397. *The Extent of Dissociation of Salts in Water. Part VIII. An Equation for the Mean Ionic Activity Coefficient of an Electrolyte in Water, and a Revision of the Dissociation Constants of Some Sulphates.*

By CECIL W. DAVIES.

An empirical extension of the Debye–Hückel limiting activity equation is proposed. A survey of all the available data for electrolytes in water at 25° shows that the equation is in good agreement with the actual values of the mean ionic activity coefficient in dilute solutions, the average deviation being about 2% in 0·1M-solution and proportionately less at lower concentrations.

The equation is applied to the activity data for zinc and cadmium sulphates, and dissociation constants are derived for these salts which agree with the values obtained from conductivity measurements.

SOME years ago (Banks, Righellato, and Davies, *Trans. Faraday Soc.*, 1931, **27**, 621) the activity data then available for ternary electrolytes in water were reviewed, and it was noted that the experimental activity coefficients ($\gamma_{\pm}$) fail to satisfy a fundamental requirement of the Debye–Hückel theory for completely dissociated electrolytes, in that they differ considerably from each other even at quite low concentrations. Thus in 0·01 molal solution the stoicheiometric activity coefficient of barium chloride is 0·724, of lead chloride 0·612, and of cadmium chloride 0·475, and the values for lead and barium nitrates and sodium sulphate fall between these extreme limits. It was also pointed out that on the evidence of conductivities none of these salts with the possible exception of barium chloride could be considered as completely dissociated, and it was shown that when the activity data are corrected for incomplete dissociation the mean ionic activity coefficients ($f_{\pm}$) derived for the different salts lie very close to a common curve up to an ionic strength of 0·1 or somewhat higher.

A similar type of departure from the requirements of the simple theory occurs amongst solubility measurements, where it is commonly found that the solubility of a salt is markedly dependent on the nature, as well as on the concentration and valency type, of added salts, and here also it has been shown (see J., 1935, 1416; this vol., p. 273) that corrections for ionic association have the effect of almost entirely eliminating the individual deviations.

It seemed likely, therefore, that an equation could be derived which could be relied upon, in the absence of experimental data, to express within specified limits of uncertainty the mean ionic activity coefficient of any electrolyte in water at fairly low ionic strengths. As such an equation would be of considerable practical value, the available data have been reviewed, and the results are summarised in the next section. In a later section the new results are applied to some bi-bivalent salts.

An Equation for the Mean Ionic Activity Coefficient.

The equation proposed for the mean ionic activity coefficient of an electrolyte in water at 25° is:

$$-\log f_{\pm} = 0{\cdot}50 z_1 z_2 \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0{\cdot}20 I \right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where z_1, z_2 are the valencies of the constituent ions and I is the ionic strength. The equation is approximate and is not intended for use at high ionic strengths, and so may be applied equally to data expressed either in mols. per litre or in mols. per kg. of water. At sufficiently high dilutions it reduces to the Debye–Hückel limiting formula.

An equation of similar form has been used by Guggenheim (*Phil. Mag.*, 1935, **19**, 588; 1936, **22**, 322), who has shown that if in place of the constant 0·20 in equation (1) there is an adjustable parameter which varies from salt to salt, the formula accurately expresses the stoicheiometric activity coefficients of both completely and incompletely dissociated salts up to $I = 0{\cdot}1$. Equation (1), on the other hand, contains no adjustable term, and although its accuracy does not approach that of the Guggenheim equation, its relative success shows that of all the factors that account for the individual differences observed in the thermodynamic properties of salt solutions, the most important, on the whole, is the effect of ion association; the others either do not exert a very great influence on the activity coefficient below an ionic strength of 0·1, or influence it to approximately the same extent for all electrolytes.

Table I shows the application of the equation to the ternary electrolytes previously discussed (*loc. cit.*); $f_{\pm}$ is the experimental mean ionic activity coefficient, and Δ is the amount by which this is greater than the value given by equation (1).

Table II gives the more recent measurements of Harned and Fitzgerald (*J. Amer. Chem. Soc.*, 1936, **58**, 2624) for cadmium chloride. The first two columns show the experimental results, $(1 - \alpha)$ is the fraction of cadmium in the form of the intermediate ion $CdCl^{\cdot}$, obtained from conductivity measurements at 18° (*loc. cit.*), and the other symbols are as before.

