

CCXV.—*Studies of the Constitution of Soap in Solution: Sodium Myristate and Sodium Laurate.**

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ONE of the most interesting classes of substances the constitution and physical properties of which require elucidation is that of electrolytic colloids. This class includes many well-known substances, such as soaps, dyes, indicators, tannin (which is a weak acid coming between carbonic and acetic acids), protein salts, many hydrolysed salts, for example, chromic and ferric derivatives, silicates, etc. The recognition of these substances as constituting a class by themselves is of recent origin, having arisen essentially out of the physico-chemical study of such materials as casein, soap, and Congo-red. Their particular interest lies in the fact that they exhibit electrolytic and colloidal properties to an equal extent, since they contain both electrolytic and colloidal constituents.†

Presumably, in each of these cases we are dealing with simultaneous electrolytic, colloidal, and hydrolytic equilibria. In no case

* Previous papers : J. W. McBain and M. Taylor, *Ber.*, 1910, **43**, 321 ; *Zeitsch. physikal. Chem.*, 1911, **76**, 1 ; R. O. Bowden, *Trans.*, 1911, **99**, 191.

† The idea has been more or less current for a decade ; the term itself is due to W. B. Hardy (*Gedenkboek van Bemmelen*, 1910, 180), who, however, employed it to express the definite assumption that the anion in soap solutions is colloidal. Here the term is used in a broader sense without prejudging the question as to the exact nature of each constituent present.

have the physico-chemical relationships been sufficiently investigated.

The soaps were selected for systematic study because of the apparent simplicity of their chemical nature and their accessibility to study from various points of view.

The study of these relationships is of the first importance in view of the question of the experimental transition of a colloid into a crystalloid, and the conditions under which this takes place. Many of the most eminent authorities deny its possibility, and the work hitherto carried out, for example, that in this laboratory on soap solutions, is capable of interpretation either from the point of view that gradual transition does take place* or (present working hypothesis) that strictly colloidal and strictly electrolytic constituents co-exist and merely vary in relative amount. A decision between these two opposite opinions would seem to be of fundamental importance for the interpretation of colloidal phenomena in general.

In the case of soaps one of the most striking results already obtained was the anomalous conductivity-curve with the dilution, which possessed both a maximum and minimum; in the case of sodium palmitate the maximum was in $N/2$ -solution, the minimum between $N/5$ and $N/10$. In the case of sodium stearate the maximum was in N -solution, the minimum between $N/2$ and $N/10$. The peculiar shape of the conductivity-curve was tentatively accounted for as being due to the changes in the degree of dispersion of the colloid and in its amount, the assumption being made that the only colloids present were acid sodium salts. Hydrolysis predominates in very dilute solutions, and in highly concentrated solutions there is presumably a great deal of normal salt formed, but its dissociation and conductivity would be relatively low, and it may even be colloidal and hence non-conducting. In intermediate solutions, the colloidal acid salt assumes so high a degree of dispersion (as is evident from the appearance of the solutions) that its sorptive powers are probably diminished, which would set free sodium hydroxide and account for the maximum in conductivity.

The effect of varying the amount of sodium hydroxide is in accordance with the hypothesis just outlined. The next step is obviously to vary the nature of the soap still further by taking the next lower homologues and observing how the shape of the conductivity-curves and the position of maxima and minima alters with diminishing molecular weight of the acid radicle.

This possesses a further source of interest in that the lowest members of this homologous series do not give rise to colloids at

* Compare the frequently met with hypothesis that ions may be colloidal.

all. An essential part of all these conductivity determinations remains that, contrary to previously accepted doctrine, the conductivities are high throughout.

EXPERIMENTAL.

The experimental method is that described by McBain and Taylor (*loc. cit.*) for solutions of sodium palmitate. They found that the conductivity of each concentration, was perfectly definite, no matter how the solutions were made up; hence it was safe to make the same assumption in the case of this lower homologue.

