119. *The Extent of Dissociation of Salts in Water. Part X. Dissociation Minima.*

By Cecil W. Davies.

In solutions in which the ionic strength increases sufficiently rapidly with increasing concentration, ion-association will increase up to a critical concentration, and thereafter will decrease. The degree of dissociation of the electrolyte will therefore have a minimum value. Evidence for this is found amongst aqueous solutions containing multivalent ions, and it is suggested that the effect will have an important bearing on the properties of colloid systems and non-aqueous solutions.

In classical theory the degree of dissociation of a binary electrolyte was governed by the condition $\alpha^2 m/(1 - \alpha) = K$, from which it followed that any increase in the concentration of the electrolyte was accompanied by a decrease in its degree of dissociation. When we formulate the equilibrium with due regard to deviations from ideal behaviour, and write $f_{\pm}^2 \alpha^2 m/f_u(1 - \alpha) = K$, this familiar consequence is no longer necessarily valid, for concentrations may be reached in which $f_{\pm}^2 m/f_u$ decreases, and in which α must therefore increase, with rise in concentration. If this occurs, the electrolyte will show a minimum degree of dissociation (a maximum extent of ion-association) at some intermediate concentration, on either side of which it will increase. The objects of the present paper are to show that this novel type of behaviour may be expected to be quite common, to bring forward experimental evidence in support of it, and to offer it as an explanation for some of the anomalies which electrolyte solutions still present.

The treatment of typical strong electrolytes on the basis of a dissociation equilibrium was used in 1926 by Bjerrum, who showed how a (somewhat arbitrary) distinction between free ions and ion pairs made it possible to correct for the " close approach " effects, for which the conventional Debye–Hückel treatment of strong electrolytes does not provide.

A more general treatment based on incomplete dissociation has been applied in the present series of papers to conductivities and to solubilities and other thermodynamic properties in pure and mixed electrolyte solutions. Concordant dissociation constants have been derived for numerous electrolytes from two or more of these independent sources; the method has predicted the sign and magnitude of the large departures from additivity found in the conductivity of certain mixtures (J., 1938, 448); and the existence of association products like KSO_4' has been demonstrated by transport numbers (*Trans. Faraday Soc.*, 1930, **26**, 592). From the practical point of view it is an advantage rather than a defect of the general treatment that it is unnecessary to distinguish between cases where association is to be attributed entirely to electrostatic influences and those where it is not. In some cases the salt though incompletely dissociated is probably completely ionised. In others this is not so, for there is a marked difference between the optical properties of the association product and those of the ions from which it is formed (J., 1938, 271); and, again, many of the measured dissociation constants would lead, on Bjerrum's treatment, to impossibly small ionic diameters (*Trans. Faraday Soc.*, 1931, **27**, 621; 1932, **28**, 609).

An important outcome of this work, for our present purpose, is the fact that the individual differences amongst measured activity coefficients in dilute solutions are almost entirely removed when the necessary allowances for incomplete dissociation are made. The equation $\log f = -0.50z^2\{\sqrt{I}/(1 + \sqrt{I}) - 0.20I\}$ (f is the ionic activity coefficient, z the valency of the ion, I the ionic strength) has been shown to give mean ionic activity coefficients in reasonably good agreement with the corrected data for a large number of salts of various valency types in water at 25° up to an ionic strength $I = 0.1$ (J., 1938, 2093). The deviations from it which appear in more concentrated solutions seem to depend on the *concentrations* (and not on the valencies) of the ions present; so that if we accept $I = 0.1$ as the limit beyond which specific deviations from it are too important to be ignored, we may expect it to be the more accurate the higher the valency type of the electrolyte to which it is applied, and this provides justification for placing some reliance on the equation when applied to high-valency type electrolytes of which experimental knowledge is scanty.

