The Electrical Conductivities of Aqueous Solutions of Sodium Dodecyl Sulphate and Sodium Hexadecyl Sulphate at Different Temperatures

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The classical work of McBain on the electrical conductivity and other properties of aqueous solutions of the soaps led him to postulate the formation of the ionic micelle.* This aggregate of ions has a greater mobility than that of the ions composing it, and its formation accounts for the characteristic increase in conductivity exhibited by colloidal electrolytes.

The conception has resulted in great advances in the study of all classes of colloidal electrolytes, e.g., protein and gelatine salts, dyes, and other substances of high molecular weight.†

The study of aqueous soap solutions is greatly restricted and complicated by the fact that soaps are hydrolysed in solution. The degree of hydrolysis, as determined from e.m.f. measurements‡ and from rates of catalysis.§ is too great in very dilute solution to enable measurements of the conductivity to be made with accuracy. Moreover, hydrolysis results in the formation of acid soaps|| which may be adsorbed on the micelle and which therefore make interpretation of the conductivity curves more difficult.

The metallic salts of the long chain alkyl sulphates are free from hydrolysis so that their conductivities may safely be measured down to infinite dilution and the curves explained in terms only of ions and the micelles formed from them.

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* McBain, 'Trans. Faraday Soc.,' vol. 9, p. 99 (1913); 'Kolloidzschr.,' vol. 12, p. 256 (1913); many subsequent papers with numerous collaborators.
When this investigation was in progress a paper appeared\(^*\) on the electrical conductivities of several metallic salts of four long chain alkyl sulphates. The results of the two investigations are in general agreement but the interpretation of the form of the conductivity curves now advanced is new.

**EXPERIMENTAL**

*The Electrical Assembly*—The electrical circuit was exactly similar to that used in previous investigations.\(^\dagger\) The source of alternating current was a valve oscillator, and the null-point was detected by means of a valve amplifier and loud-speaker. The bridge consisted of a new Tinsley non-inductive resistance box with six decade dials in conjunction with a pair of Tinsley ratio arms. A separate pair of exactly similar ratio arms was used for the Wagner earth. The resistance box was shunted with a bank of variable condensers to balance the capacity of the cell.

*Cells*—The large quartz cell with large platinum electrodes (4 cm × 3 cm; 2 mm apart) coated with grey platinum used in the previous investigations was employed for the more dilute solutions. In order to conserve material a similar but much smaller cell with electrodes 0·5 cm × 0·5 cm and 1 cm apart was used for the concentrated solutions. The cell constants were determined against N/50 pure potassium chloride solution.

*Thermostats*—Seven thermostats, one for each working temperature, were used. They were filled with water covered with a layer of oil (except that for 100° which was filled with oil) and fitted with efficient stirrers. They were heated by gas from a governed supply and maintained within ± 0·01° of the desired temperature.

*Materials*—The sodium dodecyl sulphate and sodium hexadecyl sulphate were specially made and given by Messrs. Imperial Chemical Industries (Dyestuffs Group). In both instances the alcohol was repeatedly fractionated; the purified alcohol was treated with chlorosulphonic acid and the acid ester was neutralized with sodium hydroxide. The sodium salt was crystallized and repeatedly recrystallized from methyl alcohol and from water. It was dried over phosphoric oxide in a desiccator. Analysis of the dried materials showed the salts to be of great purity (Table I).

The salts may perhaps contain homologues, but these must be present

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in small amount and, as the analysis shows, distributed evenly on either side.

Conductivity water of great purity was made by the method of fractional condensation. The block tin still used for previous investigations developed leaks due apparently to the growth of crystals followed by fracture at the interfaces. It was replaced by a still of pure silver and the block tin spray trap was also replaced by one of monel metal. The arrangement gave a steady supply of water of conductivity $0.4 \times 10^{-6}$ mhos which was used throughout the investigation.

### Table I

<table>
<thead>
<tr>
<th></th>
<th>Sodium dodecyl sulphate</th>
<th>Sodium hexadecyl sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>0.03%</td>
<td>Nil</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>Nil</td>
<td>0.07%</td>
</tr>
<tr>
<td>Hydrolysable SO$_3$</td>
<td>27.7%</td>
<td>23.1%</td>
</tr>
<tr>
<td>Theoretical</td>
<td>27.8%</td>
<td>23.2%</td>
</tr>
</tbody>
</table>

**Measurements**—Solutions were prepared in the conductivity cell itself by weighing out the requisite amount of the sodium salt, collecting the water direct from the still, and weighing again. Concentrations are expressed as the square-root of the normality by weight.

