[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WESTERN AUSTRALIA, AND THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

Ionic Hydration and Activity in Electrolyte Solutions

BY R. H. STOKES[1a] AND R. A. ROBINSON[1b]

General Introduction

There are two useful lines of approach to the problem of explaining activity data in electrolyte solutions. The first is to extend the treatment of Debye and Hückel (which was developed for dilute solutions) to moderately high concentrations by applying relevant "corrections." This method has received a great deal of attention in the past twenty years or so. The other is to examine data for very concentrated solutions, where the Debye-Hückel treatment is certainly not applicable, seeking relationships which may throw light on the general problem. In this paper it is shown that the concept of ion–solvent interaction, or ionic hydration, is capable of explaining quantitatively a large body of experimental observations in both cases. Part I discusses a modified form of the Debye–Hückel equation, introducing the effect of ion–solvent interaction in terms of "hydration," which is applicable up to ionic strengths of about 4. In Part II the effect of the solvent at concentrations above about 12 *M* is approached in another way, similar to that of the Brunauer–Emmett–Teller adsorption isotherm.

I. A One-parameter Equation for Activity Coefficients.—The evaluation by Debye and Hückel[1c] of the free energy change due to the coulomb forces between ions led to a tremendous expansion of our understanding of the behavior of electrolyte solutions. There is now no doubt that the familiar Debye–Hückel expression

$$\log f = -\frac{A\sqrt{c}}{1 + B\mathring{a}\sqrt{c}} \qquad (1)$$

gives an adequate representation of the activity coefficients of normally dissociated salts of 1:1 and 2:1 valence types in sufficiently dilute solutions, in terms of the single arbitrary parameter å (the mean distance of "closest approach" of the ions), and the volume concentration c. Equation (1) however predicts an activity coefficient which is always a decreasing function of the concentration, whereas experimentally a minimum usually occurs, followed by a more or less rapid rise of the activity coefficient at high concentrations. Hückel[2] explained this effect in terms of the change in dielectric constant of the solvent near the ions, which led to a second arbitrary constant D in the equation

$$\log f = -\frac{A\sqrt{c}}{1 + B\mathring{a}\sqrt{c}} + Dc \qquad (2)$$

Equation (2) has been of great practical value, and has been extensively employed for the extrapolation of standard potentials and for the representation of activity coefficient data.[3] Its theoretical foundations have, however, been frequently criticized. Furthermore, it usually fails to give a reasonably accurate representation of observed activity coefficients at ionic strengths much greater than unity. To overcome this, further arbitrary terms in c^2 and even higher powers are sometimes introduced, but such equations are of no theoretical value.

In recent years our knowledge of activity coefficients in concentrated solutions has been greatly extended, mainly through the application of the isopiestic vapor pressure technique. It has become increasingly clear, especially in the case of 2:1 electrolytes, that any treatment of the properties of concentrated solutions must take specific account of the hydration of the ions. There seems to be no adequate alternative explanation of the fantastically high activity coefficients often encountered at high concentrations. For instance, a 5 *M* solution of magnesium iodide at 25° has a stoichiometric activity coefficient of over 100, while that of 5 *M* sodium chloride is only 0.874. The first formally correct treatment of the effect of hydration on the activity coefficient appears to have been given by Bjerrum,[4] a few years before the appearance of the Debye–Hückel theory. Apart from recognition by Scatchard[5] in connection with hydrochloric acid, and an important discussion of a "hydration–association" model for electrolytes by Frank,[6] the subject does not appear to have been accorded the attention which its importance warrants in this connection. It will now be shown that by allowing for the ion-solvent interaction in terms of a simple hydration model it is possible to obtain as a first step a two-parameter equation, and by a slight elaboration of the model a one-parameter equation, which will represent the experimental activity coefficients up to remarkably high concentrations. These equations are derived and tested for a large number of salts in aqueous solution at 25°.

