elsewhere. Indeed it is probable that this new class contains as many members as all acids and bases put together.

In a measure the properties of this ionic micelle must apply to all colloids which possess even slight electrical charges. In the cases of proteins and soaps at high concentration, the undissociated substance is an ordinary colloid while the organic ion is a micelle. In dilute soap solutions, on the other hand, the undissociated molecules possess only the simple stöchiometric weight and the ions too are simple.

As the previous papers are somewhat scattered and as the data described in this paper derive their significance from combination with the previous work, a brief résumé is necessary.

When McBain and Taylor, in 1908, planned their attack on this subject, they chose soap as the material for their experiments because of the relative simplicity of its components, and also on account of its industrial importance. McBain had already shown that quite complicated cases, such as solutions of cadmium iodide, could be readily interpreted within the limits of the dissociation theory.<sup>1</sup> Here, however, they found a case which necessitated an extension of that theory. They recognized the importance of the conclusions towards which their results led, and decided deliberately not to adopt the explanation just outlined, as long as it was possible to maintain any other. Further, the methods of investigation were to be only the powerful incontestible ones which had served to establish the theory of solutions and of electrolytes. Viscosity measurements, for instance, and other colloidal methods were rejected as being in the nature of circumstantial evidence only.

At that time Krafft's work on the subject was universally accepted, and it was believed that soap was just an ordinary colloid. Kahlenberg and Schreiner's measurements of the conductivity of certain dilute soap solutions were simply explained away as being due to impurities, hydrolysis and dilution.

McBain and Taylor<sup>2</sup> spent several years in measuring the conductivity of sodium palmitate solutions of all concentrations, near the boiling

<sup>1</sup> *Z. Elektrochem.*, **11**, 222 (1905); *THIS JOURNAL*, **34**, 1134 (1912).

<sup>2</sup> *Z. physik. Chem.*, **76**, 179-209 (1911).

point, as Krafft's molecular weight measurements had been made at this temperature, and as the concentrated solutions were not liquid at low temperatures. They found a high conductivity in all solutions.<sup>1</sup> This showed conclusively that soap solutions consist to a large extent of something other than a neutral colloid. The next step was to show by two quite independent methods, namely by the rate of catalysis and the electromotive force of the hydrogen<sup>2</sup> electrode, that the hydroxyl ion present was negligible, its concentration being only about 0.001 *N*. Hence the high conductivity was necessarily due to the soap itself.

The present paper shows again<sup>3</sup> that Krafft's well known work is completely erroneous, and it describes measurements of the osmotic pressure of numerous soap solutions by a vapor tension method, showing that in extreme cases the sole constituent that is not a colloid is the sodium or potassium ion, although this is present in high concentration and must, therefore, be counterbalanced by a colloidal micelle of high equally opposite charge and conductivity. Other related work, to the same effect, on the freezing points of some potassium soap solutions is being described elsewhere.

No less remarkable is the demonstration that as the solutions become more dilute a gradual transition from colloid to crystalloid takes place, until in dilute solutions the soap is essentially an electrolyte just like potassium acetate. This refers to the undissociated colloid as well as to the colloidal ion or ionic micelle. In every solution again there is established a perfectly definite, completely reproducible equilibrium between all these constituents, both colloids and crystalloids.

#### The Experimental Method.

McBain and Taylor<sup>4</sup> have shown the impossibility of using the ordinary boiling-point method with these solutions, owing to the presence of a large amount of air which does not escape from the bubbles and, therefore, by its partial pressure, wholly invalidates the results. Krafft's observation that soap solutions boil just above or below the boiling point of water, although perfectly correct, is thereby wholly deprived of significance. The same consideration renders illusory the apparent vapor pressure as measured by Smits in an ordinary tensimeter. McBain and Taylor<sup>4</sup> were able to obtain direct confirmation of this by experiments which in one case extended over 3 weeks, where most of the air was eliminated and a vapor tension in agreement with that obtained here was finally observed.

<sup>1</sup> Subsequent measurements of conductivity of various soaps solution from this laboratory: *Trans. Chem. Soc.*, **99**, 191 (1911); **101**, 2042 (1912); **105**, 417 (1914).

<sup>2</sup> *Trans. Chem. Soc.*, **105**, 957-977 (1914); rate measurements not yet published, completed in 1914.

<sup>3</sup> See McBain and Taylor, *loc. cit.*, pp. 185-186.

<sup>4</sup> *Loc. cit.*

The present experimental results consist of measurements of the rise of the boiling point or lowering of the vapor pressure of soap solutions as measured by Cummings'<sup>1</sup> dew-point method suitably modified. The experiments cover an extraordinary range of concentration from very dilute solutions up to practically anhydrous solids. It is a matter of indifference when using this method whether the system studied is liquid or solid, viscous or limpid, one phase or several phases. The results are accurate to  $0.01^{\circ}$ . For instance, the vapor pressures of a number of soap solutions were measured by one of us (J. W. M.) and subsequently the other carried out the same series of measurements without being aware of this. Our results agreed either to  $0.00^{\circ}$  or  $0.01^{\circ}$  in every case. This degree of accuracy was made possible through a special treatment of the silver surface described below.

Fig. 1 shows a diagram in cross-section of the apparatus employed. A highly polished silver tube with silver bottom was closed with a cork at the top. Through the cork were inserted a thermometer and 2 tubes through which a rapid current of water was circulated by a power pump from and to a thermostat of adjustable temperature. The silver tube was held in a cork in a glass vessel which contained the solution to be studied. The top of the glass vessel rose an inch or so above the cork so that the closed space was completely immersed in the water of a thermostat which had glass sides.

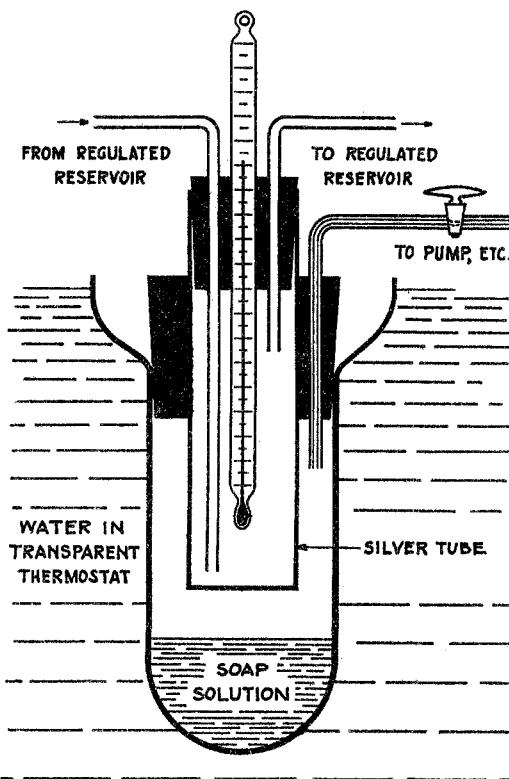


Fig. 1.

Further, a capillary glass tube passed through the cork holding the silver tube and could be connected with an air pump and thus evacuated or the pressure adjusted to any desired value. This tube was closed by a glass tap.

The following device alone rendered possible the attainment of accurate results. The silver tube was kept most highly polished; but as it was

<sup>1</sup> *Trans. Chem. Soc.*, 95, 1772 (1909).

extremely difficult to detect the first very slight dimming of the silver surface, a definite portion of the silver surface was so treated that no dew deposited on it, so that it therefore remained bright and afforded by juxtaposition a contrast with a slightly clouded surface. The test of the appearance or disappearance of the dew was then the first appearance of this sharp boundary or the attainment of perfect uniformity of the surface. To produce this effect, boiling water was run through the silver tube and the bottom corner of the tube was dipped once into boiling conductivity water. The water evaporated at once but thereafter no dew would form on this part of the surface. In this way when the tube was subsequently viewed from the front the boundary line ran diagonally across the lowest part of the side of the tube. The attempt was made to extend this essential refinement of the dew-point method to various non-aqueous solutions, but without success. In every case dew formed all over the silver surface no matter how this had been treated or contaminated.

In making a determination, the main transparent thermostat is first adjusted to say  $90.0^{\circ}$ . It has to be filled with distilled water, stirring must be very vigorous, and the whole has to be carefully covered to prevent evaporation. For the same reason a large quantity of glycerine is added. The meniscus is kept at constant level by use of a constant level reservoir. The glass sides of the thermostat are kept carefully cleaned and polished for close observation. The adjustable auxiliary thermostat is filled with water covered by a deep layer of melted paraffin or is otherwise carefully protected.

The next step is to pass practically boiling water through the prepared silver tube and insert the latter into the glass vessel to about one cm. above the surface of the solution to be studied. This prevents first, condensing large amounts of water on the silver tube; second, altering the surface of the silver; third, dimming the glass when heavy dew is evaporated; and fourth, changing the concentration of the solution. The whole apparatus with the hot water passing through it is then inserted into the transparent thermostat as in Fig. 1. The holder is not rigid and it is, therefore, possible to shake the soap solution slightly and thus renew the surface if desired.

The glass tap is kept open for a few minutes to equalize pressure outside and inside, since the vapor pressure of the solution is considerable at this temperature. The tap is then kept closed. Owing to the high vapor pressure involved it was found quite unnecessary and inadvisable to evacuate the air in the apparatus. In later work water was often deliberately removed from the solution by this method and heavy dew could be instantly dissipated. On the other hand, the temperature dis-

turbance is very considerable. Thus for normal working with apparatus kept closed, the rather small amount of air present (say 200 mm. pressure) involved no appreciable lag in the diffusion of the water vapor (say 550 mm. pressure). Doubtless again, on account of this high vapor pressure, the use of the cork was quite without influence on the results.

The determination is now begun by very gradually lowering the temperature of the water running through the silver tube, carefully noting the temperature of the thermometer contained in it and also of the one in the thermostat with its bulb close to the solution. On the first sign of dew forming (slight discontinuity of the polished surface, the boundary line becoming faintly visible under bright and carefully adjusted illumination) the temperatures of both thermometers are read.

Immediately the supply of heat to the adjustable thermostat is altered to a value which will slowly raise the temperature of the running water. There is now a lag during which the dew increases, but soon it becomes faint and the silver surface is suddenly sensibly uniform. Both thermometers are again read, and the heat supply again diminished. Thus a long series of values for the appearance and disappearance of the dew is obtained. The temperature of the outside thermometer in the transparent thermostat is of course nearly or quite constant. The mean value for a series of at least 7 or 8 readings each way is quite reproducible by different experimenters working independently.

The apparent temperatures of appearance and disappearance of the dew differ on account of the lag referred to, but since pure water is measured similarly, the results for solvent and solution are strictly comparable. In this way the method resembles the ordinary Beckmann boiling-point method, where the absolute temperatures are always very inaccurate (perhaps by a degree or more) but where the difference in temperatures or rise in the boiling point is accurate to perhaps a few hundredths of a degree. Our dew-point results are about as accurate as an ordinary Beckmann determination in dilute solution, and the latter is wholly inapplicable to the cases here studied.<sup>1</sup> For moderate concentrations of substances such as sodium chloride they are several times more accurate. Thus, from the data given in the tables of Landolt and Börnstein, the dissociations indicated for 1.0 *N* solution of potassium and sodium chlorides are 80 and 94%, respectively, whereas our method gives 78 and 76%, respectively, in agreement with our results for the corresponding acetates, namely, 78 and 74%.