Two series of measurements were made with each of the alkyl sulphates. In the first series, the solution of fixed concentration was measured at each working temperature successively. In the second series a concentrated solution was successively diluted a number of times by blowing water over from a quartz flask* and after each dilution measured at constant temperature.

**Results**

In order to economise space in recording the results, the conductivities at each temperature have been read from large-scale curves at fixed intervals. They are given in Tables II and III for sodium dodecyl sulphate and sodium hexadecyl sulphate respectively. They are plotted showing the actual determinations in figs. 1 and 2 respectively, the curves for 80° and 100° being omitted because of the greatly extended scale they would necessitate.

The results incorporate a series of check measurements made by Mr. H. Catlow, B.Sc., to whom we are indebted.

The values at infinite dilution are higher than those found by Lottermoser and Püschell, doubtless largely due to the greater water correction applied by these workers; for their concentrated solutions, they used ordinary distilled water and for the most dilute water having a conductivity ten times as high as that used for these measurements.

**Discussion**

The curve of the electrical conductivity against the square root of the concentration at each temperature consists of three well-defined sections.
Over the first range there is a gradual linear fall. This is very abruptly succeeded over the second range by an extremely rapid fall. Over the third range the conductivity remains comparatively constant; there is, indeed, a small rise in conductivity to a maximum followed by a gradual fall.

Each of these ranges will be discussed and, in seeking an interpretation of the form of the conductivity curves, reference will be made to the results of two allied investigations about to be published, viz., the transport numbers of the ions in aqueous solutions of silver dodecyl sulphate and the effect of added electrolytes on the electrical conductivity of aqueous solutions of sodium dodecyl sulphate.
First Range—The electrical conductivity falls as a linear function of the square root of the concentration of the alkyl sulphate. This behaviour is observed with all strong electrolytes and receives complete explanation in the Debye-Hückel theory of ionic interaction.

Further, the fall is of the same order as for a simple uni-univalent salt. Thus, for sodium dodecyl sulphate at 20°:

The equivalent conductivity $\Lambda_0$ at $\sqrt{C} = 0$ is 75.7

$\Lambda$ at $\sqrt{C} = 0.06$ is 70.3.

Hence the experimental slope $= 5.4/0.06 = 90.0$
Applying Onsager’s equation with the appropriate constants for 20°:

\[ \Lambda = \Lambda_0 - (0.225 \Lambda_0 + 53.2) \sqrt{C}, \]

the theoretical slope is \((0.225 \times 75.7) + 53.2 = 70.2\). These values are exactly comparable with those for simple uni-univalent electrolytes;

for nearly all the simple salts the theoretical slope is between about 70 and 80 and the experimental slope about 10 to 15 units higher. The fact that the difference between the experimental and theoretical slopes is somewhat greater for the alkyl sulphates than for the simple salts is doubtless due to the far greater size of the anion whose “period of
relaxation" is therefore greater than that of a small simple ion. The remarkable similarity in the behaviour of these long chain compounds to that of simple salts is, indeed, strong evidence in favour of Onsager's assumption that the electrophoretic effect is independent of ionic size.

There is no doubt, therefore, that in the very dilute solutions of this first range the detergent is completely ionized as a simple salt into sodium ions and long chain sulphate ions and that this initial fall of conductivity is due to interionic action.

The transport numbers of the ions confirm this view. The values for the silver ion and dodecyl sulphate ion in aqueous solution of silver dodecyl sulphate are approximately 0.6 and 0.4 respectively at infinite dilution and 0.75 and 0.25 at the end of this range. These values are similar to those for a simple silver salt, e.g., for silver nitrate for which the values of cation and anion are 0.47 and 0.53 respectively in very dilute solution. The smaller value of the transport number of the long chain anion compared with that of the nitrate ion is to be expected because of its relatively great size and therefore smaller mobility. It is also to be expected that the fall in the transport number of the long chain anion with increasing concentration should be greater than that of the smaller nitrate ion owing to relatively more rapid crowding.

Further confirmation is forthcoming from the effect of added electrolytes on the electrical conductance. The specific conductances of a series of solutions containing a fixed amount of added electrolyte with increasing concentration of sodium dodecyl sulphate were determined. From these the specific conductances of corresponding solutions containing only sodium dodecyl sulphate were subtracted. If there were no mutual effect between the two constituents, this difference should be constant and equal to the specific conductance of the added electrolyte. The departure of the conductance difference from this constant value is a measure of the mutual effect of the alkyl sulphate and the added electrolyte.

Over this first range the conductance difference falls with increasing concentration. The effect is the same as that found on addition of the same electrolyte to a simple salt, though the effect is greater owing (as will be shown) to the far larger anion of the alkyl sulphate. It is thus clearly demonstrated that the alkyl sulphate is present in very dilute solution wholly as simple ions.