In addition to these results for single salts, two series of measurements are available from which the mean ionic activity coefficient of a ternary electrolyte in the presence of other salts can be calculated. These are the measurements of Macdougall and Davies (J., 1935, 1416) and of Wise and Davies (this vol., p. 273) of the solubilities of barium and

TABLE I.

Calcium chloride	I	0·006	0·015	0·03	0·06	0·15	0·3
	$f_\pm$	0·850	0·784	0·724	0·658	0·570	0·515
	Δ	0·000	+0·001	+0·002	+0·004	+0·006	+0·007
Barium chloride	I	0·006	0·015	0·03	0·06	0·15	0·3
	$f_\pm$	0·850	0·784	0·724	0·655	0·561	0·494
	Δ	0·000	+0·001	+0·002	+0·001	−0·003	−0·014
Lead chloride	I	0·005656	0·01334	0·02474	0·04456		
	$f_\pm$	0·852	0·792	0·745	0·675		
	Δ	−0·001	−0·001	+0·005	−0·008		
Lead nitrate	I	0·01416	0·02730	0·05180	0·1167	0·2114	
	$f_\pm$	0·819	0·764	0·696	0·601	0·530	
	Δ	+0·031	+0·033	+0·028	+0·014	−0·004	
Barium nitrate	I	0·01452	0·02846	0·05512	0·1279	0·2352	
	$f_\pm$	0·789	0·733	0·670	0·584	0·519	
	Δ	+0·008	+0·006	+0·007	+0·006	−0·006	
Sodium sulphate	I	0·01457	0·02894	0·05712	0·1383	0·2688	
	$f_\pm$	0·806	0·719	0·645	0·583	0·502	
	Δ	+0·020	−0·006	−0·013	+0·012	−0·014	

TABLE II.

Cadmium chloride.

m.	$\gamma_\pm$.	$(1 - \alpha)$.	I.	$f_\pm$.	Δ.
0·002	0·7311	0·202	0·005192	0·851	−0·007
0·005	0·6113	0·345	0·01155	0·799	−0·005
0·007	0·5653	0·402	0·01537	0·779	−0·002
0·01	0·5140	0·462	0·02076	0·753	+0·002

calcium iodates in salt solutions. The figures for barium iodate are given in Table III; the results have been re-extrapolated so that the value for the saturated solution in pure water shall be in agreement with equation (1) (giving $S_0 = 1·498 \times 10^{-9}$).

TABLE III.

Barium iodate.

KCl solutions.			KNO$_3$ solutions.			KClO$_4$ solutions.		
I.	$f_\pm$.	Δ.	I.	$f_\pm$.	Δ.	I.	$f_\pm$.	Δ.
0·00346	0·882	0·000	0·00345	0·884	+0·002	0·00658	0·842	−0·002
0·00449	0·868	0·000	0·00448	0·869	+0·002	0·01153	0·806	+0·001
0·00604	0·849	−0·001	0·00602	0·850	0·000	0·03807	0·701	+0·004
0·00759	0·834	0·000	0·00755	0·835	0·000	0·07840	0·633	−0·003
0·01017	0·812	−0·001	0·01008	0·815	+0·001			
0·01272	0·795	−0·001	0·01261	0·795	−0·002	CaCl$_2$ solutions.		
0·02289	0·744	−0·003	0·02269	0·747	0·000	0·00878	0·829	+0·005
0·05328	0·661	−0·005	0·05193	0·671	+0·002	0·01764	0·774	+0·004
0·1037	0·589	−0·010	0·1001	0·593	−0·009	0·03273	0·714	0·000

Table IV gives the results for calcium iodate, shown in the same way ($S_0 = 7·119 \times 10^{-7}$)

TABLE IV.

Calcium iodate.