The "Hydration Correction" to the Activity Coefficient.[7]—The concentrations, activities, etc., of the hydrated solute will be distinguished by primed symbols, the corresponding "apparent" quantities (computed with neglect of hy-

---

[1a] Present address: Physical Chemistry Laboratories, Free School Lane, Cambridge, England.

[1b] Present address: Chemistry Department, Raffles College, Singapore.

[1c] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

(2) E. Hückel, *ibid.*, **26**, 93 (1925).

(3) See, *e. g.*, R. A. Robinson and H. S. Harned, *Chem. Rev.*, **28**, 420 (1941).

(4) N. Bjerrum, *Medd. Vetenskapsakad. Nobelinst.*, **5**, 1 (1919).

(5) G. Scatchard, THIS JOURNAL, **47**, 2098 (1925).

(6) H. S. Frank, *ibid.*, **63**, 1789 (1941).

(7) This treatment leads to a result equivalent to that of Bjerrum, though by a somewhat different route.

dration) being denoted by the usual unprimed symbols. Let 1 molecule of solute give rise in solution to ν ions. We shall now assume that the total interaction between these ν ions and the surrounding solvent, ***in all cases where this interaction is significantly large compared to*** kT, can be allowed for as a "binding" of n molecules of water in their "hydration shells." We need not at this stage discuss the manner in which this "bound" water is shared between anions and cations.

Then in a solution of molality, m, there are nm molecules of "bound" water to $(55.51 - nm)$ molecules of "free" water. The "true" molality m' (moles of hydrated solute per 1000 g. of "free" water) is therefore

$$m' = \frac{55.51\ m}{55.51 - nm} = \frac{m}{1 - 0.018\ nm} \qquad (3)$$

Then if a' be the activity of the hydrated solute, and a that of the water, the Gibbs–Duhem relation becomes

$$\mathrm{d} \ln a' = -(55.51/m')\ \mathrm{d} \ln a_\mathrm{w}$$

This is equally as valid as the ordinary form using the stoichiometric molality and activity, computed with disregard of hydration

$$\mathrm{d} \ln a = -\ (55.51/m)\ \mathrm{d} \ln a_\mathrm{w}$$

Hence, introducing the mean molal activity coefficients γ' and γ, we have

$$\mathrm{d} \ln \gamma' = -\ (55.51/\nu m')\ \mathrm{d} \ln a_\mathrm{w} - \mathrm{d} \ln m' \qquad (4)$$

and

$$\mathrm{d} \ln \gamma = -\ (55.51/\nu m)\ \mathrm{d} \ln a_\mathrm{w} - \mathrm{d} \ln m \qquad (5)$$

from which by substituting for m' from (3) we obtain

$$\begin{aligned} \mathrm{d} \ln \gamma' &= -\ (55.51/\nu m)\ (1 - 0.108nm)\ \mathrm{d} \ln a_\mathrm{w} \\ &\quad - \mathrm{d} \ln m + \mathrm{d} \ln (1 - 0.018nm) \\ &= \mathrm{d} \ln \gamma + (n/\nu)\ \mathrm{d} \ln a_\mathrm{w} + \mathrm{d} \ln (1 - 0.018nm). \end{aligned}$$

Upon integrating between molalities zero and m we obtain, remembering that both γ and γ' must approach unity at zero concentration

$$\ln \gamma' = \ln \gamma + (n/\nu) \ln a_\mathrm{w} + \ln (1 - 0.018nm) \qquad (6)$$

We shall, however, be concerned rather with the mean *rational* activity coefficient of the hydrated solute, f'. This is clearly related to γ' by the equation

$$\ln f' = \ln \gamma' + \ln (1 + 0.018\nu m') \qquad (7)$$

which is the analog of the familiar (unprimed) equation established by Scatchard[5] for the unhydrated case. Combining (7) with (6), and simplifying with the aid of (3) we obtain

$$\ln \gamma = \ln f' - (n/\nu) \ln a_\mathrm{w} - \ln [1 - 0.018(n - \nu)m] \qquad (8)$$