In his original investigations on the electrical conductivity of soap solutions, McBain did not carry his measurements down to the low concentrations within this first range owing to excessive hydrolysis of these compounds at great dilutions. His curves begin within the second range,
so that he had no evidence of these colloidal electrolytes as completely dissociated salts. In his recent work on the straight chain alkyl sulphonate acids* also McBain makes no differentiation between the first and second ranges. Lottermoser and Püschell† conclude that the metallic alkyl sulphates are completely dissociated over the initial range.

Second Range—The first range ends abruptly and over the second range the electrical conductivity falls extremely rapidly with increasing concentration. For the small increase in concentration $\sqrt{N_m} = 0.1$ the conductivity falls to about half its former value; the average fall over the second range is about four times as great as over the first range.

It is therefore clear that the alkyl sulphate is no longer present as a simple electrolyte. Moreover, the departure of a simple electrolyte from the behaviour postulated by the Debye-Hückel theory results in an increasingly greater conductivity with increasing concentration than corresponds to the linear square root relation, whereas with the alkyl sulphate the divergence is in the opposite direction and of far greater magnitude.

McBain in his original investigations observed this rapid fall in the electrical conductivity of soap solutions and accounted for it by depression of ionization. In his recent investigation on the electrical conductivity of straight chain alkyl sulphonate acids, also, he argues that dissociation is not complete over this range.

Lottermoser and Püschell observed the same steep fall for all the salts of the four long chain alkyl sulphates which they examined, and they accounted for it by postulating the formation of aggregates of neutral colloid. The explanation presupposes the formation of neutral molecules, i.e., depression of ionization as held by McBain.

The hypothesis that depression of ionization or the formation of neutral colloid or of aggregates of neutral colloid is responsible for this rapid fall in conductivity over the second range is demonstrably incorrect. If it were true, the transport numbers of the remaining ions should remain practically unchanged, whereas, in fact, as Howell and Warne have shown, they undergo a radical change, that of the cation falling to zero and that of the anion rising to unity. Again, the effect of added electrolyte having a common ion should be profound, causing greatly enhanced depression of ionization and therefore a great fall in conductivity; but Howell and Catlow have shown that the "conductance by difference" of the added electrolyte is practically unchanged over this range.

† *Kolloidzschr.*, vol. 63, p. 175 (1933).
Hartley* accounts for the rapid fall in conductivity by postulating that where the linear relation of the first range ends, micelle formation begins. Now McBain introduced the concept of the ionic micelle to explain the increase in conductivity observed over the third range, arguing from Stokes's Law that the mobility of the ionic aggregate is greater than that of the component ions moving individually. Hartley, however, points out that inclusion of the cations by the micelle removes these from solution and the consequent reduction in the cationic mobility is greater than the increase in anionic mobility, thus causing a decrease in conductivity. This theory accounts for the observed change in the transport numbers of the ions over this range, but there are several arguments against it:

1. If micelle were present, the addition of electrolytes should have a profound effect owing to adsorption (or inclusion) of ions by the micelle. Actually, however, as already stated, added electrolytes have almost no effect over this range.

2. It is generally agreed that micelle is present over the third range where the conductivity is increasing again and the increase can be explained in terms of micelle formation. It is difficult to believe that the constitution of even so variable an aggregate as the micelle can vary within such enormous limits as to account first for a fall and then for a rise in conductivity on such a scale as that observed over a comparatively small range of concentration. Indeed, having used the micelle to account for the decrease in conductivity, Hartley has no explanation for the subsequent increase and concludes that "in the present state of our knowledge we feel that it is premature to draw any definite conclusions from the behaviour of these substances in concentrated solutions". Yet, as McBain stresses, the increase in conductivity is the most characteristic behaviour of these colloidal electrolytes.

3. The simple relation between the lengths of the anions and the distance between them at the end of this range (vide infra) indicates that over the whole of this range the alkyl sulphate is still present almost entirely as simple ions.

4. Hartley† uses Bury's observation‡ that micelle formation begins at a critical concentration in support of his argument that this occurs at the end of the first range since the change of conductivity with concentration alters abruptly at this point. The discontinuities of Bury's curves for

* Hartley, 'Trans. Faraday Soc.,' vol. 31, p. 31 (1935); Moilliet, Collie, Robinson, and Hartley, ibid., p. 120.
‡ Jones and Bury, 'Phil. Mag.,' vol. 4, p. 841 (1927).
the densities of solutions of butyric acid, however, are more comparable with the transition from the second to the third range of these detergent solutions than with the abrupt change from the first to the second, and it will be shown (vide infra) that the conditions existing at the discontinuity with butyric acid are probably identical with those at the transition from the second to the third range in these detergent solutions.