Solutions were made from sodium hydroxide free from carbon dioxide, the correct amount of myristic or lauric acid being weighed into the silver tubes used for the experiments. These were sealed with cap and ring of pure silver by means of heavy clamps, and the solutions shaken at 90° until they became homogeneous. This does not take long, as they differ entirely from the highly viscous sodium palmitate solutions. The conductivity was determined by inserting dipping electrodes of Jena-glass according to the Kohlrausch method. The constant of the cell, owing to the silver tubes used, varied with the resistance of the solutions measured. They were determined by plotting the results obtained from N -, $N/10$ - and $N/100$ -potassium chloride solutions. The myristic and lauric acids (Kahlbaum) melted, not sharply, at 53·4° and 42·9° respectively. The lauric acid was recrystallised until it melted at 43·05°. All vessels and instruments were carefully calibrated and standardised.

Densities.

Densities were determined in pyknometers of about 5 c.c. capacity, so mounted that they were entirely immersed in the thermostat until the final adjustment was complete. Each result is the means of several determinations differing by a few units in the fourth decimal place. In the case of the myristate the density was found to be $D_4^{20} 0.9678$. This differs by only 0.25 per cent. from that of water (0.9653) at the same temperature, and hence the values for the other concentrations could be estimated with sufficient exactness by linear interpolation.*

The solutions of sodium laurate contained about 3.5 per cent. less sodium than was intended (see below); as the concentrations refer to the weight-normality of the laurate radicle, the density of the N -solution should be roughly 0.0020 higher. The series, however, is comparable within itself.

* Densities and older series of conductivity values of sodium laurate by R. C. Bowden, all other measurements in this communication by J. W. McBain and E. C. V. Cornish.

TABLE I.
Density of Sodium Laurate.

Concentration..	1.0	0.5	0.2	0.1	0.05	0.01
D ₄ ⁹⁰	0.9711	0.9693	0.9678	0.9669	0.9668	0.9660
D ₉₀ ⁹⁰	1.0060	1.0042	1.0026	1.0017	1.0015	1.0008
D ₄ ²⁵	—	—	—	—	0.9924	0.9973
D ₂₅ ²⁵	—	—	—	—	1.0014	1.0003

The results at 90° make a smooth curve, the difference between the observed density and that of water not increasing as fast as the concentration. F. Goldschmidt (*Zeitsch. Elektrochem.*, 1912, **18**, 386), using the potassium salt of the acids from palm kernel oil (said to be essentially potassium laurate), obtained values more nearly proportional to the concentration and distinctly larger than ours for the higher concentrations; thus, 1.001 for $N/20$, 1.004 for $N/5$, and 1.015 for N . He also obtained a distinct increase in density as referred to water of equal temperature when the measurements were carried out at 20°, although this relative increase did not exceed 0.5 per cent. The present results for the pure sodium salt, however, appear to indicate that the coefficient of expansion at least in the dilute solutions is the same as that of water (within 0.05 per cent.); thus it is possible without appreciable error to obtain the values for intermediate temperatures by using the coefficient for water; this we have done in the case of sodium myristate in calculating the conductivity. It may be noted that solutions of sodium stearate, C₁₈, and palmitate, C₁₆, are lighter than water, whilst the myristate, C₁₄, laurate, C₁₂, and acetate, C₂, are heavier, the differences being roughly in proportion to the position in the homologous series.

Conductivity.

The following table gives the experimental results for sodium myristate solutions at 90°. The first column gives the weight-normality; the second, the number of grams of sodium myristate to 100 grams of water; the third the number of the electrode; the fourth the cell constant; the fifth the specific conductivity; the sixth the average specific conductivity; the seventh the densities (obtained by interpolation, see under), and the last column the molar conductivity at 90°. The molar conductivity is derived by multiplying the weight of solution containing 1000 grams of water by the specific conductivity, and dividing by the weight-normality and the density. In each case all the corrections enumerated by McBain and Taylor were applied. The absolute values of the

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conductivities, except in the cases specified, we may regard as accurate to about 2 per cent., the relative values to about 1 per cent.*; thus the present results do not pretend to the painstaking accuracy of the sodium palmitate measurements, where equilibrium was approached from both sides, and where, further, each result was checked by many independent measurements.

TABLE II.