The Conditions for Dissociation Minima.—For a binary electrolyte we have $f_{\pm}^2\alpha^2m/f_u(1-\alpha) = K$. At ionic strengths below 0·1 we can without serious error put $f_u = 1$, and $f_{\pm}$ is given by the equation

$$-\log_{10} f_{\pm}^2 = z^2\{\sqrt{I}/(1 + \sqrt{I}) - 0.20I\},$$

where z is the valency of the constituent ions. We also have $I = \alpha mz^2$. Differentiation of these three expressions gives

$$f^2\alpha^2 + 2f^2\alpha m\frac{d\alpha}{dm} + \alpha^2 m\frac{d(f^2)}{d(\sqrt{I})} \cdot \frac{d(\sqrt{I})}{dm} = -K\frac{d\alpha}{dm} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{f^2} \cdot \frac{d(f^2)}{d(\sqrt{I})} \cdot \log_{10} e = z^2\left\{0.4\sqrt{I} - \frac{1}{(1 + \sqrt{I})^2}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$2\sqrt{I} \cdot \frac{d(\sqrt{I})}{dm} = \alpha z^2 + mz^2\frac{d\alpha}{dm} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Putting $d\alpha/dm = 0$, we obtain as the condition for a minimum in α from (3),

$$2\sqrt{I} \cdot d(\sqrt{I})/dm = \alpha z^2 = I/m, \text{ or } d(\sqrt{I})/dm = \sqrt{I}/2m.$$

Substituting in (1),

$$f^2\alpha^2 + \alpha^2 m\frac{d(f^2)}{d(\sqrt{I})} \cdot \frac{\sqrt{I}}{2m} = 0, \text{ or } \frac{1}{f^2} \cdot \frac{d(f^2)}{d(\sqrt{I})} = -\frac{2}{\sqrt{I}}$$

and substituting in (2),

$$\frac{2}{z^2\sqrt{I}}\log_{10} e = 0.4\sqrt{I} - \frac{1}{(1 + \sqrt{I})^2}$$

This gives no minimum in α for $z = 1$ or $z = 2$. For a ter-tervalent electrolyte it predicts a minimum at $\sqrt{I} = 0.13$, corresponding to $\alpha m = 0.00188$, and $m = 0.00188 + 3.50 \times 10^{-7}/K$. Although the equation gives no minimum for a bi-bivalent salt, the slope of the α–m curve decreases to a low value at $I = 0.1$. Thus for an electrolyte of dissociation constant $K = 0.005$ the values calculated from our equations are : at $I = 0.09$, $\alpha = 0.61$; at $I = 0.10$, $\alpha = 0.60$; clearly, the appearance of a minimum at somewhat higher concentrations is very possible. With regard to unsymmetrical valency types, a minimum will not be expected for uni-bivalent salts. Almost the only other unsymmetrical salts for which any data are available are calcium ferro- and ferri-cyanides, and these are considered individually in a later section.

Comparison with Experiment in Aqueous Solutions.—(a) *Activity data.* We are almost entirely restricted here to bi-bivalent electrolytes. The mean ionic activities of several sulphates have been determined at 25°, and may be inserted in the mass-action equation $a_{\pm}^2/a_u = \gamma_c^2 m/f_u(1-\alpha) = K$, where γ_c is the stoicheiometric activity coefficient on the molar concentration scale. The data given by Kielland (*J. Amer. Chem. Soc.*, 1936,

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58, 1855) for zinc sulphate, and those of LaMer and Parks (*ibid.*, 1931, **53**, 2040) for cadmium sulphate, both at 25°, are given below, recalculated to the molar concentration scale.

<table>
<tr><td colspan="8" align="center">*Zinc sulphate.*</td><td colspan="5" align="center">*Cadmium sulphate.*</td></tr>
<tr><td>m ......</td><td>0·01</td><td>0·02</td><td>0·05</td><td>0·1</td><td>0·1995</td><td>0·299</td><td>0·4975</td><td>0·01</td><td>0·03</td><td>0·05</td><td>0·1</td><td>0·4959</td></tr>
<tr><td>γ_c ......</td><td>0·387</td><td>0·298</td><td>0·202</td><td>0·148</td><td>0·1043</td><td>0·0840</td><td>0·06373</td><td>0·383</td><td>0·254</td><td>0·199</td><td>0·137</td><td>0·0610</td></tr>
<tr><td>$10^3 . \gamma_c{}^2 m$</td><td>1·497</td><td>1·776</td><td>2·041</td><td>2·191</td><td>2·170</td><td>2·110</td><td>2·019</td><td>1·467</td><td>1·935</td><td>1·981</td><td>1·877</td><td>1·845</td></tr>
</table>

In both cases $\gamma_c{}^2 m$ goes through a maximum. Unless, therefore, the values of f_u show large departures from unity, the degree of association, $1 - \alpha$, must pass through a maximum. This conclusion is independent of any assumption that might be made as to the value of the dissociation constant, or the form of the extended Debye–Hückel equation.