This gives a relation between the observed stoichiometric activity coefficient and the rational activity coefficient of the hydrated solute, in terms of the "hydration parameter" n.[8]

Application of Equation (8) to the Debye–Hückel Theory.—In order to fit equations (1) or (2) to observed activity coefficients, it is in general necessary to use values of the "mean distance of closest approach of the ions," $\mathring{a}$, which are substantially larger than the known crystallographic radius sums of the ions. This is very reasonably attributed to hydration of the ions. Consequently we should surely regard the Debye–Hückel treatment as predicting the activity coefficient of the *hydrated* ions, *i. e.*, the f' of equation (8). If the hydration effect is alone responsible for the observed increase in the activity coefficient, activity coefficients in water at 25° should be capable of representation by the equation

$$\log \gamma = -\ \frac{0.5092 z_1 z_2 \sqrt{\mu}}{1 + 0.3286\mathring{a}\sqrt{\mu}} - \frac{n}{\nu} \log a_\mathrm{w} - \log [1 - 0.018(n - \nu)m] \qquad (9)$$

where we have replaced the term $\log f'$ by the Debye–Hückel expression (1), using the modern values[9] of the physical constants involved. Here z_1 and z_2 are the valencies, μ is the ionic strength in volume units, and $\mathring{a}$ is to be expressed in ångström units. The three terms on the right of (9) may conveniently be called the "*D–H* term," the "solvent term," and the "scale term," respectively. The *D–H* term is always negative, and the solvent term is always positive since $a_\mathrm{w} < 1$. The scale term is positive, zero, or negative according as $n > \nu$, $n = \nu$, or $n < \nu$. The importance of the solvent term has often been overlooked in discussion of hydration effects. In point of fact the scale term and the solvent term are usually of the same order of magnitude.

Equation (9) still contains two adjustable parameters, a and n. In this form it proves to be capable of representing observed activity coefficients with an accuracy about as good as that of equation (2), but over a much wider range of concentration, extending in many cases to an ionic strength of 5. Its superiority to equation (2) is especially evident in the case of 2:1 halides, where equation (2) generally fails at an ionic strength of about 1 (*i. e.*, about 0.3 *M*). In Table I are listed the n and $\mathring{a}$ values giving the best fits to the experimental γ values, with the range of validity and the average and maximum deviations. The concentrations at which the comparisons are made are those listed in Tables II and III in connection with the one-parameter equation. The experimental activity coefficients with which the comparisons are made are mainly values which we have recently recomputed from our isopiestic measurements, using the most recent standard data for the reference solutions.[10,11] These activity coefficients are also listed in Tables II and III. Those of hydrochloric and hydrobromic acids are from the compilation by Harned and

---

(8) If we allow for a possible variation of n with concentration, we must replace $(n/\nu) \ln a_\mathrm{w}$ by $\int_0^m \frac{n}{\nu}\, \mathrm{d} \ln a_\mathrm{w}$.

(9) G. G. Manov, *et al.*, THIS JOURNAL, **65**, 1765 (1943).

(10) R. A. Robinson, *Trans. Roy. Soc., New Zealand*, **75** [II], 203 (1945).

(11) R. H. Stokes, *Trans. Faraday Soc.*, **44**, in press (1948).

Owen.[12] These activity coefficients are listed in Tables II and III in connection with the one-parameter equation now to be developed. The solvent term $-n/\nu \log a_w$ can *in principle* be computed from the values of f' for a given n and $\mathring{a}$, but such a procedure would be extremely arduous from the computational point of view. This term has therefore been evaluated from the experimental osmotic coefficients ϕ, since for aqueous solutions, by definition

$$-1/\nu \log a_w = 0.007824 m\phi$$

The One-parameter Equation.—Examination of the n and $\mathring{a}$ values of Table I shows that the $\mathring{a}$ values are much the same as those normally needed in equation (2). The n values, however, are substantially greater than the values we might expect to find on current ideas of hydration, which are largely based on the treatment by Bernal and Fowler[13] of the apparent molal volumes in dilute solutions. Furthermore they do not depend only on the cation as we should at first sight expect if we accept those authors' view that the large anions Cl^-, Br^- and I^- are unhydrated.