Conductivity of Sodium Myristate at 90.00°.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1.500 <i>N</i>	37.5	XIII	3.011	0.0899	0.0896	(0.9690)	84.76
		XII	5.094	0.0893			
1.000 <i>N</i>	25.0	XIII	3.010	0.0735			
		XII	3.096	0.0737	0.0735	0.9678	94.93
0.750 <i>N</i>	18.75	XII	3.097	0.0594			
		XIII	3.008	0.0598	0.0596	(0.9671)	97.57
0.500 <i>N</i>	12.5	XIII	3.008	0.0422			
		XIII	3.008	0.0429	0.0426	(0.9665)	99.15
0.2000 <i>N</i>	5.00	XIII	2.992	0.01744			
		XII	3.113	0.01761	0.01752	(0.9658)	95.23
0.1000 <i>N</i>	2.50	XIII	2.985	0.00914			
		XII	3.404	0.00904	0.00909	(0.9655)	96.51
0.0500 <i>N</i>	1.25	XIII	2.978	0.00522			
		XIII	2.978	0.00534	0.00526	(0.9654)	110.4
		XII	2.978	0.00522			
0.01000 <i>N</i>	0.250	XIII	3.033	0.001829			
		XII	3.034	0.001863	0.001846	(0.9653)	191.7

Table III gives the corresponding data for sodium laurate at 90°. The data for 0.1, 0.5, and 1.0*N* are obtained from a previous complete series for the solutions the densities of which were recorded above. From the new determinations for the 0.01, 0.05, 0.2, and 1.5*N*-solutions it was apparent that the values for the previous solutions which had been made up by mistake to a wrong standard had to have their specific conductivity increased by 9.0 per cent. This has been done in the table. This decrease in conductivity, due to a lack of more than 3 per cent. of sodium, is in accordance with the effects obtained in the numerous measurements made with sodium palmitate with excess and deficiency of alkali (J. W. McBain and M. Taylor, *loc. cit.*).

* It has already been pointed out (J. W. McBain and M. Taylor, *loc. cit.*, p. 196) that quite careful measurements of ordinary salt solutions at this temperature are not generally more accurate than this, and at room temperature, even Kohlrausch's measurements for acids and bases are incorrect by several units per cent.

TABLE III.
Conductivity of Sodium Laurate at 90.00°.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1.500 <i>N</i>	33.3	XII	3.042	0.1057			
		XIII	3.012	0.1051	0.1054	(0.9740)	96.2
0.982 <i>N</i>	21.83	XIII	3.006	0.0820			
		XIII	3.006	0.0812	0.0816	0.9711	104.2
0.496 <i>N</i>	11.01	XIII	3.005	0.04741			
		XIII	3.005	0.04743	0.04742	0.9693	109.5
0.2000 <i>N</i>	4.44	XIII	3.002	0.02101			
		XII	3.058	0.02107	0.02104	0.9678	113.4
0.0998 <i>N</i>	2.218	XIII	2.998	0.01187			
		XIII	2.998	0.01183	0.01185	0.9669	125.5
0.0500 <i>N</i>	1.111	XIII	2.982	0.00750			
		XIII	2.982	0.00751	0.00751	0.9668	157.0
0.01000 <i>N</i>	0.2222	XIII	2.956	0.001893			
		XII	3.033	0.001846	0.001870	0.9660	193.9

On comparing these values for sodium laurate with those of Goldschmidt (*loc. cit.*) for impure potassium laurate (173.5 for 0.05*N*, 135 for 0.191*N*, 141 for 0.5*N*, 137.2 for 1.02*N*, and 116.2 for 1.4*N*), his values are seen to be uniformly higher. Further, his values go through a maximum and a minimum, whilst the sodium salt exhibits merely a "step out." This is surprising, since potassium soaps on account of their greater solubility and insensibility to the precipitating action of electrolytes are expected to behave more like normal electrolytes.

The results in the tables above are compared with corresponding results obtained in this laboratory for sodium palmitate, sodium stearate, and sodium acetate in the following table.

TABLE IV.
Molar Conductivities of Sodium Salts at 90.00°.