I.	$f_\pm$.	Δ.	I.	$f_\pm$.	Δ.	I.	$f_\pm$.	Δ.
Water.			KCl solutions.			K$_2$SO$_4$ solutions.		
0·02257	0·748	(0·000)	0·03642	0·706	+0·003	0·03845	0·698	0·000
			0·05009	0·672	+0·001	0·05523	0·660	−0·002
			0·07690	0·627	−0·001	0·07215	0·630	−0·005
			0·1296	0·569	−0·008	0·08916	0·607	−0·006
NaCl solutions.			CaCl$_2$ solutions.			MgSO$_4$ solutions.		
0·03686	0·707	+0·005	0·03765	0·706	+0·006	0·04248	0·687	−0·001
0·04998	0·676	+0·004	0·08959	0·621	+0·009	0·06017	0·654	+0·001
0·07671	0·632	+0·003	0·08994	0·611	−0·002	0·07680	0·630	+0·001
0·1293	0·576	−0·001	0·1623	0·563	+0·006	0·09256	0·612	+0·002

A review of Tables I—IV shows that for the more reliable data the value of Δ rarely exceeds 0·006 at ionic strengths in the neighbourhood of 0·1, and that for the few measurements at more than double this ionic strength the average deviation, without regard to sign, is 0·008. Where large deviations are found there are reasons to suspect the accuracy of the data; for lead nitrate the large errors may be attributed to the method of extrapolating the experimental results (cf. Guggenheim; Harned and Fitzgerald; *locc. cit.*), and the large alternating positive and negative deviations found in the isolated case of sodium sulphate suggest inaccuracies in the experimental data or calculations. Excluding these two series, the average deviation for 192 measurements below $I = 0{\cdot}2$ is $0{\cdot}002_8$, and the average deviation for 17 measurements in the range $I = 0{\cdot}08$—$0{\cdot}15$ is $0{\cdot}004_8$ which corresponds to considerably less than 1% in the value of $f_\pm$. It may be concluded that equation (1) holds good for ternary electrolytes with an accuracy of at least 1% in the value of $f_\pm$ up to $I = 0{\cdot}1$, and that beyond this the error will probably increase in proportion to the ionic strength, as has been found for other equations connecting activity coefficient and concentration (see Guggenheim, *loc. cit.*, 1935).

For uni-univalent electrolytes the most reliable data have been collected by Guggenheim (*loc. cit.*, 1936, p. 334). As most of these electrolytes are completely dissociated, the stoicheiometric activity coefficients given by this author are also the mean ionic activity coefficients. In a few cases, however, allowances for ionic association are necessary; these are shown in Table V, calculated from the relation $f_\pm = \gamma_\pm/\alpha$, where α, the degree of dissociation, has previously been derived from conductivity measurements (*Trans. Faraday Soc.*, 1927, **23**, 351; 1931, **27**, 621). Combining these figures with the others given by Guggenheim, we have 20 values for $f_\pm$ at each concentration. Of these, the results for the iodates are quite abnormal, both in their being so low and in their being identical for the sodium and potassium salts; remembering that they are the earliest measurements considered, and that the iodates of calcium and barium were found to be quite normal, we have some grounds for excluding them from the comparison. For the other 18 electrolytes the values of $f_\pm$ at an ionic strength of approximately 0·1 vary from 0·752 to 0·818; the value given by equation (1) is 0·776, and the average deviation of the calculated from the experimental values of $f_\pm$ is 0·017, or 2% of the value of $f_\pm$. The average error in the calculated value is therefore more than twice as great as with the ternary electrolytes at the same ionic strength. At an ionic strength of 0·04 the calculated value is 0·833, the experimental values vary from 0·828 to 0·851, and the average deviation is 0·CC6, about the same as with ternary electrolytes of the same molar concentration but three times the ionic strength. If we are correct in regarding the dissociation constants as taking into account the short-range forces between ions, and equation (1) as covering the long-range Coulomb forces, the specific effects of the various ions, which are usually attributed to differences in dielectric constant and in solvation effects, are reflected in the foregoing treatment in the reported deviations from equation (1); and it would appear that these depend in magnitude on the concentration of the ions and are little influenced, on the whole, by their valencies. The number of measurements considered is perhaps not large enough, however, for great reliance to be placed on this generalisation.

TABLE V.