The most hopeful mode of approach to an understanding of the conditions obtaining in solution seemed to lie in a consideration of the inter-ionic distances, which are readily calculated.

Thus, for sodium hexadecyl sulphate at 60°, the sudden departure from the linear relation of the first range (hereafter referred to as the “break”) occurs at $\sqrt{N} = 0.032$, i.e., at 0.001024 N.

The compound is completely dissociated at this concentration, hence the

Number of anions per litre $= 6.06 \times 10^{23} \times 0.001024$

" " cc $= 6.06 \times 10^{20} \times 0.001024$

$= 6.205 \times 10^{17}$

" " cm $= \frac{3}{8} \sqrt{6.205 \times 10^{17}}$

$= 8.53 \times 10^{5}$

Distance between the anions $= \frac{1}{8.53 \times 10^{5}}$ cm

$= 117$ A.

Since Lottermoser and Püschell have examined the conductivity of four homologous compounds, their values can be used for a comparison of the inter-ionic distances. Their values for the concentration at the break in the dodecyl and hexadecyl compounds are in excellent agreement with ours.

The inter-ionic distance may be compared with the length of the anion. The length is not known from direct measurement. However, the distance between neighbouring carbon atoms is doubtless the same as in carboxylic acids, * viz., 1.26 A, and the distance between the last carbon atom and the sulphate group may be taken as the same without serious error. Thus, the length of the hexadecyl sulphate ion is $16 \times 1.26 = 20.16$ A.

It is seen from Table IV that there is no simple relation between the separation and the length of the anion; the ratio $d/l$ increases from 3.70

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for the dodecyl compound to 7·05 for the octodecyl. Nor is there a simple relation between the free distance \( d - l \) and the length.

The anion is free to rotate and therefore occupies a volume proportional to the cube of its length. It is seen that the free distance is proportional to the rotational volume of the ion, \( d - l/l^3 \) being constant for all four compounds within the limits of experimental error.

These compounds, therefore, cease to behave as simple electrolytes when the mean free path of the anion falls below a critical value which is proportional to its rotational volume. It is therefore suggested that at this point the anions are unable to pass one another owing to mutual electrical repulsion and that on electrolysis they therefore move as a complete lattice-like loose network. The cations no longer have complete freedom of movement and are able to move through the network only with difficulty; at the end of the second range (vide infra) their movement through the network has ceased and they are being carried along by it.

The sudden change from the behaviour as a simple electrolyte over the first range is thus clear, since the formation of the network occurs at a critical concentration determined by the relative free path and rotational volume of the anion.

The extremely rapid fall in conductivity is also explained, since, with increasing concentration, the network becomes more densely packed and therefore less mobile and also offers increasingly greater resistance to the movement of the cations in the opposite direction. The packing of the anions continues until the critical concentration at the end of this range is reached when the movement of the cation through the network is completely checked and the anions with cations fall into micelle formation. Thus over this range the mobility of the cation falls to zero and that of the anionic network is also reduced; consequently, the electrical con-

### Table IV—Sodium Alkyl Sulphates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. at break ( \sqrt[3]{N} )</th>
<th>Distance between anions ( d ), Å</th>
<th>Length of anion ( l ), Å</th>
<th>Free distance ( d - l ), Å</th>
<th>Rotational volume proport. to ( l^3 \times 10^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecyl</td>
<td>0·21</td>
<td>56</td>
<td>15·12</td>
<td>40·9</td>
<td>3·46</td>
</tr>
<tr>
<td>Tetradecyl</td>
<td>0·138</td>
<td>86</td>
<td>17·64</td>
<td>68·4</td>
<td>5·49</td>
</tr>
<tr>
<td>Hendecyl</td>
<td>0·10</td>
<td>118</td>
<td>20·16</td>
<td>97·8</td>
<td>8·20</td>
</tr>
<tr>
<td>Oodecyl</td>
<td>0·074</td>
<td>160</td>
<td>22·68</td>
<td>137·3</td>
<td>11·66</td>
</tr>
</tbody>
</table>
ductivity at the end of the second range should be less than half its value at the beginning, and this is seen to be true in each of the curves.

The change in the transport numbers over this range is also explained. The transport number of the cation falls with increasing concentration, since its passage through the network becomes increasingly difficult and eventually falls to zero when its passage is completely checked. The transport number of the anion therefore increases correspondingly until it reaches unity. Indeed, the transport number of the anion slightly exceeds unity, indicating that cations are being carried along in the network.