We are inclined to accept the idea that it is the cations rather than the anions which are hydrated, especially as it has been shown[13a] by comparing the activity coefficients of the pairs: calcium chloride–sodium sulfate, lanthanum chloride–potassium ferricyanide and thorium nitrate–potassium ferrocyanide, that polyvalent cations lead to high activity coefficients and polyvalent anions to low coefficients. We wish to emphasize, however, that our n is not the same thing as the conventional number of water molecules in the first layer round the ion. It is rather a number introduced to allow for the average effect of all ion–solvent interactions where these are large compared to kT, and may therefore very well contain contributions from solvent molecules outside the first layer. The feature of Table I which does seem difficult to explain is the *increase* of n with increasing anion size, for a given cation. Even this is, however, not necessarily impossible, when we consider that in the concentration range considered the water molecules are not bound simply by the fields of isolated ions, but rather by the resultant field of an ion and its neighbors, which of course depends on their dimensions.

It is clear from Table I that there is some sort of connection between the n and $\mathring{a}$ values, which in general increase together. $\mathring{a}$ is to be interpreted as the closest distance to which the center of the (unhydrated) anion can approach that of the (hydrated) cation. We may estimate the size of the cation from the n value as follows: From the density of pure water, we know that a "normal" water molecule occupies at 25° an effective volume of 30.0 cubic ångström units. Round the smaller cations, however, there is, as Bernal and Fowler[13] have shown, a closer-packing effect which in many cases actually makes the apparent ionic volume of the cation negative. We can allow for this close-packing effect, as well as for the volume occupied by the cation itself, by putting the volume of the n-hydrated cation equal to $(30n + V_+)$, where V_+ is the apparent ionic volume of the cation (in cubic Å. per ion). In most cases V_+ is only a small fraction of $30n$, so that it need not be determined with great accuracy, and any variation of V_+ with concentration can be ignored. To estimate V_+ from the observed apparent molal volumes, we have fol-

TABLE I

CONSTANTS OF THE TWO-PARAMETER EQUATION (9), GIVING BEST FITS TO THE EXPERIMENTAL ACTIVITY COEFFICIENTS

Salt	n	$\mathring{a}$ (ångströms)	Range fitted (molality)	Average difference in γ	Maximum difference in γ
HCl	8.0	4.47	0.01–1.0	0.001	0.0025
HBr	8.6	5.18	.1–1.0	.001	.002
HI	10.6	5.69	.1–0.7	.002	.002
$HClO_4$	7.4	5.09	.1–2.0	.001	.003
$LiCl$	7.1	4.32	.1–1.0	.001	.002
$LiBr$	7.6	4.56	.1–1.5	.001	.002
LiI	9.0	5.60	.1–1.0	.003	.008
$LiClO_4$	8.7	5.63	.2–1.0	.003	.007
$NaCl$	3.5	3.97	.1–5.0	.002	.003
$NaBr$	4.2	4.24	.1–4.0	.001	.002
NaI	5.5	4.47	.1–1.5	.002	.004
$NaClO_4$	2.1	4.04	.2–4.0	.0015	.003
KCl	1.9	3.63	.1–4.0	.002	.003
KBr	2.1	3.85	.1–4.0	.0025	.004
KI	2.5	4.16	.1–4.0	.001	.002
$RbCl$	1.2	3.49	.1–1.5	.001	.002
$RbBr$	0.9	3.48	.1–1.5	.001	.001
RbI	0.6	3.56	.1–1.5	.005	.003
$MgCl_2$	13.7	5.02	.1–1.4	.001	.002
$MgBr_2$	17.0	5.46	.1–1.0	.002	.004
MgI_2	19.0	6.18	.1–0.7	.001	.002
$CaCl_2$	12.0	4.73	.01–1.4	.001	.002
$CaBr_2$	14.6	5.02	.1–1.0	.0005	.001
CaI_2	17.0	5.69	.1–0.7	.0005	.002
$SrCl_2$	10.7	4.61	.1–1.8	.001	.002
$SrBr_2$	12.7	4.89	.1–1.4	.0015	.002
SrI_2	15.5	5.58	.1–1.0	.001	.002
$BaCl_2$	7.7	4.45	.1–1.8	.001	.003
$BaBr_2$	10.7	4.68	.1–1.5	.001	.002
BaI_2	15.0	5.44	.1–1.0	.0025	.005
$MnCl_2$	11.0	4.74	.1–1.4	.001	.004
$FeCl_2$	12.0	4.80	.1–1.4	.002	.003
$CoCl_2$	13.0	4.81	.1–1.0	.001	.001
$NiCl_2$	13.0	4.86	.1–1.4	.0015	.003
$Zn(ClO_4)_2$	20.0	6.18	.1–0.7	.001	.003