A typical experiment showing only a few readings is quoted below, Table I:

<sup>1</sup> McBain and Taylor, *loc. cit.*

TABLE I.  
Dew Point of 1.0 *N* Potassium Stearate at 90°.

Silver tube thermometer. ° C.	Thermostat thermometer. ° C.	Temperature formation. ° C.	Difference disappearance. ° C.
89.43	90.00	(0.57)	
89.75	90.01		0.26
89.68	90.01	0.33	
89.75	90.00		0.26
89.68	90.00	0.32	
89.74	90.01		0.27
89.68	90.00	0.32	
89.75	90.01		0.26
89.69	90.00	0.31	
89. 4	90.00		0.26
		Mean, 0.32	0.26
		Final mean, ---0.29°	
		Thermometer error, ---0.09°	

Hence the rise of boiling point due to the soap is 0.20° at 90° and the total concentration of all ions and molecules is 0.42 *N*.<sup>1</sup>

Two other completely independent solutions measured on different occasions and involving 18 readings gave elevations of 0.20 and 0.205°.

The thermometric error was obtained by carrying out similar experiments with pure water. It consists essentially of the error in the calibration of the thermometer, but any personal error is eliminated at the same time. With water the difference in temperature between the appearance and disappearance of the dew was only from 0.01 to 0.03°, instead of the 0.06° difference between the temperatures in the final columns of the above table.

It will be noted that the first rough reading is usually neglected in taking the mean. An important practical point is a close inspection of the silver surface after the experiment, to see that it has remained quite clean.

The solutions were prepared in silver tubes from Kahlbaum's best chemicals, employing all the precautions described in previous communications. The weight of palmitic acid required to neutralize a known amount of sodium hydroxide in aqueous alcohol was only 0.1% smaller than the theoretical amount. Each concentration up to 1.5 *N* was prepared separately and at least in duplicate. Concentrations are given invariably in weight normality (number of gram equivalent weights of soap in 1000 g. of water).

#### Method of Calculating Dew-point Results.

When the silver tube is cooled just far enough to form a little dew the pure water thus formed is in equilibrium with its own vapor. The aqueous vapor pressure in the apparatus, therefore, can be ascertained by reference to the standard tables. But this vapor is also that which is exhi-

<sup>1</sup> It will be seen later that this is entirely due to the potassium ion.

bited by the soap solution present at the somewhat higher temperature of the thermostat. In other words, the difference in temperature between the silver tube and the soap solution is the rise in boiling point of water at reduced pressure due to the substance dissolved in it. The rise predicted for a 1.0 *N* solution of a crystalloid such as sugar, according to the familiar van't Hoff formula  $RT^2/s$  is  $0.483^\circ$  at  $90^\circ$ . Since the latent heat of vaporization of water is greater at lower temperatures, and  $T$  is less, this rise is slightly less than the rise of  $0.5010^\circ$  expected in the ordinary Beckmann method at  $100^\circ$ . The values of the constant taken for lower temperatures are:  $70^\circ$ , 0.414;  $45^\circ$ , 0.353;  $25^\circ$ , 0.303;  $20^\circ$ , 0.291.

Results calculated by the related formula

$$\ln \frac{p}{p'} = \frac{n}{N}$$

gives a practically identical result. It is worth emphasizing both that these simple formulas are still approximately correct in surprisingly high concentrations, and that the osmotic effect is always somewhat greater than expected. Thus even in a 2.7 *N* solution of cane sugar containing about equal weights of water and cane sugar the error is still less than 12%.<sup>1</sup> The enhanced osmotic effect is generally accounted for by assuming hydration of the solute. Thus, in the case of cane sugar, the hydrate appears to contain 5 molecules of water to one of sugar. The point that is useful in the following is that the osmotic activity tends to be too great rather than too small.

### Experimental Results and Deductions from Them.

I. *In concentrated soap solutions the only crystalloidal or electrolytic constituent is the potassium or sodium ion.*—This means that nearly half of the current is carried by the negative colloid, which must be as good a conductor as an ordinary ion. How this can be is explained later (see Section II).

For convenience, we shall discuss one particular example first, taking for this purpose the measurement of the 1.0 *N* potassium stearate solution recorded in Table I. This solution has at  $90^\circ$  an equivalent conductivity of 113.4 reciprocal ohms,<sup>2</sup> that of 1.0 *N* potassium acetate being 176.9 at the same temperature. It is evident that in this concentration the stearate conducts about  $\frac{2}{3}$  as well as the acetate itself and that it must, therefore, be recognized as an excellent conductor.

We now pass to the quantitative evaluation of these conductivity data in order to arrive at the concentration of the potassium ion present.

If the negative ion were an ion at all, the high molecular weight of the stearate radical would lead us to predict that the stearate ion would not

<sup>1</sup> *Trans. Faraday Soc.*, 11, 39 (1915).

<sup>2</sup> *Trans. Chem. Soc.*, 105, 424 (1914).



conduct as well as the acetate ion (116 reciprocal ohms at  $90^{\circ}$ ). In accordance with the extensive knowledge we possess of the dependence of mobility upon molecular weight and chemical constitution we should predict for the stearate ion a mobility at  $90^{\circ}$  of about 90 reciprocal ohms. This, with a mobility of 188 reciprocal ohms for the potassium ion, would make the conductivity of potassium stearate 278 for complete dissociation.

Using this result, the concentration of potassium ion is found to be  $\frac{113}{278} \times 1.0 N = 0.41 N$ . This equals the observed total concentration of crystalloidal constituents,  $0.42 N$ , within the experimental error. Hence everything else, that is, the whole of the stearate, including whatever carries the equivalent of this large amount of electricity, must be colloid and not simple unpolymerized stearate of any sort.

II. *These highly mobile ionic micelles may be plausibly predicted or explained on mechanical grounds.*—The conception of these highly mobile heavily hydrated micelle, outlined above, was originated by McBain in a general discussion on colloids and viscosity held by the Faraday Society in 1913.<sup>2</sup> It was put forward to remove one of the chief difficulties in interpreting the properties of acid and alkali albumens, since it reconciles their enormous viscosity with their quite good conductivity.

Stokes' law applied to a sphere of radius  $a$  moving through a liquid of viscosity  $\eta$  may be expressed as follows:  $V = \frac{E}{6\pi\eta a}$ , where  $V$  is the velocity caused by the action of a force  $F$ . Perrin and others have shown that this law applies to colloidal particles. In conductivity experiments the force  $F$  is due to the electric charge on the ion which is 96540 coulombs per gram ion. If this charge could be varied without other alteration of the ion, the driving force, velocity, and mobility or conductivity would vary in direct proportion.

If, on the other hand, a number of ions, say a dozen, were to coalesce, the resulting particles would be driven by a force equal to  $12F$ . The velocity would not be proportionally great, for the radius of the sphere would now be increased by a  $x^3/12 = 2.3a$ . The new velocity, therefore, would be  $12/2.3 = 5.2V$ . This 5-fold increase in mobility of the aggregate as compared with the separate ions would in practice be counterbalanced by the effect of the greatly enhanced electrostatic potential of the aggregate in attracting water molecules and other material, so that such an aggregate would become a heavily hydrated micelle. This great hydration would usually more than offset the extra mobility expected, and the results would be a colloidal particle of somewhat less mobility than a rather slow true ion. The hydration accounts for the enormous

<sup>1</sup> *Trans. Chem. Soc.*, 105, 423 (1914).

<sup>2</sup> *Trans. Faraday Soc.*, 9, 99 (1913); *Kolloid-Z.*, 13, 56 (1913).

mechanical viscosity observed in all the systems mentioned and also for its variation with the concentration of the constituents, etc. Such hydration has been commonly deduced by workers in this field for other reasons.

What is essentially new in the conception of a mobile micelle here presented, is the mechanism by which the micelle is built up round an aggregate of simple stearate ions which still retain their original electrical charges. In the study of such electrolytic colloids as the proteins it has long been assumed that an ion could be colloidal or associated with colloidal matter, but that was chiefly because quite enormous values are taken for the molecular weights of proteins, and molecules of such bulk must be expected to behave like colloids. Only a relatively low conductivity has ever been ascribed to them.<sup>1</sup>

III. *In dilute solutions on the contrary the colloid breaks up into simple ions and simple undissociated soap.*—On account of the limitations of the dew-point method in dilute solutions 0.2 *N* soap solutions were the most dilute measured. The result of measurements of potassium palmitate solutions of this concentration at 90° was as follows: Lowering of dew point = rise of boiling point at 90° = 0.12°. Hence total concentrations of all ions and molecules present = 0.25 *N*. Now the molar conductivity of 0.2 *N* potassium palmitate at 90° is 111.0 reciprocal ohms.<sup>2</sup> If the conductivity at infinite dilution is 304, the concentration of potassium ions is 0.072 *N*; if it be 278, the concentration is 0.080 *N*. Hydrolysis does not affect this result by more than about 2%,<sup>3</sup> and this may be neglected for our present purpose.

Taking the second result,  $K = 0.080$  *N*, the concentration of total crystalloids present being 0.25 *N*, leaves a concentration of 0.25 — 0.08 = 0.17 *N* for crystalloids other than the potassium ion. The total undissociated soap is 0.200 — 0.080 = 0.120 *N*. Thus, even if all the undissociated soap here is in simple crystalloidal form there is still a 0.17 — 0.12 = 0.05 *N* concentration of crystalloid to account for, and this must be afforded by simple palmitate ions, since the hydroxyl ions have been shown to be only about 0.01 *N*. The small balance of 0.03 is all that can be colloid.

Whether this relatively small amount of colloid is due to remaining

<sup>1</sup> It is a well known and striking fact that many mechanical suspensions as well as colloidal particles have an actual mobility in the electrical field comparable with that of an ion. This has not, however, been associated with high conductance, for it has been generally explained on the Helmholtz conception of the shearing of an electrical double layer, water upon water, not on the possession of such high electrical charge as we are here forced to recognize. Thus high mobility has not meant high conductivity although both must be attributed to an ionic micelle.

<sup>2</sup> *Trans. Chem. Soc.*, 105, 428 (1914).

<sup>3</sup> *Ibid.*, 105, 966 (1914). Confirmed by unpublished measurements of catalysis.

micelle or to neutral colloid will be discussed below. The point to notice is that not more than a quarter of the undissociated palmitate, nor more than  $\frac{3}{8}$  of the palmitate ion can be in colloidal form. If there be some of each in colloidal form this amount has to be divided up between them so as not to exceed a total of 0.03 *N*.

It is quite clear that in 0.2 *N* palmitate solution the break-down of the colloid has gone moderately far, and that further dilution would rapidly complete it. In other words, we have a clear case of transition from colloid to crystalloid in the same solution, depending only on the concentration, and forming a true, stable, reversible equilibrium in each concentration. That a colloid can thus enter into true equilibria would appear to be of great importance for the theory of colloids.

IV. "*Molecular weights*" of typical solutions of potassium and sodium salts of fatty acids at 90°.—Before further discussion a body of data may be presented for 77 typical potassium and sodium soap solutions giving the final results of measurements of the dew point carried out as described above. Almost every number in Table II and Table III is the mean of several such tables as Table I, carried out on independent solutions. Further results for concentrated solutions and other cases are given later. The total work done so far involves several thousand individual readings.

TABLE II.  
Rise of Boiling Point at 90° for Potassium Salts.