The effect of added electrolytes over this range is also explained. The added cations can pass through the anionic network only with difficulty; the added anions, on the other hand, increase the charge of the network without appreciably altering its frictional resistance. The two effects are opposed and the effect of added electrolyte over this range should be very small. As already stated, this is found to be so, the "conductance by difference" of the added electrolyte being almost constant over the whole range.

The relation between the mean free path and the rotational volume holds at each temperature as the values given in Table V for 40° and 50° clearly show.

**Table V—Sodium Alkyl Sulphates**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature 40° C</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d</td>
<td>d - l</td>
<td>(d - l)/l^2</td>
<td></td>
</tr>
<tr>
<td>Dodecyl</td>
<td>62</td>
<td>47</td>
<td>0.0136</td>
<td></td>
</tr>
<tr>
<td>Tetradecyl</td>
<td>92</td>
<td>75</td>
<td>0.0136</td>
<td></td>
</tr>
<tr>
<td>Hexadecyl</td>
<td>135</td>
<td>115</td>
<td>0.0140</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature 50° C</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d</td>
<td>d - l</td>
<td>(d - l)/l^2</td>
<td></td>
</tr>
<tr>
<td>Dodecyl</td>
<td>58</td>
<td>43</td>
<td>0.0124</td>
<td></td>
</tr>
<tr>
<td>Tetradecyl</td>
<td>89</td>
<td>71</td>
<td>0.0129</td>
<td></td>
</tr>
<tr>
<td>Hexadecyl</td>
<td>122</td>
<td>102</td>
<td>0.0124</td>
<td></td>
</tr>
</tbody>
</table>

It is seen that the ratio of the mean free path to the rotational volume is constant at each temperature. The value decreases with increase of temperature (about 0.7% per degree); this is to be expected, since with increasing temperature the mobility of the ions increases and they have therefore to be brought closer before the mutual repulsive force of the anions is sufficient to prevent their movement past one another.

Confirmatory evidence of the formation and persistence of an anionic network over the second range is probably best sought by measurements
of the rigidity of the solution,* and it is hoped that this investigation may be made in the near future.

Third Range—The sudden fall in conductivity is arrested and, over the third range, the conductivity rises to a maximum and then falls again.

It was to explain this increase in conductivity which he found exhibited by soap solutions that McBain was led to postulate the formation of the ionic micelle.

If \( n \) univalent spherical ions each of radius \( r \) coalesce to form a spherical micelle carrying \( n \) charges, then it follows from Stokes's Law that the conductivity of the micelle will be \( n^{2/3} \) times as great as that of the \( n \) individual ions.

It is therefore possible to calculate the conductivity at infinite dilution of a compound dissociated into simple ions and micelles.

Thus using the values 45.7 and 30.1, as before, for the mobility of the sodium and dodecyl ion, respectively, at 20°, the conductivity at infinite dilution of sodium dodecyl sulphate dissociated into \( 10\text{Na}^+ + [\text{D}_{10}]^{10-} \) will be

\[
\frac{1}{10} \left[ (10 \times 45.7) + (10 \times 30.1 \times 10^{2/3}) \right] = 185.4.
\]

The values have been calculated for the series up to \( \text{D}_{10} \) and are given in Table VI, from which it is seen how the conductivity increases with the size of the micelle.

Such a highly charged unit as the type of micelle so far considered will have a most powerful adsorption effect. McBain postulated that the micelle is heavily hydrated and adsorbs undissociated molecules from

* Suggestion of Professor Rideal, F.R.S., in a private communication.
solution. There is every reason to believe (*vide infra*) that the long chain alkyl sulphates are still practically completely dissociated at the moment micelle formation begins, so that adsorption of neutral molecules does not occur. Evidently, the most marked effect will be the adsorption of the oppositely charged sodium ions.

It is possible to calculate in the manner already indicated the conductivity at infinite dilution of the salt dissociated into simple cations and ionic micelles with adsorbed cations, assuming that, so far as size is concerned, the mobility of the micelle remains unchanged. Thus the conductivity at infinite dilution of sodium dodecyl sulphate dissociated into $4\text{Na}^+ + [\text{D}_{10}\text{Na}_6]^{4-}$ will be

$$\frac{1}{10} [(4 \times 45 \cdot 7) + (4 \times 30 \cdot 1 \times 10^{2/3})] = 74 \cdot 2.$$

The values have been calculated for the D$_{10}$ series with from none to nine sodium atoms in the micelle and are given in Table VII from which it is clearly seen how the conductivity decreases with adsorption of the cation on the micelle.

Now the conductivity of sodium dodecyl sulphate at $20^\circ$ at the point where micelle formation begins is about $27 \cdot 0$. It is therefore possible to rule out those ionic combinations which are not of about this order. The nearest values for all possible combinations with from two to ten dodecyl groups in the micelle are collected in Table VIII.