Concentration.	1.5	1.0	0.75	0.50	0.35	0.20	0.10	0.05	0.01
NaStr C ₁₈	81.5*	88.3	—	76.1	—	77.4	76.0	78.0	125.9
NaP C ₁₆	84.5	84.66	87.48	89.48	87.04	82.38	82.51	88.61	137.7
NaM C ₁₄	84.8	94.9	97.6	99.2	—	95.2	96.5	110.4	191.7
NaL C ₁₂	96.2	104.2	—	109.5	—	113.4	125.5	152.0	193.9
NaAc C ₂	—	129.7	—	—	—	178.9	195.0	—	228.2

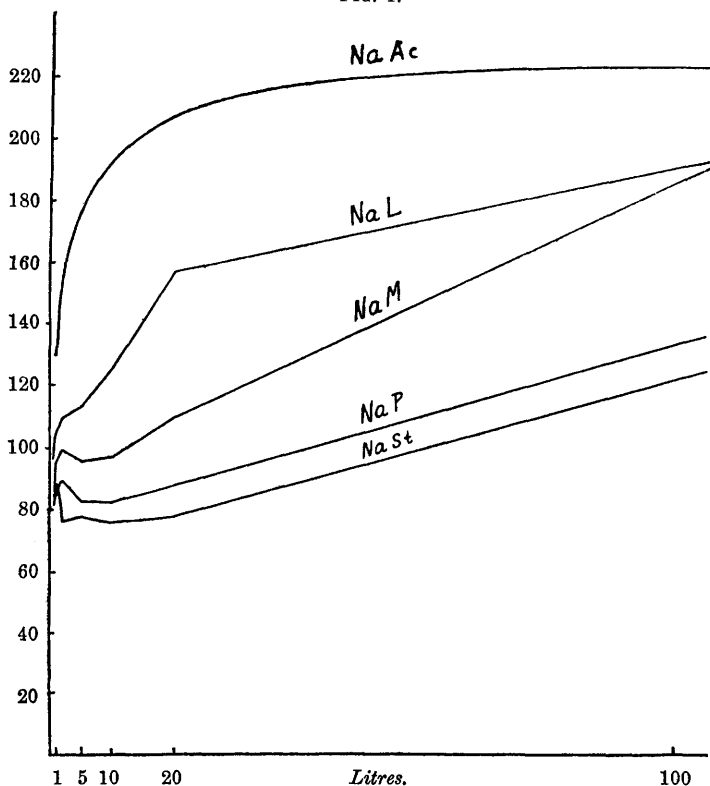
* Two independent measurements by Miss Taylor; the actual data were: weight-normality, 1.451*N*; grams per 100 grams of water, 44.44; electrode No. IX; cell constant, 3.44 and 3.2; specific conductivity, 0.0781 and 0.078; estimated density, 0.950; molar conductivity, 81.5. The solution is a viscid gum; an accurate measurement would require special study. This suffices to show that the maximum lies near 1.0*N*.

From this table and the accompanying graphs, it will be seen how very similar, both in magnitude and behaviour, are the results

obtained with sodium myristate and sodium palmitate in all but the 0.01*N*-solution.

This is unexpected and somewhat remarkable, since the solutions themselves are quite dissimilar in consistency, and even in appearance, the palmitates being viscid, gummy solutions, whilst all the myristates, even the *N*-solution, are quite mobile at 90°. Also the fact that the conductivity diminishes regularly as one ascends the

FIG. 1.



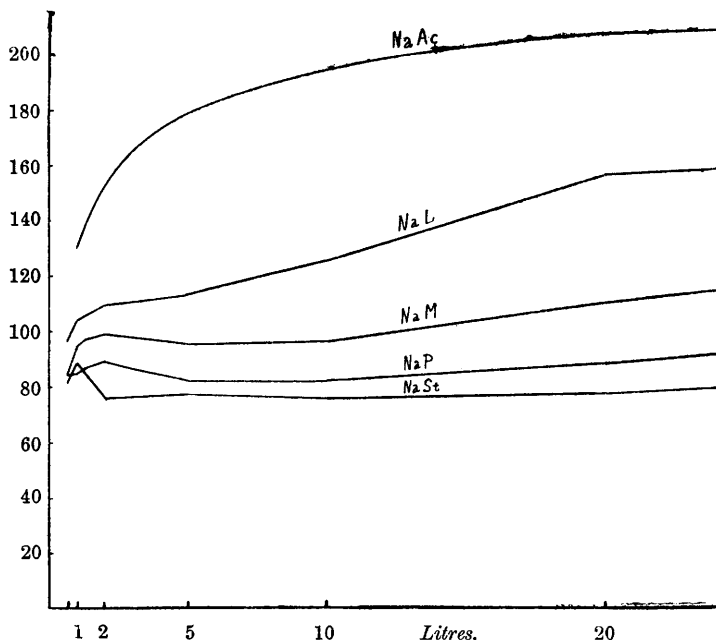
Molar conductivities of sodium salts of fatty acids at 90°.