Weight normality.	Stearate, C <sub>18</sub> , °C.	Palmitate, C <sub>16</sub> , °C.	Myristate, C <sub>14</sub> , °C.	Laurate, C <sub>12</sub> , °C.	Decoate caprate, C <sub>10</sub> , °C.	Octoate caprylate, C <sub>8</sub> , °C.	Hexoate caproate, C <sub>6</sub> , °C.	Acetate, C <sub>2</sub> , °C.
0.2	0.10	0.12	0.13	0.15	0.16	0.17	0.17	0.185
0.5	0.17	0.19	0.23	0.26	0.31	0.35	0.38	0.46
0.75	0.19	0.23	0.27	0.30	0.42	0.48	0.53	....
1.0	0.20	0.24	0.28	0.32	0.52	0.60	0.66	0.86
1.5	0.16	0.21	0.25	0.31	(0.65)	....	....	....
2.0	0.18	0.27	0.32	0.48	(0.72)	....	....	....
3.0	0.23	....	....	1.02	....	....	....	....

TABLE III.  
Rise of Boiling Point at 90° for Sodium Salts.

Weight, normality.	Behenate, C <sub>22</sub> , °C.	Stearate, C <sub>18</sub> , °C.	Palmitate, C <sub>16</sub> , °C.	Myristate, C <sub>14</sub> , °C.	Laurate, C <sub>12</sub> , °C.	Caprylate, C <sub>8</sub> , °C.	Acetate, C <sub>2</sub> , °C.	Any non-electrolyte by theory.
0.2	0.09	0.11	0.13	0.14	0.15	0.17	....	0.10
0.5	0.11	0.18	0.20	0.24	0.28	0.37	0.45	0.24
0.75	....	0.22	0.24	0.28	0.32	0.50	....	0.36
1.0	0.09	0.23	0.25	0.29	0.34	0.62	0.84	0.48
1.5	....	0.18	0.22	0.27	0.33	....	....	0.72
2.0	0.11	0.19	0.50	....	....	....	....	0.97
3.0	....	0.30	1.23	....	....	....	....	1.45

Tables IV and V give the total amounts of crystalloidal matter (ionized and otherwise), indicated by the data of Tables IV and V and expressed

in mols per 1000 g. of water. These are calculated as shown on page 435.

TABLE IV.

Total Crystalloidal Matter in Potassium Salt Solutions at 90°.

Weight normality.	Mols per 1000 g. of Water.							
	Stearate, C <sub>18</sub> .	Palmitate, C <sub>16</sub> .	Myristate, C <sub>14</sub> .	Laurate, C <sub>12</sub> .	Caprate, C <sub>10</sub> .	Caprylate, C <sub>8</sub> .	Caproate, C <sub>6</sub> .	Acetate, C <sub>2</sub> .
0.2	0.21	0.25	0.27	0.31	0.33	0.35	0.35	0.38
0.5	0.35	0.39	0.48	0.54	0.64	0.72	0.79	0.95
0.75	0.39	0.48	0.56	0.62	0.87	0.99	1.10	....
1.0	0.42	0.50	0.58	0.66	1.08	1.24	1.37	1.78
1.5	0.33	0.44	0.52	0.64	1.35	....	....	....
2.0	0.37	0.56	0.66	0.99	1.50	....	....	....
3.0	0.48	....	....	2.11	....	....	....	....

TABLE V.

Total Crystalloidal Matter in Sodium Salt Solutions at 90°.

Weight normality.	Mols per 1000 g. of Water.						
	Behenate, C <sub>22</sub> .	Stearate, C <sub>18</sub> .	Palmitate, C <sub>16</sub> .	Myristate, C <sub>14</sub> .	Laurate, C <sub>12</sub> .	Caprylate, C <sub>8</sub> .	Acetate, C <sub>2</sub> .
0.2	0.19	0.23	0.27	0.29	0.33	0.35	....
0.5	0.23	0.37	0.41	0.50	0.58	0.77	0.93
0.75	....	0.46	0.50	0.58	0.66	1.04	....
1.0	0.19	0.48	0.52	0.60	0.70	1.28	1.74
1.5	....	0.37	0.46	0.56	0.68	....	....
2.0	0.23	0.39	1.04	....	....	....	....
3.0	....	0.62	2.55	....	....	....	....

Far better than any further discussion of the reliability and reproducibility of these independent measurements is a glance at a graph of the results. Fig. 2 presents the directly observed dew-point lowerings plotted against the dilution<sup>1</sup> in liters as abscissas. The curves for the sodium soaps are only dotted in, for convenience of comparison. It is evident that the salts fall into two classes. From the acetate up to the caprate (C<sub>10</sub>) the curves are regular, showing dissociation, although in the more concentrated caprate solutions the lowering only slightly exceeds that of an ordinary non-electrolyte. On the other hand, from the laurate (C<sub>12</sub>) upwards, each curve passes through a pronounced maximum lowering at about 1.0 N<sup>2</sup> and a definite minimum lowering again at 1.5 N. Above these concentrations the lowering rapidly increases again.

It is worth while remembering that the stearate above 1.5 N is hardly a solution; 1.5 N sodium stearate at 90° is a viscid gum. On the other hand, 2.0 N potassium laurate solution with a similarly shaped curve, is a clear oily liquid. The form of the curve is thus definitely due to the constituents in solution, not to mechanical effects such as formation of

<sup>1</sup> The concentrations are in grams per kg.

<sup>2</sup> The exact concentration is slightly higher than 1.0 N for the lower members, and slightly lower than 1.0 N for the behenate. This agrees with the previous work on conductivity published from this laboratory (*Trans. Chem. Soc.*, 105, 435 (1914)).

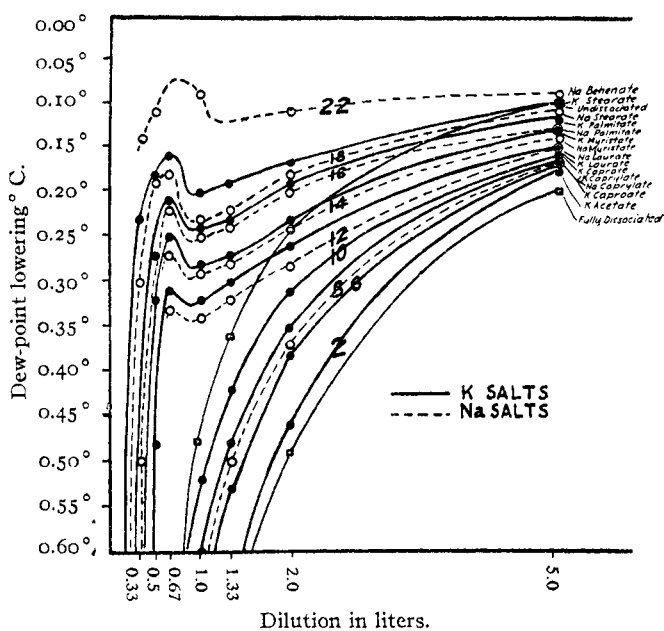


Fig. 2.—Dew-point lowerings of potassium and sodium salts of fatty acids at  $90^{\circ}$ .

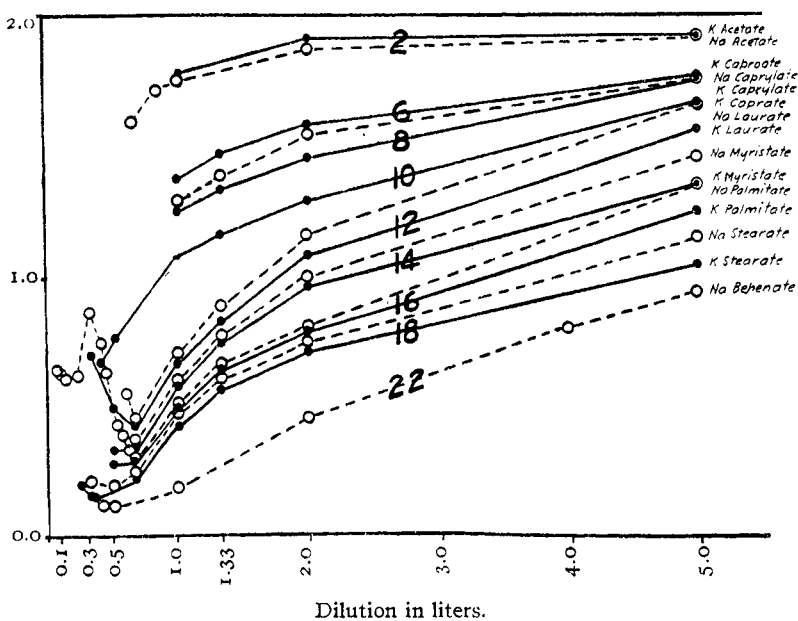


Fig. 3.—Osmotic activity.

gel or change of state. The effect is also not due to hysteresis, as is the case in the dehydration of certain gels, for it is independent of the age or method of preparation of the soap solution or whether water may have been previously added or taken away.

Fig. 3 presents the results in a wholly different form. Here the ratios of the lowerings to that predicted for the same concentration of any non-electrolyte, in other words van't Hoff's factor  $i$ , are plotted against the dilution in liters. The curves for the sodium salts are dotted as before. The significance of these results is that they give directly, for each concentration, the proportion of total crystalloids present, relative to that in the case of a non-electrolyte which is taken as unity, that of a completely dissociated binary electrolyte being 2.

It will be noted that the present consideration differs from the crude treatment almost invariably accorded to osmotic data whether in aqueous or non-aqueous solution, where the data are simply scanned for evidence of association or dissociation. The usual interpretation would be to jump to the conclusion that a 0.20  $N$  potassium stearate or a 0.5  $N$  sodium myristate, for example, consists of simple undissociated molecules, a result which is of course irreconcilable with the conductivity, as in the case of many non-aqueous solutions. Similarly, a normal solution of sodium or potassium palmitate would be regarded as being composed of undissociated double molecules, again irreconcilable with the high conductivity. It will be seen how the method developed under Sections I and III will probably clear up many otherwise unexplained anomalies in non-aqueous solutions where such cases constantly occur.

The results cover a very wide range, from the ordinary highly dissociated electrolytes represented by the acetates, to the concentrated solutions of the behenate ( $C_{22}$ ) where the total amount of crystalloid, ionized and non-ionized, is only a tenth of the total concentration. The data for the behenate will be discussed in a separate communication in conjunction with other data.

It is quite striking with what regularity the phenomena set in. The transition from any one type to the other is quite gradual as we ascend the homologous series. Again, the curves for each fatty acid run in pairs for the sodium and potassium salts. Only in concentrations above 1.5  $N$  do the potassium and sodium soaps diverge appreciably, although in every case the potassium salt solution contains slightly more colloid. This last result had been already deduced from our study of conductivity.<sup>1</sup>

V. In 1.0  $N$  solutions at 90° the total colloid present equals at least 15% in the case of the hexoate, increasing to nearly the whole in the cases of the

<sup>1</sup> *Trans. Chem. Soc.*, 105, 435(1914).

*higher soaps, but falling off rapidly on dilution.*—We have now in Tables IV and V the total amount of crystalloid in each solution ( $K^+$  or  $Na^+$ , simple soap ion such as palmitate ion  $P^+$ , as simple undissociated neutral soap such as  $NaP$ ). Next come the results of the conductivity measurements which give the concentrations of the potassium or sodium ions, (Tables VI and VII). The values taken for the mobilities of the negative radicals are, behenate to laurate 90, caprate 92, caprylate 94, caproate 98, acetate 116, also sodium 139 and potassium 188. (See page 434 and also below.<sup>1</sup>)

TABLE VI.