It is clear that for the smaller micelles the charge must be unity and that even for a micelle composed of as many as ten anions the charge is not greater than two.

The combination which gives almost perfect agreement with the observed value is $\text{Na}^+ + [\text{D}_4\text{Na}_3]^-$. The Onsager slope for this uni-univalent electrolyte at $20^\circ$ is $70 \cdot 04$ so that the calculated conductivity at $0 \cdot 0536$ N, the concentration at which micelle formation begins, is $30 \cdot 4 - 3 \cdot 75 = 26 \cdot 65$ as against $27 \cdot 0$ observed. It is therefore possible that the initial aggregation is of four dodecyl ions, with three sodium ions. With increasing concentration of the alkyl sulphate, the size of the micelle increases. Addition of dodecyl ions results in increased conductivity; adsorption of sodium ions causes decreased conductivity. These effects alone are sufficient to account for the increase and the subsequent decrease in conductivity over this range.

Interesting information is obtained from a consideration of the inter-ionic distances when micelle formation begins. It may be noted here that the change of direction in the conductivity curve (hereafter called the bend) in passing from the second to the third range is not so abrupt as
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that (the break) between the first range and the second. Nevertheless, the concentration at which the transition occurs is obtained without appreciable error from the point of maximum change of direction.

The positions of the bends for the long chain alkyl sulphates were taken from the conductivity curves of Lottermoser and Puschell and used for calculating the data given in Table IX.

**Table VIII**

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Lambda_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-1}]^1_-$</td>
<td>46.7</td>
</tr>
<tr>
<td>$\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-2}]^2_-$</td>
<td>36.1</td>
</tr>
<tr>
<td>$2\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-2}]^2_-$</td>
<td>72.2</td>
</tr>
<tr>
<td>$\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-2}]^1_-$</td>
<td>30.4</td>
</tr>
<tr>
<td>$2\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-2}]^1_-$</td>
<td>60.8</td>
</tr>
<tr>
<td>$\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-2}]^1_-$</td>
<td>26.7</td>
</tr>
<tr>
<td>$2\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-2}]^1_-$</td>
<td>53.5</td>
</tr>
<tr>
<td>$\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-2}]^1_-$</td>
<td>24.2</td>
</tr>
<tr>
<td>$2\text{Na}^+ + [\text{D}<em>n\text{Na}</em>{n-2}]^1_-$</td>
<td>48.3</td>
</tr>
</tbody>
</table>

**Table IX—Sodium Alkyl Sulphates**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration at bend $^a$</th>
<th>Distance between anions $^b$</th>
<th>Length of anion $^c$</th>
<th>$d/l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecyl</td>
<td>0.377</td>
<td>31</td>
<td>15.12</td>
<td>2.05</td>
</tr>
<tr>
<td>Tetradecyl</td>
<td>0.330</td>
<td>36</td>
<td>17.64</td>
<td>2.04</td>
</tr>
<tr>
<td>Hexadecyl</td>
<td>0.285</td>
<td>41</td>
<td>20.16</td>
<td>2.03</td>
</tr>
<tr>
<td>Octodecyl</td>
<td>0.255</td>
<td>45</td>
<td>22.68</td>
<td>2.00</td>
</tr>
</tbody>
</table>

It is seen that, within the limits of error in reading the concentrations from the curves, the ratio $d/l$ is constant. The anionic network therefore falls into micelle formation when the distance between the anions has been reduced to a critical value which is proportional to the length of the anion.

Fortunately the necessary information is available for testing the truth of the relation with another homologous series. Using the concentration at the bend read from McBain’s curves for the sodium soaps, the values shown in Table X are obtained.
It is seen that the same relation holds for this series also. Indeed, even with so low a member as the octoate, the ratio is not very different. There is no information for the sodium salt but potassium octoate forms micelles in about 0.5 N solution.* The distance \( d = 15 \) A, the length of the anion \( l = 8.82 \), and the ratio \( d/l = 1.70 \).

Since the formation of micelle is an ionic combination, the reaction should be exothermic and should therefore be retarded by increasing temperature.

**Table X—Sodium Soaps**

<table>
<thead>
<tr>
<th>Soap</th>
<th>Concentration at bend ( \sqrt{N} )</th>
<th>Distance between anions ( d ), A</th>
<th>Length of anion ( l ), A</th>
<th>( d/l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laurate</td>
<td>0.45</td>
<td>20</td>
<td>13.86</td>
<td>1.44</td>
</tr>
<tr>
<td>Myristate</td>
<td>0.35</td>
<td>24</td>
<td>16.38</td>
<td>1.47</td>
</tr>
<tr>
<td>Palmitate</td>
<td>0.28</td>
<td>28</td>
<td>18.90</td>
<td>1.48</td>
</tr>
<tr>
<td>Stearate</td>
<td>0.23</td>
<td>31</td>
<td>21.42</td>
<td>1.45</td>
</tr>
</tbody>
</table>

The data given in Table XI calculated from the concentrations at the bends in the conductivity curves for sodium dodecyl sulphate at different temperatures show that the temperature coefficient of micelle formation is negative.