homologous series, is not what would have been expected, since the conductivity is probably largely due to free sodium hydroxide, and the stearates are always assumed to be most hydrolysed. Consequently the stearates should give a higher conductivity than the palmitates, etc., particularly in dilute solution, whilst the contrary is the case. According to this view it is evidently necessary to assume that sorption operates in the opposite direction, being

greatest for the stearate. It is not certain that stearic acid is appreciably weaker than, say, lauric acid; increased hydrolysis would, therefore, have to be ascribed to the increasing insolubility of the products of hydrolysis (not the acids themselves).

On comparing the positions of the maxima and minima in the molar conductivities of the homologues (see graphs), it is evident that the chief feature is the development in the extent and importance of the depression imposed on the curve at $N/5$ ($N/2$ to $N/10$) as we pass down the homologous series from the stearate.

FIG. 2.



Molar conductivities of sodium salts of fatty acids at 90°.

The depression in the curve for the stearate extends from $N/2$ to $N/20$, whilst in the lower members of the series the maximum is attained in $N/2$ -solution, although in the case of the laurate the depression is not great enough to produce a maximum.

Equally significant is the fact that this depression seems to be imposed on each curve at about the same region of concentration. This is very surprising, since one would have expected a pronounced displacement as the number of carbon atoms in the acid decreased, a change in concentration making up for a falling off in colloidal

properties. We expect to extend these measurements to the other homologues and to the potassium salts.

Effect of Temperature on the Conductivity-curve.

It seemed desirable to estimate the effect of temperature on the shape and position of the curve for, say, sodium myristate, as all the results hitherto have been determined at 90.0° . One might quite well expect to find that the temperature-coefficients would also exhibit anomalous changes with the concentration, and thus the conductivity-curve and the equilibria underlying it would depend very much on the temperature.

The following are the experimental results for the temperature-coefficients. They were obtained by taking solutions of each concentration, measuring them at 90.0° ; then, without removing the electrode, measuring them at successive temperatures. The results italicised were obtained from duplicate solutions measured successively at 90.0° , 80.0° , 90.0° , 80.0° , 90.0° , 70.0° , 90.0° , 70.0° , 90.0° , 60.0° , 90.0° , 60.0° , 90.0° , 50.0° , 90.0° , 50.0° , 90.0° , etc. In accordance with the results of a preliminary study, periods ranging from six hours at 40° to three-quarters of an hour at 80° were allowed for the conductivity to adjust itself to its final value, although even at 40° the results would have been correct to within 1 or 2 per cent. within one hour. McBain and Taylor, who worked only at 90.0° , found the conductivity to be independent of the time. In the light of these new results, this is evidently due to their having worked at the highest temperature. The significance of their discovery, that the conductivity assumes a true reversible equilibrium value, is not impaired, but rather augmented, by the fact that the equilibrium conductivity at lower temperatures is attained only after the lapse of a measurable period.

For some reason, the conductivity requires more and more careful measurement in order to obtain trustworthy results as the temperature is lowered; thus the temperature-coefficients at 50.0° are uncertain to the extent of several units per cent. It was noticed that the conductivities at 90.0° did not change very much, except in the case of more dilute solutions, in spite of the prolonged exposure to the Jena-glass of the dipping electrodes during the treatment outlined above. In table V the results are expressed in terms relative to the specific conductivity at 90.0° , which is taken as unity for each concentration.

TABLE V.

Weight-normality.	90°.	80°.	70°.	60°.	50°.	40°.
1.5	1.000	1.121	1.279	1.505	—	—
1.0	1.000	1.118	1.273	1.498	1.800	—
0.5	1.000	1.126	1.308	1.560	1.872	—
0.2	1.000	1.118	1.311	1.545	1.861	2.40
0.1	1.000	1.132	1.311	1.559	—	—
0.05	1.000	1.126	1.312	1.599	1.863	2.22
0.01	1.000	1.126	1.316	1.547	1.853	less than 2.35

These results have been smoothed out as shown in table VI:

TABLE VI.