## Concentrations of Potassium Ion in Salts at 90°.

Weight normality.	Stearate, $C_{18}$ .	Palmitate, $C_{16}$ .	Myristate, $C_{14}$ .	Laurate, $C_{12}$ .	Caprate, $C_{10}$ .	Caprylate, $C_8$ .	Caproate, $C_6$ .	Acetate, $C_2$ .
0.2	0.072	0.080	0.094	0.103	0.135	0.135	0.140	0.145
0.5	0.205	0.202	0.243	0.262	0.278	0.298	0.310	0.324
0.75	0.305	0.345	0.366	0.384	0.399	0.389	0.426	0.454
1.0	0.408	0.446	0.489	0.515	0.521	0.527	0.523	0.582
1.5	.....	.....	.....	0.696	.....	0.728	.....	0.800
2.0	.....	.....	.....	0.885	.....	0.898	.....	1.01

TABLE VII.

## Concentrations of Sodium Ion in Salts at 90°.

Weight normality.	Stearate, $C_{18}$ .	Palmitate, $C_{16}$ .	Myristate, $C_{14}$ .	Laurate, $C_{12}$ .	Acetate, $C_2$ .
0.2	0.053	0.079	0.085	0.099	0.140
0.5	0.166	0.195	0.216	0.239	0.303
0.75	0.272	0.286	0.324	0.350	0.409
1.0	0.386	0.369	0.405	0.455	0.511
1.5	0.553	0.553	0.543	0.615	0.664

By subtracting corresponding values in Tables VI and VII from those in Tables IV and V, we arrive at the values in Tables VIII and IX, which give all crystalloidal constituents other than potassium or sodium ions. The remainder of the soap must, of course, be colloidal and the values for this are given in Tables X and XI.

TABLE VIII.

Concentrations of Crystalloidal Constituents other than  $K^+$  at 90°.

Weight normality.	Stearate, $C_{18}$ .	Palmitate, $C_{16}$ .	Myristate, $C_{14}$ .	Laurate, $C_{12}$ .	Caprate, $C_{10}$ .	Caprylate, $C_8$ .	Caproate, $C_6$ .	Acetate, $C_2$ .
0.2	0.14	0.17	0.18	0.21	0.20	0.22	0.21	0.24
0.5	0.15	0.19	0.23	0.28	0.36	0.43	0.43	0.63
0.75	0.08	0.11	0.19	0.24	0.47	0.58	0.67	.....
1.0	0.01	0.05	0.09	0.15	0.56	0.72	0.85	1.20
1.5	.....	.....	.....	0.05	.....	.....	.....	.....
2.0	.....	.....	.....	0.11	.....	.....	.....	.....

<sup>1</sup> Direct determinations of these values were being carried out in this laboratory in the early summer of 1914. It is hoped ultimately to complete them.

TABLE IX.  
Concentrations of Crystalloidal Constituents other than Na<sup>+</sup> at 90°.

Weight normality.	Stearate, C <sub>18</sub> .	Palmitate, C <sub>16</sub> .	Myristate, C <sub>14</sub> .	Laurate, C <sub>12</sub> .	Acetate, C <sub>2</sub> .
0.2	0.18	0.19	0.20	0.23	....
0.5	0.20	0.22	0.28	0.34	0.63
0.75	0.18	0.1	0.26	0.31	....
1.0	0.09	0.15	0.20	0.25	1.23
1.5	-0.20	-0.11	0.02	0.07	....

TABLE X.  
Concentrations of Total Colloid in Potassium Salt Solutions at 90°.

Weight normality.	Stearate, C <sub>18</sub> .	Palmitate, C <sub>16</sub> .	Myristate, C <sub>14</sub> .	Laurate, C <sub>12</sub> .	Caprate, C <sub>11</sub> .	Caprylate, C <sub>8</sub> .	Caproate, C <sub>6</sub> .	Acetate, C <sub>2</sub> .
0.2	0.06	0.03	0.02	-0.01	0.00	-0.02	-0.01	-0.04
0.5	0.35	0.31	0.27	+0.22	0.14	+0.07	+0.02	-0.13
0.75	0.69	0.64	0.56	0.51	0.28	0.17	0.08	....
1.0	0.99	0.95	0.91	0.85	0.44	0.28	0.15	-0.20
1.5	....	....	....	1.55	....	....	....	....
2.0	....	....	....	1.89	....	....	....	....

TABLE XI.  
Concentrations of Total Colloid in Sodium Salt Solutions at 90°.

Weight normality.	Stearate, C <sub>18</sub> .	Palmitate, C <sub>16</sub> .	Myristate, C <sub>14</sub> .	Laurate, C <sub>12</sub> .	Acetate, C <sub>2</sub> .
0.2	0.02	0.01	0.00	-0.03	....
0.5	0.30	0.28	0.22	+0.16	-0.13
0.75	0.57	0.54	0.49	0.44	....
1.0	0.91	0.85	0.80	0.75	-0.23
1.5	(1.70)	1.61	1.48	1.43	....

It is necessary to pause again to consider the validity of this comparison of osmotic with conductivity data. It is undoubtedly the case that the osmotic values are too high, presumably, as already mentioned, on account of hydration of the solute. The ebullioscopic method shows this particularly, for Beckmann, by this method, obtained values from sodium acetate corresponding to dissociations which actually increased from 78% in 0.25 *N* solution to 95% in 1.9 *N* solution. The apparent dissociations of potassium and sodium chlorides pass through minima of 76 and 84% at about 0.1 *N*, rising to 89% for 2.5 *N* potassium chloride and the impossible value of 106% for 2.1 *N* sodium chloride.

The dew-point method is much more reliable than the ebullioscopic method since the latter measures only a very rough dynamic thermal equilibrium instead of a true static one. But even so, the dissociation deduced for sodium acetate from the conductivity falls short of the osmotic activity by 20 to 23%. Even were this all due to hydration, 7 or 8 molecules of water would have combined with the acetate and its ions, a not improbable result in the light of other evidence.

On the other hand, the results of conductivity measurements are definitely too low, on account of the retarding influences of viscosity on the



mobility of ions. The form which the viscosity correction should take is still a matter of speculation<sup>1</sup> but it follows from the present paper that those in use are not universally correct. For example, the solutions often have their observed conductivities corrected directly by multiplying these values by the ratio between the viscosities of solvent and solution; more usually a fractional power of this ratio is employed. The former is certainly the correction required by Stokes' Law. But in some of the soap solutions here discussed the viscosity is 1000 times greater than that of water, and it is very obvious that the high observed conductivity cannot be increased even a few fold without exceeding 100% dissociation. The viscosity correction ought certainly to be made in all solutions, but it is evident that its exact formulation has still to be ascertained. Even in viscous soap solutions the correction cannot be very large. It may be legitimate to take the viscosity of the solution itself in a molecular, homogeneous, crystalloidal solution, but it must be that of the intramolecular liquid in the case of a colloidal electrolyte.

In the case of the acetates here measured the viscosities of 1.0 *N* solutions of potassium and sodium acetates at 18° and 25° exceed that of water by 26 and 39%, respectively. Although this would be somewhat less at 90°, it is ample to account for any divergence between the conductivity and osmotic effect, but probably both viscosity and hydration each contribute a share.

We have seen then that the osmotic activity is certainly too great, and that conductivity data are certainly too small. And yet in concentrated solutions of the higher soaps the osmotic effect is not enough even for the sodium and potassium ions alone as deduced from the conductivity. This is satisfactory in establishing the main thesis of this paper.

However, looking at Tables X and XI, we see that 1.5 *N* solutions of potassium laurate, sodium stearate and sodium palmitate give more colloid than is possible when calculated by taking the conductivity and dew point without correction. The permissible correction as just discussed would operate in the wrong direction. The obvious course is to admit that the basis of the calculation of the concentration of the sodium and potassium ions in concentrated solutions is incorrect, in that the ionic micelle (it cannot be the potassium ion) has a mobility even higher than that assumed above 90 mhos at 90°.

To reconcile the data for 1.5 *N* sodium stearate it is necessary to assume for the micelle a mobility at least as great as that of potassium ion (188 mhos). This could easily be effected through diminishing hydration of the micelle in concentrated solution according to the data of Section II. Other evidence in support of this plausible assumption will be discussed below. (See Section XIV.)

<sup>1</sup> Cf. *Trans. Chem. Soc.*, 105, 433 (1914).

The only alternative would appear to be the assumption of a positive as well as a negative micelle, to replace some of the potassium ion. However, it is not in accordance with what we know of the behavior of colloids that two oppositely charged colloids should be simultaneously present in a solution.<sup>1</sup>

On the whole then, the tables presented appear to be substantially correct for all dilute solutions, and in every case in Tables X and XI to indicate minimum values for the amounts of colloid present.

The first point to notice is that every 0.1 *N* solution, from the caproate ( $C_6$ ) upwards, contains colloid. In the caproate only 15% is present in this form, while in the potassium stearate 99% is colloid. This is in accordance with former work from this laboratory, on appearance, washing power, density and conductivity.<sup>2</sup> The great increase in amount of colloid is in passing from the caprate ( $C_{10}$ ) to the laurate ( $C_{12}$ ) which about doubles it.

Again, in every case the amount of colloid falls off steadily and very readily with decrease in concentration. It appears to become inappreciable as measured at 0.2 *N* laurate; but since an error of 0.01° in the dew point is equal to 10% in the concentration in this dilute solution, it follows from previous work that some colloid is still present.

VII. *Only within certain limits can we at present allot the total colloid between micelle and neutral colloid.*—What we have so far established is the approximate total amounts of colloid and crystalloid present and the existence of ionic micelles which conduct as well as ordinary ions; and since the micelles conduct much better in concentrated solution, the total amount of colloid in such solutions as given in Tables X and XI, is somewhat too great.

The next step is to attempt to allot the total colloids and crystalloids among the 5 constituents which are present in concentrations of at least 0.01 *N*, namely sodium or potassium ion (given in Tables VI and VII), micelle, simple fatty ion, undissociated neutral colloid, and undissociated crystalloid. The results are given in Tables XII to XV according to each of 3 different assumptions. The upper figure in each case assumes that micelle tends to be formed much more than undissociated colloid, and so ascribes the total colloid to micelle as far as possible; the third makes the opposite assumption and favors undissociated colloid at the expense of micelle; the second allots the available colloid to both in the proportion of one fatty ion to one and a half molecules of undissociated soap. This middle value is certainly not far from correct in the concen-

<sup>1</sup> Bancroft thinks this possible (*Trans. Amer. Electrochem. Soc.*, 27, 184 (1915)). It is, however, not worth while considering the question at any length for we expect to be able to decide it by experiment (see *Trans. Chem. Soc.*, 105, 976 (1914), footnote).

<sup>2</sup> *Trans. Chem. Soc.*, 105, 435 (1914).

TABLE XII.  
 Limits<sup>a</sup> of Concentration of Colloidal Constituents of Potassium Salts.