(b) *Conductivity data.* When the concentration of an electrolyte is increased beyond that for minimum dissociation, the concentration of free ions will increase more rapidly than before, and so will the ionic strength

Fig 1
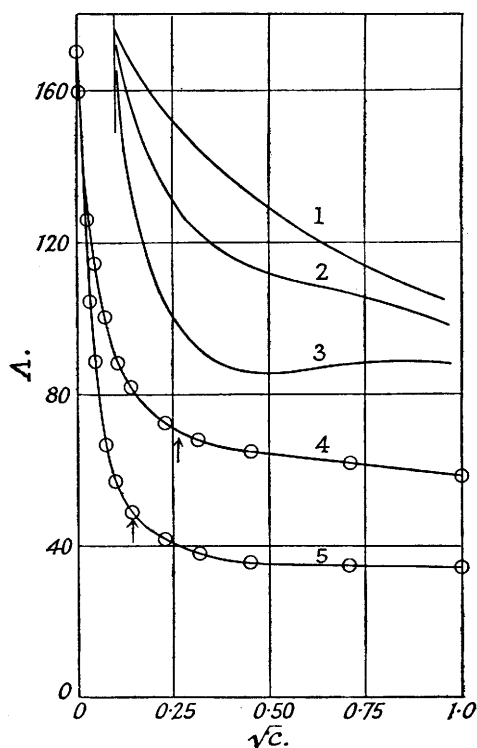
of the solution and the magnitude of ionic atmosphere effects. The first effect will tend to increase the equivalent conductivity, and the second to reduce it. In extreme cases these opposing influences may result in a minimum, succeeded by a flat maximum, in the conductivity curve; more generally, a region of abnormally small slope, followed by a point of inflexion, will be expected. These possibilities are illustrated in curves 2 and 3 of Fig. 1, where curve 1 is intended to represent the conductivity of the completely dissociated electrolyte; the extent of divergence of curve 2 or 3 from this is an approximate measure of the degree of ion-association, and is greatest in the region of minimum dissociation. Curves 4 and 5 show the data of Shoch and Felsing (*J. Amer. Chem. Soc.*, 1926, **38**, 1916) for calcium ferricyanide and ferrocyanide in water at 25°. At first both curves fall far more rapidly than would be expected for completely dissociated salts, indicating extensive ion association; at higher concentrations they show just the peculiarities expected, and at the highest concentrations reached they are probably very highly dissociated. The calculated points of minimum dissociation are shown by arrows.

The approximate points of minimum dissociation have been calculated as follows. Calcium ferrocyanide will dissociate in two stages :

$$Ca_2Fe(CN)_6 \rightleftharpoons CaFe(CN)_6'' + Ca^{\cdot\cdot} ;$$
$$CaFe(CN)_6'' \rightleftharpoons Ca^{\cdot\cdot} + Fe(CN)_6''''.$$
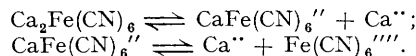
For the most dilute of Shoch and Felsing's solutions ($m = 0·00025$, $\Lambda = 105·1$) the first-stage dissociation is taken as approximately complete and the second-stage is estimated from the mobilities : $Ca^{\cdot\cdot}$, 59·5 (Shedlovsky and Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 1066); $Fe(CN)_6''''$, 110·3 (Davies, *ibid.*, 1937, **59**, 1760); $CaFe(CN)_6''$, 60 (assumed); on this (infinite dilution) basis complete formation of $CaFe(CN)_6''$ would reduce the equivalent conductivity from 169·8 to 59·8. The observed decrease, approximately corrected for mobility changes, corresponds to just under 50% association; this gives $[Ca^{\cdot\cdot}][Fe(CN)_6'''']/[CaFe(CN)_6''] = 1·5 \times 0·00025$, and the activity correction being applied, $K_2 = 2 \times 10^{-4}$. K_1, which is less important in the calculations, is assumed to be 0·005, the value found for several bivalent metal sulphates. If now we write $[Ca_2Fe(CN)_6] = (1 - \alpha)m$ and $[CaFe(CN)_6''] = \alpha m(1 - \beta)$, then $[Fe(CN)_6''''] = \alpha\beta m$ and $[Ca^{\cdot\cdot}] = \alpha(1 + \beta)m$. Hence