**Table XI—Sodium Dodecyl Sulphate**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Concentration at bend ( \sqrt{Nw} )</th>
<th>Distance between anions ( d ), A</th>
<th>( d/l )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.185</td>
<td>36.4</td>
<td>2.41</td>
</tr>
<tr>
<td>30</td>
<td>0.200</td>
<td>34.6</td>
<td>2.28</td>
</tr>
<tr>
<td>40</td>
<td>0.215</td>
<td>32.9</td>
<td>2.18</td>
</tr>
<tr>
<td>50</td>
<td>0.235</td>
<td>31.1</td>
<td>2.06</td>
</tr>
<tr>
<td>60</td>
<td>0.250</td>
<td>29.9</td>
<td>1.98</td>
</tr>
<tr>
<td>80</td>
<td>0.300</td>
<td>26.4</td>
<td>1.74</td>
</tr>
<tr>
<td>100</td>
<td>0.340</td>
<td>24.3</td>
<td>1.61</td>
</tr>
</tbody>
</table>

It is seen that with increasing temperature the value of the ratio \( d/l \) decreases (0.41% per degree over the range examined) showing that the anions have to be brought increasingly closer before micelle formation begins.

With a partially dissociated electrolyte, on the other hand, micelle formation is accompanied by further dissociation of the electrolyte and this is an endothermic reaction, so that if the absorption of heat due to ionization is greater than the evolution of heat due to micelle formation, the temperature coefficient will be positive. An example is given later (vide infra).

The force tending to prevent micelle formation is the charge on the anion. This is the same (unity) for the anions in the two homologous series considered, and it is seen that the ratio \( d/l \) is very similar for the two series at the same temperature; thus at 90° it is 1.46 for the sodium soaps and 1.67 for the sodium salts of the long chain alkyl sulphates.

The value of the ratio is also about the same for the long chain alkyl sulphates and the long chain alkyl sulphonic acids. The concentration at the bend in the conductivity curves for the sulphonic acids* cannot be read with accuracy since the experimental points are too widely spaced, but the data shown in Table XII are calculated from the approximate values.

<table>
<thead>
<tr>
<th>Table XII—Sulphonic Acids</th>
<th>Temperature 25° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphonic acid</td>
<td>Conc. at bend</td>
</tr>
<tr>
<td>Undecyl</td>
<td>0.25</td>
</tr>
<tr>
<td>Myristyl</td>
<td>0.15</td>
</tr>
</tbody>
</table>

It is seen that the ratio 2.3 is practically identical with that for the alkyl sulphates at 25°, viz., 2.35.

The force tending to promote micelle formation is the hydrophobous nature of the chain, and this is proportional to its length. Hence the tendency for two long chain anions to coalesce is proportional to the square of the length. The restraining force, the mutual repulsion due to the charges, is inversely proportional to the square of the distance between them. At the point where micelle formation begins, therefore, these two opposing forces just balance so that \( d^2/l^2 \) and therefore \( d/l \) is a constant.

It follows that with a partially dissociated electrolyte, since the repulsive force is less, micelle formation should begin earlier, i.e., when the inter-molecular distance is greater. It further follows that, since micelle formation results in further dissociation of the electrolyte, increase of temperature should facilitate micelle formation.

These two effects are clearly seen by comparing butyric acid with the soaps. The data in Table XIII have been calculated from the discontinuities in the curves for the partial specific volume of butyric acid in aqueous solution at different temperatures.*

\[
\begin{array}{cccc}
\text{Temp.} & \text{Concn.} & \text{Distance between molecules} & \text{Length of anion} & d/l \\
{\degree C} & \% & d & l & \\
0 & 15.0 & 9.86 & 3.78 & 2.61 \\
12 & 13.7 & 10.2 & 3.78 & 2.70 \\
18 & 13.0 & 10.4 & 3.78 & 2.75 \\
25 & 12.3 & 10.6 & 3.78 & 2.80 \\
35 & 12.0 & 10.7 & 3.78 & 2.83 \\
\end{array}
\]

It is seen that the ratio \(d/l\) is far greater than that for the soaps; thus at 90\(\degree\) the value would be about 3.1, which is more than double that for the soaps (1.46) at the same temperature. It is also seen that the temperature effect is in the direction anticipated and is appreciable (0.24\% per degree over the range given).