Weight normality.	Stearate, C <sub>18</sub> .	Palmitate, C <sub>16</sub> .	Myristate, C <sub>14</sub> .	Laurate, C <sub>12</sub> .	Caprate, C <sub>10</sub> .	Caprylate, C <sub>8</sub> .	Caproate, C <sub>6</sub> .
Micelle. <sup>b</sup>							
0.2	0.06	0.03	0.02	0.00	0.00	0.00	0.00
	0.02	0.01	0.01	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.5	0.21	0.20	0.24	0.22	0.14	0.07	0.02
	0.14	0.12	0.10	0.08	0.06	0.07	0.01
	0.06	0.01	0.01	0.00	0.00	0.00	0.00
0.75	0.31	0.35	0.37	0.38	0.28	0.17	0.08
	0.28	0.26	0.22	0.20	0.12	0.07	0.03
	0.23	0.24	0.18	0.14	0.00	0.00	0.00
1.0	0.41	0.45	0.49	0.52	0.44	0.28	0.15
	0.40	0.38	0.36	0.34	0.18	0.11	0.06
	0.40	0.40	0.40	0.37	0.00	0.00	0.00
1.5	....	....	....	0.70	....	....	....
	....	....	....	0.62	....	....	....
	....	....	....	0.75	....	....	....
2.0	....	....	....	0.89	....	....	....
	....	....	....	0.76	....	....	....
	....	....	....	0.78	....	....	....
Neutral Colloid. <sup>c</sup>							
0.2	0.00	0.00	0.00	0.00	0.00	0.00	....
	0.04	0.02	0.01	0.00	0.00	0.00	0.00
	0.06	0.03	0.02	-0.01	0.00	-0.02	-0.01
0.5	0.14	0.11	0.03	0.00	0.00	0.00	0.00
	0.21	0.19	0.17	+0.14	0.08	+0.04	+0.01
	0.29	0.30	0.26	0.22	0.14	0.07	0.02
0.75	0.38	0.29	0.19	0.13	0.00	0.00	0.00
	0.41	0.38	0.34	0.31	0.16	0.10	0.05
	0.46	0.40	0.38	0.37	0.28	0.17	0.08
1.0	0.58	0.50	0.42	0.33	0.00	0.00	0.00
	0.59	0.57	0.55	0.51	0.26	0.17	0.09
	0.59	0.55	0.51	0.48	0.44	0.28	0.15
1.5	....	....	....	0.85	....	....	....
	....	....	....	0.93	....	....	....
	....	....	....	0.80	....	....	....
2.0	....	....	....	1.00	....	....	....
	....	....	....	1.13	....	....	....
	....	....	....	1.11	....	....	....

<sup>a</sup> The upper number of each trio is calculated by ascribing the largest available proportion of the total colloid to micelle; the lowest similarly to undissociated colloid; the middle one, which gives the most probable general idea, assumes that 1.5 mols of undissociated soap are agglomerated for every mol of fatty acid that is so.

<sup>b</sup> Calculated as weight normality of agglomerated palmitate ion.

<sup>c</sup> This represents all the colloid other than agglomerated fatty acid ion. Whether a part of the whole is involved in the ionic micelle, or has a separate existence is a question which cannot be settled by the data presented here (see VII and VIII).

trated solutions, and altogether gives the fairest general picture of the composition of all solutions.

It will be noted that in some cases, especially where either colloid or crystalloid largely predominates, the concentrations are fixed within narrow limits; in some other cases these limits although definite are quite wide apart.

TABLE XIII.

Limits of Concentration of Crystalloidal Constituents of Potassium Salts at 90°.

Weight normality.	Stearate,	Palmitate,	Myristate,	Laurate,	Caprate,	Caprylate,	Caproate,	Acetate,
	C <sub>18</sub> .	C <sub>16</sub> .	C <sub>14</sub> .	C <sub>12</sub> .	C <sub>10</sub> .	C <sub>8</sub> .	C <sub>6</sub> .	C <sub>2</sub> .
Simple Fatty Acid Ion.								
0.2	0.01	0.05	0.07	0.11	0.14	0.15	0.15	0.19
	0.05	0.07	0.08	0.10	0.14	0.14	0.14	0.00
	0.07	0.08	0.09	0.10	0.14	0.14	0.14	0.15
0.5	0.00	0.00	0.00	0.04	0.14	0.23	0.29	0.45
	0.07	0.08	0.14	0.18	0.22	0.27	0.30	0.00
	0.15	0.19	0.23	0.26	0.28	0.30	0.31	0.32
0.75	0.00	0.00	0.00	0.00	0.12	0.22	0.35	0.00
	0.03	0.09	0.15	0.18	0.28	0.32	0.40	0.00
	0.08	0.11	0.19	0.24	0.40	0.39	0.43	0.45
1.0	0.00	0.00	0.00	0.00	0.08	0.25	0.37	0.78
	0.01	0.07	0.13	0.18	0.34	0.42	0.46	0.00
	0.01	0.05	0.09	0.15	0.52	0.53	0.52	0.58
1.5	....	....	....	0.00	....	....	....	0.00
	....	....	....	0.08	....	....	....	0.00
	....	....	....	0.05	....	....	....	0.80
2.0	....	....	....	0.00	....	....	....	0.00
	....	....	....	0.13	....	....	....	0.00
	....	....	....	0.11	....	....	....	1.01
Simple Neutral Undissociated Salt.								
0.2	0.13	0.12	0.11	0.10	0.06	0.07	0.06	0.01
	0.09	0.10	0.10	0.11	0.06	0.08	0.07	0.00
	0.07	0.09	0.09	0.11	0.06	0.08	0.07	0.05
0.5	0.15	0.19	0.23	0.24	0.22	0.20	0.19	0.05
	0.08	0.11	0.09	0.10	0.14	0.16	0.18	0.00
	0.00	0.00	0.00	0.02	0.08	0.13	0.17	0.18
0.75	0.08	0.11	0.19	0.24	0.38	0.36	0.32	0.00
	0.05	0.02	0.04	0.06	0.19	0.26	0.27	0.00
	0.00	0.00	0.00	0.00	0.07	0.19	0.24	0.30
1.0	0.01	0.05	0.09	0.15	0.48	0.47	0.48	0.22
	0.00	-0.02	-0.04	-0.03	0.22	0.30	0.39	0.00
	0.00	0.00	0.00	0.00	0.04	0.19	0.33	0.42
1.5	....	....	....	-0.05	....	....	....	0.00
	....	....	....	-0.13	....	....	....	0.00
	....	....	....	0.00	....	....	....	0.75
2.0	....	....	....	+0.11	....	....	....	0.00
	....	....	....	-0.62	....	....	....	0.00
	....	....	....	0.00	....	....	....	0.99

TABLE XIV.

Limits of Concentration of Colloidal Constituents of Sodium Salts at 90°.

Weight normality.	Stearate,	Palmitate,	Myristate,	Laurate,	Acetate,
	C <sub>18</sub> .	C <sub>16</sub> .	C <sub>14</sub> .	C <sub>12</sub> .	C <sub>2</sub> .
	Micelle.				
0.2	0.02	0.01	0.00	-0.03	0.00
	0.01	0.00	0.00	0.00	0.00
	0.00	0.00	0.00	0.00	0.00
0.5	0.17	0.20	0.22	+0.16	-0.03
	0.12	0.11	0.09	0.06	-0.05
	0.00	0.00	0.00	0.00	0.00
0.75	0.27	0.29	0.32	0.35	0.00
	0.23	0.22	0.19	0.17	0.00
	0.09	0.08	0.06	0.04	0.00
1.0	0.39	0.37	0.41	0.46	-0.23
	0.36	0.34	0.32	0.30	-0.09
	0.30	0.22	0.21	0.21	0.00
1.5	0.53	0.55	0.54	0.62	0.00
	0.68	0.64	0.79	0.58	0.00
	0.73	0.66	0.52	0.55	0.00
	Neutral Colloid.				
0.2	0.00	0.00	0.00	0.00	0.00
	0.01	0.01	0.00	-0.03	0.00
	0.02	0.01	0.00	-0.03	0.00
0.5	0.13	0.08	0.00	0.00	0.00
	0.18	0.17	0.13	+0.10	-0.08
	0.30	0.28	0.22	0.16	+0.13
0.75	0.30	0.25	0.17	0.09	0.00
	0.34	0.32	0.30	0.27	0.00
	0.48	0.46	0.43	0.40	0.00
1.0	0.52	0.48	0.39	0.29	0.00
	0.65	0.51	0.48	0.45	-0.14
	0.61	0.63	0.59	0.54	-0.23
1.5	1.17	1.06	0.94	0.81	0.00
	1.02	0.97	0.69	0.86	0.00
	0.97	0.95	0.96	0.88	0.00

Whatever assumption is made, the absolute concentration of simple fatty ion is seen to rise at first with concentration, pass through a maximum and then nearly disappear; except that in extremely high concentration it may possibly increase again. The simple crystalloidal undissociated salt is similar but disappears rather more definitely.

Some ionic micelle and perhaps some of the other colloid are present in moderate dilution, but the amounts rapidly and steadily rise with concentration tending towards about  $\frac{2}{5}$  of the total soap in the form of micelle and the other  $\frac{3}{5}$  in the form of undissociated colloid. This is, by the way, a frequent approximate proportion for the union of sodium and

fatty acid radical, as is shown by the analyses of precipitates and sediments from soap solutions.

TABLE XV.

Limits of Concentration of Crystalloidal Constituents of Sodium Salts at 90°.					
Weight normality.	Stearate, C <sub>18</sub> .	Palmitate, C <sub>16</sub> .	Myristate, C <sub>14</sub> .	Laurate, C <sub>12</sub> .	Acetate, C <sub>2</sub> .
Simple Fatty Acid Ion.					
0.2	0.03	0.07	0.09	0.13	0.00
	0.04	0.08	0.09	0.10	0.00
	0.05	0.08	0.09	0.10	0.00
0.5	0.00	0.00	0.00	0.08	0.43
	0.05	0.09	0.13	0.18	0.35
	0.17	0.20	0.22	0.24	0.30
0.75	0.00	0.00	0.00	0.00	0.00
	0.04	0.07	0.13	0.18	0.00
	0.18	0.21	0.26	0.31	0.00
1.0	0.00	0.00	0.00	0.00	0.74
	0.03	0.03	0.09	0.16	0.60
	0.09	0.15	0.20	0.25	0.51
1.5	0.00	0.00	0.00	0.00	0.00
	—0.15	—0.09	—0.25	0.05	0.00
	—0.20	—0.11	+0.02	0.07	0.00
Simple Neutral Undissociated Salt.					
0.2	0.15	0.12	0.11	0.10	0.06
	0.14	0.11	0.11	0.13	0.06
	0.13	0.11	0.11	0.13	0.06
0.5	0.20	0.22	0.28	0.26	0.20
	0.15	0.13	0.15	0.16	0.28
	0.03	0.02	0.06	0.10	0.33
0.75	0.18	0.21	0.26	0.31	0.34
	0.14	0.14	0.13	0.13	0.34
	0.00	0.00	0.00	0.00	0.34
1.0	0.09	0.15	0.20	0.25	0.49
	—0.04	0.12	0.11	0.09	0.63
	0.00	0.00	0.00	0.00	0.72
1.5	—0.20	—0.11	0.02	0.17	0.84
	—0.05	—0.02	0.27	0.12	0.84
	0.00	0.00	0.00	0.10	0.84

The question now arises as to whether the undissociated colloid unites with the agglomerated fatty ions or whether, on the contrary, there are two independent colloids present, one highly charged and mobile, the other an ordinary colloid. The first view is certainly the more likely approximation to the facts but the question cannot be decided by the experimental data so far presented.