	$NaClO_3$.	$KClO_3$.	$NaNO_3$.	KNO_3.	$NaIO_3$.	KIO_3.	
$\gamma_\pm$	0·764	0·734	0·758	0·723	0·700	0·700	at $I = 0{\cdot}1$
α	0·986	0·968	0·985	0·961	0·984	0·976	
$f_\pm$	0·775	0·758	0·770	0·752	0·711	0·717	
$\gamma_\pm$	0·828	0·815	0·825	0·810	—	—	at $I = 0{\cdot}04$
α	0·992	0·980	0·992	0·978	—	—	
$f_\pm$	0·835	0·832	0·832	0·828	—	—	

Very few measurements are available for the mean ionic activity coefficients of electrolytes of other types. The only data for a bi-bivalent electrolyte are those derived for barium oxalate in the following paper, where it is shown that these are in satisfactory agreement with equation (1) up to the highest ionic strength measured, *viz.*, 0·1225.

The only other suitable data available are some measurements by LaMer, King, and Mason (*J. Amer. Chem. Soc.*, 1927, **49**, 363) of the solubility of the ter-tervalent salt luteocobaltic ferricyanide in salt solutions. The stoicheiometric activity coefficients derived from these measurements are shown in Table VI. It is impossible to calculate the corresponding mean ionic activity coefficients, as the dissociation constants of the salts involved are not known; it is only possible to say that they will be larger than the $\gamma_{\pm}$ values, but that the corrections are not likely to be very important on account of the extremely small solubility of the saturating salt and the low concentration at which the tervalent ions can interact with the added salt. The last line of the table compares the $\gamma_{\pm}$ values with the values given by equation (1), which here has the form $-\log f_{\pm} = 4{\cdot}5\sqrt{I}/(1 + \sqrt{I}) - 0{\cdot}9I$; the differences except at the lowest concentrations are all negative, as they should be, and are of reasonable magnitude, so that, so far as can be judged, the equation survives this very drastic test satisfactorily.

TABLE VI.

I	0·00079	0·00133	0·00339	0·00548	0·01059	0·02080
$\gamma_{\pm}$	0·767	0·670	0·577	0·459	0·373	0·277
$\gamma_{\pm} - f_{\pm}$ calc.	+0·014	−0·023	+0·007	−0·036	−0·015	−0·006
I	0·03105	0·05144	0·06160	0·07187	0·1026	
$\gamma_{\pm}$	0·210	0·156	0·137	0·117	0·085	
$\gamma_{\pm} - f_{\pm}$ calc.	−0·016	−0·008	−0·007	−0·013	−0·015	

It can be concluded from this survey of the data that, where the mean ionic activity coefficient of an electrolyte is unknown, it can be calculated from equation (1) with an uncertainty not greatly exceeding 2% at a concentration of 0·1M, and proportionately less at lower ionic strengths; at higher concentrations the equation is of little value, as specific effects become too great to be ignored. That this degree of accuracy is sufficient for many purposes, and that the equation enables measurements in different fields to be correlated successfully, is shown in the next section.

The Dissociation Constants of some Sulphates.

In Part I (1927, *loc. cit.*) the dissociation constants of some bi-bivalent salts at 18° were derived. The method was to calculate the extent of ion association from the conductivity measurements of Kohlrausch (see Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454), and then to extrapolate to zero ionic strength by plotting $\alpha^2 m/(1 - \alpha)$ against the square root of αm and drawing the best straight line through the points. This line in every case had a greater slope than that given by the Debye–Hückel activity formula, and now that the validity of the latter as a limiting equation is established, it is clear that the dissociation constants reported were somewhat too low, and that the conductivity results were probably affected by some small errors. Sources of error that might reasonably be expected to have a significant effect at the two or three lowest concentrations measured (up to $m = 0{\cdot}00025$) are inaccuracies in the solvent correction (see Davies, "Conductivity of Solutions," 1933, p. 73), and hydrolysis.