The values of the transport numbers confirm the presence of the micelle over this third range. The transport number of the anion does not change appreciably but retains the high value of about unity. This is to be expected since the micelle carries with it adsorbed cations.

It has been shown that the most probable ionization at the moment of micelle formation for sodium dodecyl sulphate is \(\text{Na}^+ + [\text{D}_4\text{Na}_3]^\cdot\). It is possible to calculate the transport number of the anion in this solution:

\[
\text{Mobility of Na}^+ = 45.7 \\
[\text{D}_4\text{Na}_3]^\cdot = 75.85.
\]

Hence the simple transport number of the anion \(= \frac{75.85}{121.55} \times \frac{7}{4} = 1.09\).

The gain in concentration at the anode, however, will be due not only to the attack by the four dodecyl ions but will include the three sodium ions carried by the micelle.

Hence the observed transport number of the anion

\[
= \frac{75.85}{121.55} \times \frac{7}{4} = 1.09.
\]

This is in almost perfect agreement with the transport number reached by the anion at the beginning of the third range in solutions of silver dodecyl sulphate, viz., 1.10.

The effect of added electrolytes on the conductivity also confirms the existence of the micelle over this third range. The "conductance by difference" of the added electrolyte increases extremely rapidly to values far exceeding its conductance alone. The effect is readily explained by the adsorption of ions of the added electrolyte by the micelle which is present over this range.

We are indebted to Messrs. Imperial Chemical Industries for a research grant and for permission to publish this paper.

**Summary**

The electrical conductivities of aqueous solutions of sodium dodecyl sulphate and of sodium hexadecyl sulphate have been measured over a wide range of concentration at different temperatures from 20° to 100° C. The conductivity has been plotted against the square root of the concentration and, at each temperature, the curve consists of three distinct ranges.

Over the first range the fall in conductivity is linear as for a simple electrolyte and is of the same order of magnitude. The alkyl sulphate is therefore completely ionized and the fall in conductivity is due to ionic interaction as postulated in the Debye-Hückel theory. Confirmation is obtained from the fact that the transport numbers are normal and that the "conductance by difference" of an added electrolyte falls as on the addition of one simple electrolyte to another.

At the point where the first range is abruptly succeeded by the second, it is shown that the mean free path of the anion is proportional to its rotational volume. At higher concentrations the anions are prevented by their mutual repulsion from passing one another and they therefore move as a loose network.

Over the second range the fall in conductivity is extremely rapid. Previous theories to account for this fall are discussed and shown to be untenable. The anionic network now postulated offers a satisfactory explanation and is in accordance with other properties observed over this range. The cations are unable to move freely through the network; with increasing concentration the network becomes more densely packed, so that the movement of the cations is increasingly hindered and eventually stopped. The contribution of the cations in carrying the current is
The Electrical Conductivities of Aqueous Solutions

therefore reduced to zero and, since the network is less mobile than an equal number of ions moving individually, the conductivity at the end of this range is less than half the value at the beginning.

Confirmation is obtained from the fact that the transport number of the cation falls and that of the anion increases to more than unity. Further confirmation is afforded by the fact that the "conductance by difference" of an added electrolyte is practically constant, since the cation is hindered by the network and the anion increases the mobility of the network.

At the point where the second range is succeeded by the third, it is shown that the distance between the anions in the network is proportional to their length. It is shown that the same relation holds for aqueous solutions of the soaps. In any homologous series the tendency to form micelle is proportional to the length of the anion. This is the point, therefore, at which the network falls into micelle formation.

Over the third range the conductivity rises to a small maximum and falls again. The conductivities of micelles of varying constitution have been calculated, and it has been shown that the increase in conductivity due to aggregation and the decrease due to adsorption of cations are sufficient to explain the observed changes over this range.

Confirmation of the existence of micelle over this range is given by the fact that the transport number of the anion retains its high value of about unity and that the "conductance by difference" of an added electrolyte increases very rapidly owing to adsorption of its ions by the micelle.

It is shown that for a completely dissociated substance the temperature coefficient of micelle formation is negative.

It is argued that a partially dissociated electrolyte should form micelles when the distance between the molecules is greater than the distance between the ions in a completely dissociated electrolyte of similar constitution; further, that the temperature effect may be positive. By comparison of butyric acid with the soaps this is shown to be true.

The ionic micelle is not highly charged. The charge is probably not more than one or two units. Thus it is shown from the conductivity and from transport numbers that initial formation of micelle with sodium dodecyl sulphate most probably yields Na' + [D₄Na₃].