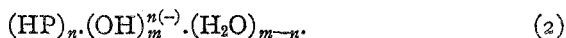
VII. *Some conceptions of the ionic micelle. Various hypotheses as to the genesis of the micelle lead to nearly the same result.*—Various views may well be taken with regard to the formation of the ionic micelle. For in-

stance, the simplest is to consider it as an agglomeration of palmitate ions, heavily weighted by water, a complex solvate:



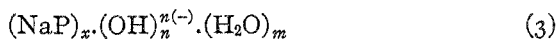
The water sphere, collected round these enormous electrical charges, is as inevitable as the collection of a droplet of water round an electron in saturated water vapor. Probably some at least of the undissociated colloid would also join in (see below).

This selfsame micelle can also be formulated thus:



Here the assumption is complete hydrolysis of the palmitate ion followed by complete adsorption of the hydroxyl ions by the fatty acid. It is a question of taste as to whether such juggling attracts or repels the investigator. We personally appreciate it more when it appears to represent a difference in experimental result, not merely in words or even in standpoint.

Bancroft,<sup>1</sup> in discussing the preliminary accounts of our data, which had appeared before the outbreak of war suddenly stopped our scientific work, says: "As I see the matter, the sodium palmitate is hydrolyzed and the hydroxyl ions are adsorbed to a great extent by the undissociated palmitate and possibly by the insoluble palmitate acid also, though this seems less probable." The latter assumption is represented by Formula 2; the former by

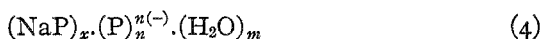


leaving either  $n$  equivalents of insoluble palmitic acid or  $n$  equivalents of (insoluble) acid salt, say  $n$  NaHP<sub>2</sub>, free in the solution. The former alternative of this pair for the solution is untenable since previous papers from this laboratory have shown conclusively that palmitic acid cannot exist in the free state in the presence of even the low concentrations of free hydroxyl ion characteristic of all these solutions. The latter alternative would mean that our undissociated colloid as tabulated in Tables XII and XIV consists of insoluble acid salt such as NaHP<sub>2</sub> or something intermediate between this and neutral NaP. One asks at once why NaHP<sub>2</sub> cannot adsorb hydroxyl ions too when it is exactly intermediate between the two substances HP and NaP which are proposed for this purpose in Formulas 2 and 3.

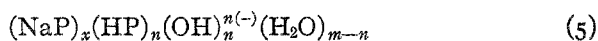
Much more important, however, is that Bancroft has evidently overlooked the existence of hydrogen soaps such as Reychler's cetyl sulfonic acid, of which hydrolysis is either out of the question or else becomes as arbitrary an assumption as that of a 100% hydrolysis of potassium chloride with ions such as KOH, H<sup>-</sup> + HCl.OH<sup>+</sup> instead of K<sup>-</sup>.H<sub>2</sub>O + Cl<sup>+</sup>.H<sub>2</sub>O. Reverting to the idea expressed in Formula 1, that the micelle is built

<sup>1</sup> *Trans. Amer. Electrochem. Soc.*, 27, 184 (1915).

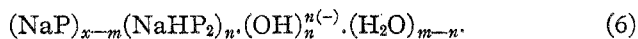
up around palmitate ions (or, if preferred, around other things adsorbing palmitate ions) the following formula seems the most plausible, where all or nearly all the colloid collects to form the micelle:



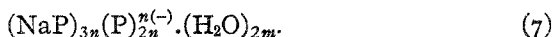
which is the same as follows:



or



The middle values given in Tables XII to XIV represent the micelle for the particular case:



The only argument that occurs to us for regarding adsorbed hydroxyl ion as the basis of the micelle is that it is in general comparatively readily adsorbed. However, a more than 99% adsorption in a highly concentrated solution would differ wholly and remarkably from hitherto investigated cases of sorption.

The formulas above present only a general scheme for the micelle. Their composition must alter continuously with the concentration or upon the addition of salts. Thus in very concentrated solution or in the presence of large amounts of another electrolyte such as sodium hydroxide (see below), the soap must be nearly all colloid of approximately the composition



In other words, the question left open is as to whether in moderate concentrations the micelle has Formula 4, corresponding to (8) less the sodium which has gone to form ions and plus the equivalent number of electrical charges on the palmitate radicals left, or, on the other hand, has a formula such as (1) (where the value of  $x$  in Formula 4 has become very small). If the first is the case, the micelle alters gradually from (4) to (8) as the dissociation is driven back; on the second alternative, driving back the dissociation does not alter the composition of the ionic micelle so much, but replaces it by producing neutral colloid instead. Here it must be remembered that in dilute solution simple, neutral, crystalloidal, undissociated soap does exist independently.

With regard to the value of  $n$ , the number of negative charges on one micelle, it must be at least 10, and may be much greater. There the "molecular weight" of one ionic micelle must be nearly 3000 anyway since the true molecular weight of the palmitate ion is 255. Similarly the enormous molecular weights ascribed to various substances which occur only in colloidal form may be derived from the aggregation of comparatively small molecules.

VIII. *The effect of concentration upon the ionic micelle explains the anoma-*



*lous conductivity curves of soap solution.*—This will be discussed upon the assumption that the micelle, starting in dilute solution, essentially as  $P_n^{n(-)}.mH_2O$ , Formula 1, gradually alters to  $xNaP.yH_2O$ , Formula 8, through  $(NaP)_xP_n^{n(-)}.mH_2O$ , Formula 4, as  $x$  increases by means of the ionic micelle steadily taking up more and more NaP when dissociation is driven back.

Further, we have seen that if the facts are to be reconciled at all, we must assume that the ionic micelle conducts better and better the higher the concentration, probably through diminution of the hydration  $m$ .

This whole conception gains strong support from several sources. Important confirmation is given by the conductivity. It is definitely a fact that the higher soap solutions, quite apart from the small amount of free alkali present, exhibit minimum conductivity in 0.1 or 0.2  $N$  solutions (see previous papers from this laboratory, also independent confirmation in the experiments of F. Goldschmidt and co-workers).<sup>1</sup> In higher concentrations the conductivity rises appreciably up to 0.5  $N$  or  $N$  solutions, where a maximum is observed. This is direct evidence that the ionic micelle which is replacing the fatty acid ion is a better conductor than that ion. The ultimate falling off in very concentrated solutions is the effect of the diminishing dissociation of the electrolytic colloid.

Now the higher soaps are the most colloidal and the potassium soaps contain more colloid than the sodium salts. It is just these cases that exhibit the minimum in 0.1  $N$  solution. The better conducting and less colloidal potassium laurates ( $C_{12}$ ) and the sodium soaps do not show a minimum until 0.2  $N$  concentration of solution is attained.

Similarly, the lowering of vapor pressure passes through a maximum in normal solution where the total concentration of crystalloid is at a maximum. Diminishing hydration and diminishing dissociation of the colloidal electrolyte combine to reduce the lowering of vapor pressure and it, therefore, falls to the minimum observed in 1.5  $N$  solution. There must be a limit to this action as the proportion of total water present gets less, hence the minimum at 1.5  $N$ .

This diminishing hydration with increasing concentration of the micelle or some other alteration in the formula of the micelle is a necessary assumption on account of the principle of mass action, for otherwise within a very narrow range of concentration the colloidal electrolyte would pass completely into an undissociated form and no longer conduct. (See the discussion of protein in Section XIV below.)

The diminishing hydration is not due to water becoming scarce, for

<sup>1</sup> Ubbelohde und Goldschmidt, "Handbuch der Oele und Fette," Band 3, Leipzig 11 (1910); *Z. Elektrochem.*, 18, 380 (1912); *Kolloid-Z.*, 12, 18 (1913); *Kolloid-Chem. Beihefte*, 5, 427 (1914).

the fact that the vapor pressure of a 1.5 *N* solution is greater than a 1.0 *N* solution, means that the water is more available in the 1.5 *N* solution. The hydration being less in 1.5 *N* when the water is there most active and available can only be explained by alteration in the formula or structure of the micelle such as the increasing proportion of undissociated soap in it.

Another argument for the last assumption is the divergence in behavior between the potassium and sodium soaps. This cannot be so readily explained if the micelle in both is identical— $n(\text{P})^{n(-)}.m\text{H}_2\text{O}$ —Formula 1. But if it is  $(\text{KP})_x.n\text{P}^{n(-)}.m\text{H}_2\text{O}$ —Formula 4, it becomes quite possible that the sodium and potassium soap micelle should distinctly differ, as they do.

Decrease of hydration with rise of temperature explains other conductivity data of the previous papers; it is discussed in a separate experimental communication.

The alternative hypothesis of the last heading that the micelle contains but little of the undissociated soap which can exist independently as a colloid, can also give an account of the chief facts although not so readily.

IX. *Ammonium soaps, as far as studied, agree with the conception here presented.*—The study of ammonium soap prepared from palm kernel oil (which is largely laurate with some higher constituents) by Franz Goldschmidt and L. Weissman in 1913,<sup>1</sup> has given very interesting results. Like the potassium soaps, they exhibit fairly high conductivity which, in this case, cannot possibly be due to products of hydrolysis. The conductivity curve differs greatly from those of the sodium and potassium soaps in that it steadily rises with increasing concentration from 0.2 up to 1.0 *N*, the total increase in conductivity being about 38%. The rise is rapid at first, then more gradual. Dilute solutions were not measured. The rise is accompanied by an increase in viscosity of several hundred fold. All these solutions are appreciably hydrolyzed, as is shown by the increase in conductivity effected by addition of excess of ammonia, which in itself is a poor conductor. These results can be interpreted as showing that the simple fatty ion existing in more dilute solutions is being replaced in stronger solutions by an ionic micelle which is a better conductor. This is quite in accord with the conclusion to which we were driven in Section V above, that the micelle in strong solutions must conduct as well as a good conducting ion such as the potassium ion.

However, measurements of conductivity of a series of solutions containing excess of ammonia would be required for definite deductions to be made. We have measured the dew points of a few ammonium salts of pure fatty acids for comparison, although the conductivity of pure solu-

<sup>1</sup> *Kolloid-Z.* 12, 18 (1913).

tions had not been studied. The results are presented in Table XVI. It was not considered necessary to correct the dew points for the effect of the partial pressure of the ammonia as it was evidently too small.

TABLE XVI.  
TABLE XVI.—DEW-POINT MEASUREMENTS ON AMMONIUM SOAPS.

Soap.	Weight normality.	Temperature. ° C.	Rise in boiling point. ° C.	Concentration of total crystalloid. <i>N</i> .	Van't Hoff's factor. <i>i</i> .
NH <sub>4</sub> Laurate C <sub>12</sub> .....	1.0	25	0.37	1.22	1.22
NH <sub>4</sub> Laurate C <sub>12</sub> .....	0.5	25	0.16	0.53	1.06
NH <sub>4</sub> Laurate C <sub>12</sub> .....	0.25	25	0.09	0.30	1.20
NH <sub>4</sub> Laurate C <sub>12</sub> .....	1.0	45	0.42	1.19	1.19
NH <sub>4</sub> Palmitate C <sub>16</sub> .....	1.0	25	0.08	0.26	0.26
NH <sub>4</sub> Palmitate C <sub>16</sub> .....	1.0	45	0.07	0.20	0.20
NH <sub>4</sub> Palmitate C <sub>16</sub> .....	1.0	90	0.13	0.27	0.27

In warm weather the *N* and 0.5 *N* laurates were quite clear solutions, showing none of the usual appearances of soap solutions except that they gave a very good lather. On cooling under the tap the 0.5 *N* laurate solution deposited feathery crystal-like flakes; the *N* solution would not do this, but in very cold weather is set to a semi-transparent jelly similar to a potassium soap. The 0.2 *N* palmitate was somewhat similar but the *N* solution was practically solid at all temperatures and resembled fine, white, solid foam.