$$\log \frac{[Ca^{\cdot\cdot}][CaFe(CN)_6'']}{[Ca_2Fe(CN)_6]} = \log \frac{(1 + \beta)(1 - \beta)\alpha^2 m}{1 - \alpha} = \log 0·005 + 4\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0·20I \right) \quad . \quad . \quad (5)$$

$$\log \frac{[Ca^{\cdot\cdot}][Fe(CN)_6'''']}{[CaFe(CN)_6'']} = \log \frac{(1 + \beta)\alpha\beta m}{1 - \beta} = \log 2 \times 10^{-4} + 8\left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0·20I \right) \quad . \quad . \quad (6)$$

$$\log I = \log (4 + 8\beta) + \log \alpha m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Elimination of αm from equations (6) and (7) gives an equation from which β can be found graphically for various values of I; αm can then be found from equation (7), and hence α from (5). Table I gives some of the calculated values.

The calculations show that β (the fraction of second-stage dissociation) decreases rapidly to a minimum value of 0·305 at $m = 0·005$ ($\sqrt{c} = 0·141$); α, which is 0·83 at this point, continues to decrease slowly, so that the minimum in the total relative number of free ions occurs at $m = 0·015$ ($\sqrt{c} = 0·245$), where $\beta = 0·347$, $\alpha = 0·77$.

TABLE I.

I	0·0004	0·001	0·005	0·01	0·02	0·04	0·05	0·07	0·09	0·10
β	0·807	0·668	0·408	0·339	0·307	0·311	0·322	0·341	0·361	0·370
a	0·998	0·991	0·941	0·896	0·843	0·795	0·783	0·767	0·757	0·754
$m \times 10^5$	3·8	10·8	73·2	166	367	776	970	1357	1725	1905
$[Ca^{\cdot\cdot}] \times 10^5$	6·9	17·9	96·9	199·5	404·8	808·3	1005	1395	1778	1968

$\Delta[Ca^{\cdot\cdot}]/\Delta m$		1·57	1·27	1·10	1·02	0·99	1·01	1·01	1·04	1·06

The calculations for calcium ferricyanide are similar. Only one dissociation constant need be taken into account, *viz.*, that for the process $Ca^{\cdot\cdot} + Fe(CN)_6''' \rightleftharpoons CaFe(CN)_6'$, and for this the conductivity measurements give the approximate value $K = 0.001$. This leads to a flat dissociation minimum in the neighbourhood of 0·012M. ($\sqrt{c} = 0.268$), $Fe(CN_6)'''$ and $CaFe(CN)_6'$ being present in approximately equal proportions.

(c) *Solubility data* (Measurements by I. J. BUCKLAND). The solubility of a sparingly soluble salt may be affected in two ways by the addition to the solution of a soluble electrolyte. The increase in the ionic strength of the solution normally causes an increase in the solubility; but if the added electrolyte contains an ion common to the saturating salt it will depress its solubility by an amount which usually far outweighs the simultaneous