Weight-normality.	90°.	80°.	70°.	60°.	50°.	40°.
1.5	1.00	1.121	1.279	1.505	—	—
1.0	1.00	1.118	1.272	1.498	1.800	—
0.5—0.01	1.00	1.126	1.311	1.561	1.862	2.32

Using table VI, the molar conductivities of sodium myristate for varying temperatures become the following, as shown in table VII, where the coefficient of expansion with the temperature has been taken into account, taking it equal to that of water.

TABLE VII.

Molar Conductivities of Sodium Laurate Solutions at Various Temperatures.

Weight-normality.	90°.	80°.	70°.	60°.	50°.	40°.	25°.
1.5	84.8	75.1	65.4	55.2	44.8	—	—
1.0	94.9	84.3	73.6	62.2	51.5	—	—
0.5	99.2	87.5	74.6	62.3	52.1	—	—
0.2	95.2	84.0	71.5	59.8	50.0	40.0	—
0.1	96.5	85.1	72.6	60.6	50.7	40.5	—
0.05	110.4	97.3	83.1	69.4	58.0	46.4	(34.6)
							(see under)
0.01	191.7	169.0	144.3	120.5	100.6	80.3	—

The results in tables VI and VII show that the effect of temperature on the anomalous shape of the conductivity-curve is quite unimportant, although there is a very slight tendency for the maximum to move towards a higher concentration at lower temperatures. The latter result is in accordance with the single series of measurements of F. Goldschmidt (*loc. cit.*) for the potassium salt of the fatty acids of palm kernel oil at 90° and 20°.

It is interesting to note that Goldschmidt observed a time lag of several units per cent. in the adjustment of the viscosity of his solutions when suddenly cooled from 90° to 20°, although no mention is made of a similar result having been looked for in his conductivity measurements at 20°. The initial viscosity observed when his solutions were cooled from 90° to 20° was greater than that attained on further keeping at 20°; in other words, starting

from 90° the viscosity of his solutions must have risen enormously and then have diminished slightly. This is exactly analogous to our own observations in the case of conductivity, where the after-effect is of the order of magnitude of 1 per cent., although often it is not observed at all. If the conductivity has been decreased by changing, say, from 90° to 50° , the conductivity after the first hour is rising slightly; similarly, the conductivity falls slightly after a solution has been at 50° for some time after bringing it from room temperature (liquid or solid).

The exact significance of these residual phenomena is not clear, although evidently one of the minor subsidiary equilibria is displaced towards low conductivity and high viscosity at higher temperatures. Possibly it may be found to be an absorption property of the colloids present (as distinguished from adsorption). Goldschmidt's qualitative observations would make it appear a supersaturation in the state of coagulation or dispersion of the colloids present. Against this may be urged that in the case of conductivity it occurs both with rising and falling temperatures, and, further, data below show that coagulation acts in the opposite direction, since it is induced by falling temperature whilst it raises the viscosity and lowers the conductivity.

Since the last communication from this laboratory, measurements of the conductivity of sodium and potassium oleates by Dennhardt (*Diss.*, Erlangen, through Ubbelohde and Goldschmidt, "Handbuch der Chemie und Technologie der Oele und Fette," Vol. III) have come to our notice. Dennhardt also observed a slight displacement of the minimum in the sodium oleate curves toward more concentrated solution with falling temperature. On the other hand, his temperature-coefficient varied by 40 per cent., being at a minimum in $N/10$ -solution. His results may, however, be placed out of court, since his conductivity results are only half as great as those of Kahlenberg and Schreiner (*Zeitsch. physikal. Chem.*, 1898, **27**, 552). Equally untenable is his hypothesis of the existence of an emulsion of free oleic acid in alkaline solution and his assumption that the replacement of a salt by sodium hydroxide would cause a falling off in conductivity and explain the observed minima.

The most important feature of the present temperature-coefficients is their high value. This is brought out when we compare the ratios of the specific conductivities at 90° and 50° for typical classes of electrolytes. The value for nitric acid is interpolated from data in the literature, the other three values were directly determined for this purpose; the coefficients refer to $N/20$ -solutions. The value for nitric acid is 1.36, that for sodium hydroxide 1.473,

that for sodium acetate 1.656, whilst that for sodium myristate is no less than 1.862. The abnormally high value for soap would appear to be due to probable increase of hydrolysis on heating, accompanied by diminished adsorption of alkali by the colloidal matter.