A glance at the results shows that, independent of the temperature, there is a very big difference between the two kinds of soap, very much greater than that observed in the potassium soap solutions. The total crystalloids are about twice as great for the laurates and half as great for the palmitates as compared with the case of the potassium or sodium soaps. An appreciable fraction of the total crystalloid will be undissociated ammonia.

Further investigation would evidently be well repaid, particularly if pure fatty acids be used for making the solutions and hydrolysis be avoided as suggested above. Enough has been presented to show that the relationships here agree with our general conception of colloidal electrolytes.

X. *In mixtures of soaps the tendency is to form more micelle. Additions of electrolytes exert opposing influences, dehydrating and driving back dissociation.*—All commercial soaps are mixtures, hence the importance of the study of mixtures, which must, however, be preceded by a knowledge of pure constituents. Our data for the conductivity of mixtures of sodium soaps are very scanty, but they show that the conductivity differs but slightly from that calculated from the components separately. Thus a 0.1 *N* soap solution which is 0.05 *N* each with regard to palmitate and to myristate or laurate conducts at least 98% as well as the mean of 2

pure 0.1 *N* solutions alone.<sup>1</sup> These concentrations are of course too low for the effect of the micelle to be observed.

The usual tendency is for the conductivity of the mixture to be just slightly higher than expected, as appears from measurements recently published by Kurzmann,<sup>2</sup> working with F. Goldschmidt. In mixtures of 0.6 *N* potassium oleate with 0.2 *N* potassium laurate, he found an increase in conductivity above that of the constituents separately of 5% and 3.6% at 20° and 90°, respectively. Using 0.4 *N* oleate and 0.6 *N* laurate, the effect is an increase of about 4% in the conductivity at 20° but a lowering of about the same amount at 90°.

TABLE XVII.—MISCELLANEOUS DEW-POINT RESULTS.

Substances.	Weight normality.	Temperature. °C.	Rise in boiling point. °C.	Concentration of total crystalloid. <i>N</i> .	van't Hoff's <i>i</i> .
NaCl <sup>a</sup> .....	0.25	90	0.23	0.48	1.92
NaCl <sup>a</sup> .....	0.5	90	0.45	0.93	1.86
NaCl <sup>a</sup> .....	1.0	90	0.85	1.76	1.76
KCl <sup>a</sup> .....	1.0	90	0.86	1.78	1.78
K Caprylate (C <sub>8</sub> ).....	3.0	20	1.01	3.47	1.16
Na Palmitate (C <sub>16</sub> ).....	0.25	90	0.14	0.29	1.16
Na Palmitate (C <sub>16</sub> ).....	1.0	90	0.25	0.52	0.52
Na Palmitate (C <sub>16</sub> ).....	1.0	70	0.23	0.56	0.56
K Laurate (C <sub>12</sub> ).....	0.2	20	0.11	0.38	1.90
K Laurate (C <sub>12</sub> ).....	0.2	90	0.15	0.31	1.55
K Oleate (C <sub>18</sub> -H <sub>2</sub> ).....	0.6	20	0.21	0.72	1.20
K Oleate (C <sub>18</sub> -H <sub>2</sub> ).....	0.	90	0.25	0.52	0.86
{ Na Palmitate (C <sub>16</sub> ).....	{ 0.25	90	0.21	0.43	0.86
{ K Palmitate (C <sub>16</sub> ).....	{ 0.25				
{ Na Palmitate (C <sub>16</sub> ).....	{ 0.25	90	0.34	0.70	1.55
{ NaCl.....	{ 0.20				
{ Na Palmitate (C <sub>16</sub> ).....	{ 1.0	90	0.49	1.01	0.81
{ NaCl.....	{ 0.25				
{ Na Palmitate (C <sub>16</sub> ).....	{ 1.0	90	0.87	1.80	0.93
{ NaOH.....	{ 0.927				
{ K Laurate (C <sub>12</sub> ).....	{ 0.2	20	0.33	1.13	1.51
{ K Oleate (C <sub>18</sub> -H <sub>2</sub> ).....	{ 0.6				
{ K Laurate (C <sub>12</sub> ).....	{ 0.2	90	0.36	0.74	0.93
{ K Oleate (C <sub>18</sub> -H <sub>2</sub> ).....	{ 0.6				

<sup>a</sup> The sodium and potassium chlorides agree within the experimental error with the acetates.

<sup>1</sup> E. C. V. Cornish, 1913, unpublished work.

<sup>2</sup> J. Kurzmann, Dissert. 1914, also *Kolloid Chem. Beihefte*, 5, 427 (1914). He finds the conductivity of 0.6 *N* potassium oleate to be nearly that we have found for potassium palmitate, but judging from the difference between his and our conductivity data the conductivity might possibly be nearer that of potassium myristate (C<sub>14</sub>). Our dew-point lowering is like that of potassium myristate. Thus the effect of the one unsaturated bond is to lower the oleate which corresponds to stearate (C<sub>18</sub>) in the homologous series. This agrees with its other properties.

Table XVII contains a few measurements of the dew-point lowering of mixtures, including the first pair just cited. This mixture exhibits at  $90^{\circ}$  a dew-point lowering of  $0.36^{\circ}$  as compared with  $0.40^{\circ}$ , the sum of the constituents taken separately. At  $20^{\circ}$  this is reversed, for the mixture gives  $0.33^{\circ}$  instead of  $0.3^{\circ}$  calculated.

It is evident that several factors would be involved. First would come the driving back of dissociation owing to the increase in total concentration of the common ion. Second, another influence tending to form micelle is the opportunity for formation of mixed ionic micelle, comprising both constituents. Third comes the dehydrating effect which all crystalloid mixtures must exert (see below); this will be greatest when the soap is most crystalloidal, and will tend to diminish formation of micelle.

The solution in Table XVIII containing  $0.25 N$  sodium palmitate together with  $0.25 N$  potassium palmitate gives a lowering of  $0.21^{\circ}$ , as compared with  $0.20^{\circ}$  and  $0.19^{\circ}$  for  $0.5 N$  solutions of the pure constituents respectively, or with  $0.27^{\circ}$ , which is the sum of the results for  $0.25 N$  solutions taken separately.

The small experimental effect upon conductivity and osmotic activity when soaps are mixed does not preclude fairly extensive alterations in the equilibria involved and to be expected from our explanation. This is illustrated by Kurzmann's<sup>1</sup> observations on the viscosity of the mixture of oleate and laurate we have discussed above. Both at  $20^{\circ}$  and  $90^{\circ}$  the viscosity is intermediate between solutions of the two constituents if taken separately but in the same total concentration. If merely taken separately the viscosity of the mixture at  $90^{\circ}$  is not quite the sum of that of the constituents. At  $20^{\circ}$ , however, the  $0.6 N$  oleate alone has a viscosity equal to 1573, the  $0.2 N$  laurate alone 1.4, the mixture 32.9, which is over 6 times the viscosity of  $0.8 N$  laurate 4.97.

In the case of mixtures with electrolytes, the influences are at least two-fold and in the opposite direction. First comes the dehydrating effect which every lowering of vapor pressure must exert and to which these heavy hydrated micelles must be extraordinarily sensitive. This will tend to diminish their formation and also to make the solution less viscous. Opposed to this is the second effect which tends to drive back dissociation and which ultimately salts out the greater part or all of the soap. In appreciably concentrated solutions, as already fully explained, the observed osmotic results will tend to appear greater than they really are, owing to the hydration.

The first effect discussed is already familiar through the work of F. Goldschmidt and co-workers<sup>1</sup> and also of Farrow<sup>2</sup> on viscosity. This viscosity of  $0.25 N$  sodium palmitate is lowered at  $70^{\circ}$  by about 10%

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Trans. Chem. Soc.*, 101, 347 (1912).

when it contains 0.07 *N* sodium chloride; further addition rapidly increases the viscosity above this minimum to values many times greater than that of the original soap solutions. The explanation given at the time by Farrow recognized this as a general property of colloids (the illustrations cited were really colloidal electrolytes) and likewise attributed it to dehydration, but he discussed it from the now rather discredited standpoint of the emulsion theory of colloids. The second effect is also clear from the ultimate salting out.

Both effects will be most pronounced when there is most micelle and when the micelle is most hydrated. On turning up Kurzmann's data we found as expected, that the dip in viscosity was greater for oleate and less for laurate, that the subsequent large rise in viscosity occurred sooner when adding electrolyte to oleate than to laurate, that both minimum and subsequent rise requires more addition at higher than at lower temperatures where we consider hydration to be greatest. In the case of the ammonium soap from palm kernel oil the second effect appears to over-ride everything else when ammonium chloride is added. In the cases in Table XVII, the dew-point lowering of the mixtures with 0.20 and 0.25 *N* sodium chloride exceeds the sum of the constituents by an amount 0.01°, within the experimental error. On the other hand, with stronger solution, namely 0.1 *N* sodium palmitate and 0.93 sodium hydroxide, the observed lowering of 0.87° exceeds that of the alkali alone by only 0.05° instead of the 0.25° which the palmitate alone would produce. Here it is evident that the palmitate is already largely pushed back into undissociated soap or that the micelle is tending towards Formula 8, that is, undissociated neutral soap as discussed above. Data on this question will be contained in another communication from this laboratory.

XI. *At lower temperatures there is more micelle and it is more hydrated.*—As can be observed even from the data of Table XVII, in every case the apparent osmotic effect is relatively somewhat greater at lower temperatures, but this will be dealt with in a separate experimental communication.

However, it is worth pointing out that the very high temperature coefficient of conductivity which we have established in earlier papers and which has also been formed by F. Goldschmidt and others, is apparently due to hydration increasing as the temperature falls. This is strongly supported by the enormous increase in viscosity with lowering of temperature which has been measured by F. Goldschmidt and his collaborators.

On heating a soap solution to a constant high temperature, the lowering of dew point is at first slightly too great, but it rapidly falls to a constant value. On cooling the opposite is observed. Similarly, in an earlier paper from this laboratory, the conductivity of a sodium soap suddenly raised to a higher temperature is at first slightly too great and *vice versa*.

XII. *Some data for extreme concentration.*—Table XVIII presents the dew-point lowering and the vapor pressures of sodium palmitate solutions measured to quite extreme concentrations. Up to 0.5 *N* solutions the data are found in Table III. There each solution was made up independently, maximum lowering being observed in 1.0 *N* solution, a minimum in 1.5 *N* solution. Owing to the great difficulty in preparing and handling these "solutions," the higher concentrations were attained by pumping out the water vapor through weighed tubes containing calcium chloride. The amount of water remaining in the soap solution, and hence the concentration, was determined sometimes by direct weighing, sometimes by weighing the calcium chloride tubes, sometimes by both methods. The table combines 4 series of measurements. In every case time was allowed for the vapor pressure to become constant (usually one hour was found sufficient for this). Addition of small amounts of water proved that the operation was quite reversible. Using a good water pump and keeping the soap at 90° for many hours, the proportion of water never was reduced below H<sub>2</sub>O:NaP = 1:1. In 2.3 weight-normal solution (24 mols of H<sub>2</sub>O to one of NaP) small star-shaped clusters of crystals appeared on the side of the tube, the bulk of the soap was silky, resembling 0.2 *N* sodium laurate, and would not foam easily. On further evaporation these crystals disappeared, the soap became more liquid and foamed more readily, but ultimately became more solid again. The fourth and fifth columns of Table XVIII have probably no real meaning but assist in appreciating the order of magnitude of the results and in showing that the lowering finally becomes proportional to the weight normality.