The data of J. H. Jones, *J. Phys. Chem.*, **51**, 516 (1947), have been used for lithium and sodium perchlorate.

---

[12] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.

[13] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[13a] R. A. Robinson and B. J. Levien, *Trans. Roy. Soc. N. Z.*, **76**, 295 (1947).

lowed the procedure of Bernal and Fowler with slight modifications. The apparent molal volumes at 1*M* were computed from the density data of "International Critical Tables." It turns out that the values for cesium and rubidium chloride, bromide and iodide can be represented within a few per cent. by $V_{\text{app}} = 6.47(r_+^3 + r_-^3)$ cu. Å. per molecule, where r_+ and r_- are Pauling's[14] crystallographic radii (in Å.). The molal volumes in the solid state are also fairly close to this. Since these salts have anions and cations of not greatly differing sizes, it is reasonable to attribute to the anions in other salts a contribution of 6.47 r_-^3 cu. Å./ion toward the apparent molal volume. The contribution of the cation, including the closer-packing effect on the water, is then calculated as $V_+ = (V_{\text{app}} - 6.47 z_1 r_-^3)$ where z_1 is the cation valence.

We can now calculate a kind of "idealized" radius r_1 for the *n*-hydrated cation, given by $4/3\pi r_1^3 = 30n + V_+$. Upon adding r_1 to the crystallographic radius of the anion, we obtain an "idealized" distance of closest approach. When this calculation is carried out, we find a clear connection between these "idealized" distances and the $\mathring{a}$ values actually needed (Table I) for the best fit. The sum $(r_1 + r_-)$ exceeds $\mathring{a}$ by a matter of 0.7 Å. for the alkali halides and 1.3 Å. for the alkaline-earth halides. The variation in this difference from salt to salt is scarcely more than can be accounted for by the usual elasticity of a two-parameter equation. We can interpret this difference in two ways: as a penetration of the hydration shell of the cation by the anion (following a suggestion of Frank[6]) or as a distortion of the ions by the field. Either explanation will also cover the fact that the difference is nearly twice as great for doubly charged as for singly charged cations. It is to be noted that the three halide anions considered have radii varying only from 1.81 to 2.16 Å. so that we should expect them all to penetrate to much the same extent.

This admittedly empirical relation between *n* and $\mathring{a}$ turns out to be of sufficient accuracy to make possible the evaluation of $\mathring{a}$ from *n*, the densities of the solutions, and the known crystallographic radii of the ions. We therefore have the activity coefficient in terms of the single parameter *n*, as follows

$$\log \gamma = -\frac{0.5092 z_1 z_2 \sqrt{\mu}}{1 + 0.3296\sqrt{\mu}\left\{\left[\frac{3}{4\pi}(30n + V_+)\right]^{1/3} + r_- - \Delta\right\}} - (n/\nu)\log a_w - \log[1 - 0.018(n - \nu)m] \ldots \quad (10)$$

where $\Delta = 0.7$ Å. for the univalent halides and 1.3 Å. for the bivalent metal halides.