The essential uniformity of the effect of temperature on the conductivity over so very large a range of concentrations would tempt one to the conclusion that, therefore, the degree of dissociation was independent of the temperature. This may indeed be the case, even although, of course, the temperature-coefficient of μ_{∞} , the conductivity at infinite dilution, must possess a normal value. The conclusion which may be drawn is that temperature affects the hydrolytic equilibria of all concentrations much in the same way, and not, as one might have expected, in relation to the absolute concentration of the alkali formed.

*Conductivity at Room Temperature.**

N/20-Sodium myristate can be kept for about half an hour at 25.0° before it solidifies. Solidification takes place from numerous points throughout the liquid; it occurs very rapidly when it once sets in, the change taking only two or three minutes. The molar conductivity of *N*/20-solution at 25.0° (after it has been at 25.0° for about twenty minutes brought from 90.0° in a silver tube) varies from 34.2 to 35.1 mhos. On solidification the conductivity is halved, being about 16 to 17 mhos; this value further diminishes during the course of the next two hours by a fraction of 1 mho.

In the case of *N*/5-solution, which alters only slowly after the second minute, the conductivity becomes appreciably constant between the fourth and sixth minute, but between the seventh and tenth minute it increases about five-fold, solidification, of course, taking place. The conductivity at the end of an hour has become constant, as it only decreases 1 or 2 per cent. in the course of a further sixteen hours. The values for the molar conductivity are 34 mhos at five minutes while liquid; 6.3 mhos at one hour; 6.1 mhos at seventeen hours. Presumably the much greater effect of solidification in this concentration as compared with *N*/20-solution is due to the much greater mechanical resistance resulting from solidification. Kahlenberg and Schreiner (*loc. cit.*) found at 25° an increase of ten-fold in the resistance of a *N*/8-potassium stearate solution on solidification.

* Allowing the myristate solutions, or, at least, the more dilute ones, to solidify without removing the electrode, does not break the glass, as happens with the palmitate.

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A $N/2$ -solution of sodium myristate was measured in the solid state; at the end of half an hour at 25° it had a value of about 8 mhos.

*Appearance and Behaviour of Sodium Myristate and Laurate Solutions.**

Sodium Myristate.

	1.5 <i>N</i>	1.0 <i>N</i>	0.8 <i>N</i>	0.5 <i>N</i>	0.2 <i>N</i>	0.1 <i>N</i>	0.05 <i>N</i>	0.01 <i>N</i>
90°...	vis.; not op.	f. fl.; not op.	fl.; not op.	fl.; not op.	v. fl.; not op.	v. fl.; not op.	v. fl.; sl. op.	v. fl.; sl. op.
60°...	vis.; not op.	tr.; gr. susp.	f. fl.; tr.; gr. susp.	—	fl.; op.	—	—	—
50°...	white solid	v. vis.; gr. susp.	tr.; sl. vis.; tr.; cell. - susp.	fl.; gr.	—	—	—	—

v.=viscous; sl.=slightly; v.=very; f.=fairly; fl.=fluid; op.=opalescent; not op.=absolutely clear and transparent; tr.=transparent, that is, not milky; gr. susp.=granular suspension; cell.=suspension of obvious cellular structure.

The appearance at 40° or 50° depends on whether the solution has previously been at a higher or lower temperature; thus a 0.5*N*-solution at 50° cooled from 90° is as shown in the table, but if it has been raised from room temperature it contains remains of a cellular structure, the translucent network floating near the bottom of the solution and being so soft that bubbles readily rise through it. At room temperature 0.01*N*- and ("undercooled") 0.05*N*-solutions of myristate are partly coagulated; white, jelly-like masses separate out and leave a clear liquid.