The data have therefore been reconsidered by a modified procedure which enables less weight to be attached to the doubtful measurements at the lowest concentrations. Instead of using the Onsager limiting formula $\Lambda_0 - \Lambda_x = b\sqrt{I}$, the mobility changes have been calculated from the equation $\Lambda_0 - \Lambda_x = b\sqrt{I}/(1 + \sqrt{I})$; this equation is found to fit the data of Shedlovsky for potassium, sodium, lithium, and hydrogen chlorides (*J. Amer. Chem. Soc.*, 1932, **54**, 1411), and those of Shedlovsky and Brown (*ibid.*, 1934, **56**, 1066) for calcium, magnesium, and strontium chlorides up to $I = 0{\cdot}02$ with an accuracy of at least 2% in the value of $\Lambda_0 - \Lambda_x$; and although its form cannot be justified theoretically, it is undoubtedly sufficiently accurate for our purpose, and enables the six conductivity measurements up to $c = 0{\cdot}005$ to be taken into account instead of only the three lowest concentrations for which the limiting equation is approximately valid. Similarly, the mean ionic activity coefficient was calculated from equation (1). Λ_0 was obtained by an extrapolation method described in a previous paper (J., 1933, 645). The results are in Table VII. They are all somewhat higher than those previously derived. The mean dissociation constants, the values shown in parentheses being neglected, are: $MgSO_4$, $0{\cdot}007_8$; $CuSO_4$, $0{\cdot}005_0$; $CdSO_4$, $0{\cdot}004_9$; $ZnSO_4$, $0{\cdot}005_3$.

TABLE VII.

c.	0·0001.	0·0002.	0·0005.	0·001.	0·002.	0·005.
	Magnesium sulphate. $\Lambda_0 = 112·7$. $b = 202·6$.					
Λ	109·80	108·01	104·15	99·85	94·12	84·53
α	0·999	0·993	0·977	0·958	0·931	0·888
$10^3 . K$	—	(12)	8·1	7·5	7·6	8·1
	Copper sulphate. $\Lambda_0 = 113·5$. $b = 203·1$.					
Λ	109·85	107·89	103·50	98·52	91·92	80·98
α	0·993	0·985	0·964	0·938	0·901	0·839
$10^3 . K$	(6·3)	5·4	4·8	4·8	4·9	5·1
	Cadmium sulphate. $\Lambda_0 = 112·6$. $b = 202·6$.					
Λ	109·74	107·54	102·87	97·68	90·90	79·70
α	0·999	0·990	0·966	0·938	0·899	0·833
$10^3 . K$	—	(8·2)	5·1	4·8	4·8	4·9
	Zinc sulphate. $\Lambda_0 = 113·3$. $b = 203·0$.					
Λ	109·6	107·64	103·44	98·54	92·18	81·90
α	0·992	0·985	0·965	0·940	0·906	0·852
$10^3 . K$	(5·8)	5·3	5·1	5·1	5·2	5·7

Dissociation constants for cadmium and zinc sulphates can also be calculated from the stoicheiometric activity coefficients obtained by LaMer and Parks (*J. Amer. Chem. Soc.*, 1931, **53**, 2040), and Cowperthwaite and LaMer (*ibid.*, p. 4333), by electrometric measurements. The stoicheiometric and mean ionic activity coefficients are related by the equation: $\gamma_\pm = \alpha f_\pm$, so that if $f_\pm$ is assumed to be given by equation (1), α can be found by a method of successive approximations. The dissociation constant is then given by $K = \gamma_\pm{}^2 m/(1 - \alpha)$, if we assume, as before, that the activity coefficient of the undissociated part of the salt is unity in dilute solutions. The results of this treatment are given in Table VIII.

TABLE VIII.

			Cadmium sulphate.					
m	0·0005	0·001	0·003	0·005	0·01	0·03	0·05	
$\gamma_\pm$	0·774	0·699	0·551	0·476	0·383	0·254	0·199	
α	0·935	0·905	0·825	0·783	0·730	0·644	0·574	
$10^3 . K$	4·6	5·1	5·2	5·2	5·4	5·4	4·7	Mean 5·1
			Zinc sulphate.					
m	0·0005	0·001	0·002	0·005	0·01			
$\gamma_\pm$	0·780	0·700	0·608	0·477	0·387			
α	0·943	0·906	0·860	0·785	0·740			
$10^3 . K$	5·4	5·2	5·3	5·3	5·7	Mean 5·4		

The constancy of these K values provides further support for equation (1), on which they are based. As regard their magnitudes, it will be seen that they agree, within experimental error, with the dissociation constants reported in Table VII and derived by a totally different method. The comparison is not strictly justifiable, since the activity data refer to 25° and the conductivity measurements were at 18°, but the errors, especially in the conductivity figures and their treatment, are so large as to mask any probable change in dissociation constant over a small temperature interval.

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