FIG. 2.
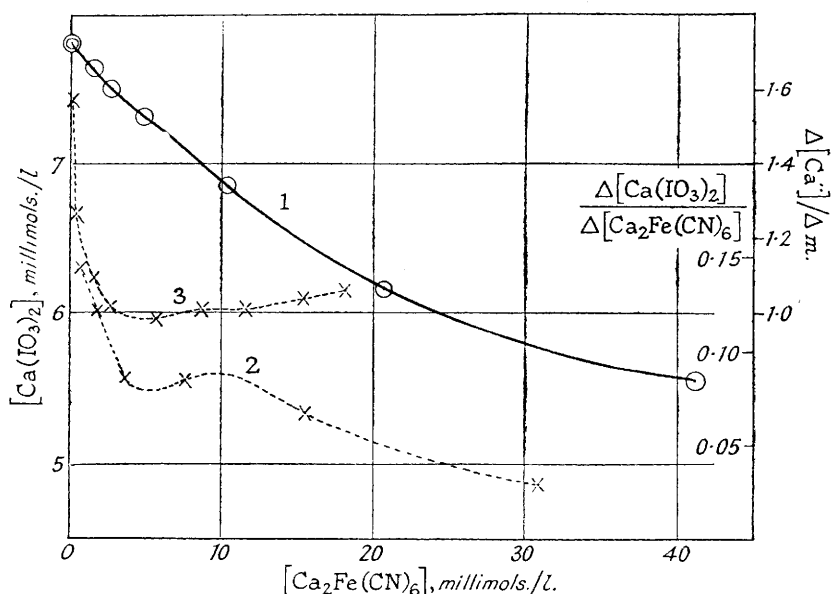
effect of the increasing ionic strength. This appeared to offer a simple means of testing the dissociation minimum reported in the previous section for calcium ferrocyanide, and we have accordingly measured the solubility of calcium iodate in solutions of this electrolyte at 25°.

The calcium iodate was prepared, and its solubility measured, as described in previous papers (cf. Davies, J., 1938, 277). The calcium ferrocyanide was a Kahlbaum specimen; crystals showing a green coloration were rejected. Blank experiments showed that the iodate estimation was unaffected by the presence of ferrocyanide.

The solubilities are plotted in Curve 1 of Fig. 2, and it will be seen that this is of very unusual type, showing a marked point of inflexion at $m = 0.006$. The results are in Table II, in which col. 1 gives the concentration

TABLE II.

$[Ca_2Fe(CN)_6]$.	$[Ca(IO_3)_2]$.	$\dfrac{\Delta[Ca(IO_3)_2]}{\Delta[Ca_2Fe(CN)_6]}$.	$[Ca_2Fe(CN)_6]$.	$[Ca(IO_3)_2]$.	$\dfrac{\Delta[Ca(IO_3)_2]}{\Delta[Ca_2Fe(CN)_6]}$
0	7·850		10·320	6·858	
		0·145			0·0671
1·198	7·676		20·639	6·166	
		0·122			0·0295
2·397	7·530		41·278	5·558	
		0·0859			
4·794	7·324				
		0·0845			

of calcium ferrocyanide, and col. 2 the solubility of calcium iodate, both in millimols. Each solubility is the mean of three measurements, the average deviation from the mean being 0·1%. Col. 3 of the table gives the values of the average slope of the curve for the intervals between measurements. These slopes are plotted in Fig. 2, Curve 2, against the mean concentration of calcium ferrocyanide for the interval to which they apply,

and in Curve **3** are plotted the values of $\Delta[Ca^{\cdot\cdot}]/\Delta[Ca_2Fe(CN)_6]$ from Table I. Curves **2** and **3** both show minima in the same region of concentration, and this agreement leaves little room for doubt that the dissociation minimum calculated for calcium ferrocyanide in Table I actually occurs, and is the explanation of the anomaly in the solubility curve. The gradual divergence between these derivative curves, which becomes marked after the minima have been passed, is due to the effect upon the solubility of the increasing ionic strength of the solution.

It is concluded from this examination of the evidence that a minimum, followed by an increase, in electrolytic dissociation is to be expected in aqueous solutions containing ions of high valency; and, more generally, the effect will be looked for wherever the ionic strength of a solution changes rapidly with change of concentration. It is believed that this is a significant factor in the stability of colloid systems, and, more particularly, that it may explain many apparently anomalous properties of colloidal electrolytes. It also provides a possible explanation for some of the conductivity minima found in non-aqueous solutions. It is hoped to discuss these applications in later papers.

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