It is an important fact that "supersaturation" or "undercooling" of the gelatinisation may readily occur; thus a 0.2*N*-sodium laurate solution which has been liquid for days at room temperature at once turns solid on jarring, or scratching the side of the bottle. A 0.1*N*-sodium laurate solution which has been mostly liquid for months "sets" in a few hours after being jarred and shaken. It will be noticed that these periods are much longer than those discussed in connexion with the conductivity measurements at 40° and 50° . There is no room left for doubt that gelatinisation is not identical in kind with the process of attainment of equilibrium within the liquid sol. The latter may have ceased to alter in conductivity, and McBain and Taylor (*loc. cit.*) have shown that a true reversible equilibrium is attained from both sides at least at higher temperatures, whilst the sol is "supersaturated" with respect to gelatinisation. This would appear to show that the gelatinisation

* Compare McBain and Taylor (*loc. cit.*) for palmitates.

is not a process continuous with the adjustment of the degree of dispersion of a colloid. S. Odén (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 100) found that coagulation and "redissolving" colloidal sulphur in dilute sols did not affect the diameter of the sulphur particles, thus showing the analogous behaviour of suspensoid colloids.

The distinctive appearance of 0.5*N*-sodium laurate at room temperature is worthy of mention. This solution (solid) after a day at room temperature (in a Jena-glass bottle with glass stopper heavily smeared with vaselin, as usual) develops a striking and beautiful lustrous surface against the glass, like white satin or even like a polished piece of white metal. 0.2*N*-Sodium laurate is the only other soap that we have observed to possess this property at all.

The "melting" points of the sodium myristate solutions when the temperature is raised about 1° in ten minutes are as follows, if we take as "melting point" the temperature at which the solid loses its hold of the inner surface of a Jena-glass bottle. Even the 0.05, 0.1, and 0.2*N*-jellies show no tendency to form a level surface when tilted, until a temperature 1.5° higher has been attained. Soon after, say, at 2° above the temperature tabulated, much liquid is formed, but at this rate of heating the solid white jelly does not wholly disappear until 4.0° above the temperatures given in each case.

1.0 <i>N</i>	0.5 <i>N</i>	0.2 <i>N</i>	0.1 <i>N</i>	0.05 <i>N</i>	0.01 <i>N</i>
51.7°	50.2°	45.4°	41.5°	41.0°	(compare p. 2054)

These "melting points" are, of course, very ill-defined* and they bear but little relationship to Krafft's so-called "temperature of crystallisation" (*Ber.*, 1895, **28**, 2566; 1899, **32**, 1596) in the dilute solutions. In the more concentrated solutions, however, they must, apart from undercooling effects, be nearly identical with these. Krafft obtained for 0.8*N*-sodium myristate 52° to 53°, but for 0.04*N* 31.5°; the latter solution must have been quite appreciably undercooled. Our results show a marked similarity of melting temperature over a fairly wide range. There seems to be no explanation as yet for the fact that the melting points of all pure solutions of sodium soaps melt a little below the melting point of the corresponding acid (1.5*N*-sodium laurate melts at 42°, lauric acid at 42.9°). Goldschmidt (Ubbelohde and Goldschmidt, "Hand-

* Thus, a 0.5*N*-solution kept for many hours at 40° (from room temperature) consists of white flocks, touching, and forming, say, 9/10ths of the solution, suspended in a colourless coagulum. Sometimes this solution would flow (0.5 cm. per minute under 15 cm. head through a hole 3 mm. in diameter).

buch der Chemie und Technologie der Oele und Fette," p. 412—414) attempts to explain Krafft's results by assuming that the solid "crystallising" out is a solid solution of neutral soap in fatty acid. A glance at the quantitative data of Donnan and White (Trans., 1911, 99, 1675) serves to exhibit the inadequacy of this explanation.

Summary of Results.

The anomalous conductivity-curve for sodium palmitate at 90° is closely paralleled by that of the very much more mobile myristate solutions. The laurate curve is much less anomalous in that the maximum and minimum are obliterated. Only the degree, and not the position, of the abnormality in the curves is altered in passing down the homologous series from stearate to laurate. The conductivity curves of sodium myristate at a number of temperatures between 90° and 40° reveal a very high temperature-coefficient which, however, is nearly uniform for all concentrations, so that the position and degree of development of maximum and minimum is largely unaffected. Finally, a number of qualitative observations closely bearing on the colloid theory of soap solutions and "supersaturation" of gelatinisation have been discussed. The coagulation of a suspensoid or gelatinisation of an emulsoid does not appear to be connected with change in the degree of dispersion of the colloid in certain cases.

In conclusion, we desire to take this opportunity of expressing our thanks to the Research Fund Committee of the Chemical Society, and to the Colston Society of the University of Bristol, for grants towards the purchase of materials and apparatus.

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