TABLE XVIII.

Dew-Point Lowering of Extreme Concentrations of Sodium Palmitate at 90°.

Weight normality.	Mols. H <sub>2</sub> O to 1 NaP.	Lowering. °C.	Concentration of crystalloid.	van't Hoff's <i>i</i> factor.	Actual vapor tension. Mm.
1.5	36.65	0.22	0.455	0.30	521.9
1.62	34.27	0.27	0.56	0.35	520.6
1.74	31.89	0.33	0.68	0.39	519.4
1.9	29.21	0.40	0.83	0.44	518.1
2.0	27.75	0.50	1.04	0.52	516.1
2.41	23.02	0.86	1.78	0.74	509.1
3.0	18.49	1.23	2.55	0.85	501.9
4.22	13.15	1.32	2.73	0.65	500.3
8.12	6.83	2.64	5.48	0.67	475.4
12.56	4.42	4.26	8.82	0.70	446.5
14.29	3.88	4.72	9.77	0.68	438.6

XIII. *The action of typical dyestuffs and indicators such as congo red may be similarly explained.*—As we have for many years insisted, any final theory of soap solutions must be capable of affording a basis for un-

derstanding the properties of dyes, acid and alkali albumens and many other complicated cases.

According to the theory of colloidal electrolytes here presented, in every case we expect to find pronounced electrical conductivity co-existing with deficient osmotic activity.

All recent work on the osmotic activity of dyes has been based upon the use of an osmometer. The results require much interpretation on account of various factors such as Donnan's "membrane equilibrium" which may completely obscure the purely osmotic effect in question. It is a distinctive advantage which our dew-point measurements on soaps possess, that all such complications are excluded. This is the reason why the present data constitute by far the most definite study yet made of the osmotic pressure of colloids.

The work of Donnan and Harris,<sup>1</sup> in agreement with that of Bayliss<sup>2</sup> and Biltz and Vegesack,<sup>3</sup> shows that the osmotic pressure of congo red is considerable, but does not exceed that of a simple non-electrolyte. On the other hand, the conductivity was unexpectedly high, being nearly equal to that of sodium chloride. Donnan's interest was chiefly attracted to the important theory of membrane equilibria, which he thought might be sufficient explanation of the discrepancy, since the sodium ions were not expected to contribute in the ordinary way to the osmotic pressure. He discussed the formation of high complexes such as  $(\text{Na}_2\text{R})_{20} \rightleftharpoons 20\text{Na} + (\text{NaR})_{20}'$ , but added, "it is difficult to reconcile such an assumption with high values obtained for the molar conductivities." The explanation we advance is that described under Section II.

On the other hand Bayliss,<sup>4</sup> whose paper, unfortunately, we have only recently read, writes, after making various alternative suggestions, "The possibility of aggregated simple ions carrying the sum of the charges of their components is suggested in order to explain the experimental results." Further, "These large organic ions may aggregate while retaining the combined charges of their components. This seems to imply, however, so great a density of the charge on the surface of the aggregates as to be improbable. \* \* \* \* \* The difficulty as to the large charge on the aggregated anion remains \* \* \* \* \* It may be tentatively suggested that aggregation of molecules may play some part in the mode of ionization."

Again, the mechanism<sup>5</sup> suggested by one of us removes the theoretical difficulty, and this hypothesis reconciles the osmotic effects, the colloidal effects, and the conductivity data.

<sup>1</sup> *Trans. Chem. Soc.*, **99**, 1554 (1911).

<sup>2</sup> *Proc. Roy. Soc.*, B, **84**, 229 (1911) and earlier papers.

<sup>3</sup> *Z. physik. Chem.*, **73**, 481 (1910); **77**, 91 (1911), etc.

<sup>4</sup> *Loc. cit.*

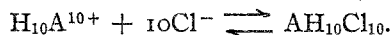
<sup>5</sup> *Loc. cit.* and Section II above.



The existing data for other dyes and for indicators are of a similar nature and may be similarly accounted for. Many of the unexplained reactions of indicators, particularly with reference to the sometimes enormous effect of neutral salts, are now seen to be probably due to disturbance of the equilibria between colloid and crystalloid and hence between the various possible crystalloidal forms of the indicator radical. We have proven that such true equilibria occur, and that every change in the colloid, conditions a corresponding alteration in the position of equilibrium.

XIV. *The explanation here advanced accords with the data for proteins. Very slight alteration in concentration may condition large displacements of the equilibria.*—In 1913, in a general discussion held by the Faraday Society, W. Pauli summarized the data hitherto obtained relating to investigations of the viscosity and electrochemical properties of protein solutions<sup>1</sup> and deduced a heavily hydrated polyvalent ion. McBain pointed out how the outstanding conflicting data were reconciled by the explanation advanced in Section II. Reference must be made to the papers cited for the details of Pauli's masterly summary, to see how far these investigations have already been carried. A point of great interest for the case of soap solutions may, however, be mentioned; that is, the effect of concentration upon equilibria involving micelles. Manabe and Matula, working with Pauli, have re-examined electrometrically the combination of albumen with each ion of hydrochloric acid.<sup>2</sup> The maximum difference between the amounts of hydrogen and chlorine ions taken up by 1% albumen occurs at about 0.02 *N* hydrochloric acid showing maximum formation of ionized salt. This maximum coincides with maximum viscosity and maximum osmotic effect in an osmometer. Further addition of hydrochloric acid drives back the ionization with extreme rapidity.

This very great influence of concentration is only what is to be expected from the principle of mass action. The law of mass action will probably never apply in quantitative form, but it will possess semi-quantitative or at least qualitative value. Thus, in the equilibrium between albumen and its ions where A represents the albumen radical, supposing for example the micelle to be decaivalent and neglecting the hydration,



Here the ionization should depend upon the tenth power of the chlorine ion, so that doubling the concentration of hydrochloric acid may quite well have the very great effect found by Pauli. Were the case of the soap micelle exactly similar, doubling the concentration of say a 0.5 *N* sodium palmitate solution should have an extremely great effect on the dissocia-

<sup>1</sup> *Trans. Faraday Soc.*, **9**, 54 (1913); and *Kolloid-Z.*, **13**, 22 (1913).

<sup>2</sup> *Biochem. Z.*, **52**, 369 (1913).

tion of the electrolytic colloid. This, however, is not observed (see Tables VII, XIV and XV). We must conclude that there is some partly compensating factor, and the obvious suggestion is a difference in amount of hydration of the palmitate micelle as the concentration increases. This had already been deduced in Section V on quite different grounds.

We should like to point out that in the case of most ions and of ionic micelles in general where there may be a series of solvates containing up to many molecules of solvent in one particle, a similar consideration must apply. That is, even the very small relative lowerings of vapor pressure of solvent observed in ordinary solutions must exert a large influence on the composition as well as upon the amounts of each solvate present. For example, if the solvation of lithium ion is, say, 10 molecules of water in 0.1 *N* salt solution, for which the vapor-pressure lowering is about 0.3%, doubling the concentration of the salt nearly doubles the vapor-pressure lowering, making it, say, 0.6%. This altered vapor pressure has to be raised to about the tenth power according to the mass law in order to compute its influence on the solvation of the decahydrate. The tenth power of 99.4% is 94.2%; therefore, the equilibrium will be shifted so that about 6% of the decahydrate disappears owing to this cause. This result is not affected by any other possible co-existing equilibria with, say, nono- or octahydrate, and it is a very large effect. We hope to return at another opportunity to the bearing upon the dissociation theory of this suggestion for a solvate theory.

Pauli, in correspondence with one of us in 1914, expressed his concurrence in the general explanation of colloids which we have described in the present communication. Apparently he has applied it to the case of sols of ferric hydroxide,<sup>1</sup> finding them to consist of a moderately dissociated electrolytic colloid with chlorine ion as anion and an ionic micelle as cation. If our explanation is correct, there will almost certainly be a gradual transition from typical ionic micelles to ordinary ions, on the one hand, and to electrically neutral suspension colloids on the other.

#### Summary.

1. For the first time a comprehensive theory of soap solutions has been set up.
2. This has led to a definition of colloidal electrolytes, a class whose members will probably prove more numerous than acids and bases put together.
3. These colloidal electrolytes are salts in which one of the ions has been replaced by an ionic micelle.
4. It is evident that this is an extension of the dissociation theory, in that there is a gradual transition from ordinary electrolytes (true salts) and complex ions to typical colloidal electrolytes.

<sup>1</sup> *Kolloid-Z.*, 21, 49-63 (1917); through *J. Chem. Soc. Abs.*, 112, II, 563 (1917).

5. This is exemplified by any one of the higher soaps simply on change of concentration. Thus in concentrated solution there is little else present than colloid plus cation, whereas in dilute solution both undissociated and dissociated soap are crystalloids of simple molecular weight.

6. Similarly, there is a continuous transition from typical colloidal electrolytes through slightly charged colloids to typical neutral colloids.

7. For the summary of the chief properties of the soap solutions, reference should be made to the numbered statements used as headings in the present paper. These follow from the mass of dew-point data here presented, by which Krafft's well known but erroneous results for "molecular weights" of soaps are at last superceded.

8. The ionic micelle in the case of soaps exhibits an equivalent conductivity quite equal to that of potassium ion. Its formula may correspond to  $P_n^{n(-)}.mH_2O$  but more probably it is  $(NaP)_x.P_n^{n(-)}.(H_2O)_m$ , where  $P^-$  is the anion of the fatty acid in question.

In conclusion, we desire to express our thanks to the Colston Society of the University of Bristol for substantial grants towards the purchase of materials and apparatus. Finally, our thanks are due to Miss M. E. Laing for her assistance in preparing this paper for publication, without which its appearance would still have been indefinitely delayed.

BRISTOL, ENGLAND.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## THE COAGULATION OF CLAY SUSPENSIONS AND SILICIC ACID.<sup>1</sup>

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An explanation is given in this paper of why many turbid river waters require at certain periods excessive amounts of coagulants for clarification and how purification may be most efficiently accomplished. The action of electrolytes commonly occurring in natural waters upon the stability of colloidal clay suspensions and silicic acid and their effect when alum is used as a coagulant, is discussed. Colloidal clay and silicic acid are more prevalent in the surface waters of the Mississippi valley<sup>2</sup> and the western states, and the need of research in this line has been emphasized in several papers.<sup>3</sup>

The experimental work was carried out along 3 well defined lines, and is discussed in the following order: 1. The removal of silicic acid

<sup>1</sup> Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

<sup>2</sup> *Water Supply Paper* No. 236.

<sup>3</sup> Fuller, "Water Purification at Louisville, Ky.," *Elms, Eng. Record*, 51, 552; Black and Veach, *ibid.*, 72, 292; and Catlett, *ibid.*, 73, 741.