By choosing the appropriate value of *n* by a trial-and-error process, equation (10) will give a satisfactory representation of the observed activity coefficients (over a usefully wide range of concentrations) as shown in Tables II and III and Fig. 1.

It is noteworthy that in the majority of cases the equation breaks down when the product of *n* and the molality exceeds about 10 or 15. This is to be expected, as there are only 55.51 moles of water altogether for *m* moles of salt, and the effects of "competition" between neighboring ions of the same sign must become noticeable. To proceed to higher concentrations we would have to use an *n* which was a suitably decreasing function of concentration. It is important to note that when equation (10) begins to fail by more than 1% or so, the predicted γ values are *higher* than the experimental values, as a natural consequence of the use of too large an *n* value. The only exceptions to this last statement occur in the case of the rubidium halides, where the predicted γ values become too *low* above 2 *M*. Here of course the relation between *n* and $\mathring{a}$ is being stretched to rather absurd lengths, in treating the ions as spherical with such small *n* values as are needed. The activity coefficients of the cesium halides cannot be reconciled with equation (10); they are equally difficult to fit with the conventional equation (2), requiring $\mathring{a}$ values substantially *less* than the radius sums.

One cannot claim that the accuracy of fit obtainable with the one-parameter equation (10) is quite as good as can be done with equation (9) using two parameters; but it is at least able to predict activity coefficients within about twice the experimental error, and with an accuracy nearly always better than 1% up to remarkably high concentrations.

The simplicity of the physical model makes its success the more striking. Though there are many obvious criticisms which can be made, the empirical value of the one-parameter equation is clear from the figures, and is sufficient to justify the decidedly *ad hoc* arguments used in its development.

II. Water Activities in Very Concentrated Electrolyte Solutions.—In the course of isopiestic measurements on very concentrated calcium nitrate solutions it was found that, while the solution is saturated at 8.4 *M* at 25°[15] it readily supersaturates. These supersaturated solutions, on further concentration (by isothermal evaporation at 25°) pass into semi-solid gels. The transition from a freely flowing solution to a transparent, rigid gel is marked by no visible discontinuity, and the vapor pressure–concentration curve is also continuous. The measurements were extended to 21 *M*, at which concentration the clear homogeneous gel broke down into a striated form. Vapor pressure measurements were not made on these striated gels, because equilibrium was not reached sufficiently rapidly. These phenomena suggested the possibility that at high concentrations the system could be treated as an adsorbent (calcium nitrate)–adsorbate (water) system.

---

(14) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1944.

(15) H. Bassett and H. S. Taylor, *J. Chem. Soc.*, **101**, 576 (1912).

TABLE II

COMPARISON OF EXPERIMENTAL ACTIVITY COEFFICIENTS OF UNI-UNIVALENT HALIDES AT 25° WITH THOSE CALCULATED BY THE ONE-PARAMETER EQUATION (10)

The value of n is given below the formula of each salt. In all cases the "penetration distance" is taken as 0.7 Å.

	HCl		HBr		HI		LiCl		LiBr		LiI		NaCl		NaBr	
	n = 7.3		n = 8.6		n = 10.6		n = 6.5		n = 7.1		n = 10.0		n = 3.5		n = 4.15	
	(4.84)		(5.18)		(5.69)		(4.66)		(4.92)		(5.59)		(3.97)		(4.30)	
m	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
0.1	0.796	0.799	0.805	0.807	0.818	0.820	0.790	0.795	0.796	0.800	0.815	0.817	0.778	0.776	0.782	0.783
.2	.767	.770	.782	.784	.807	.806	.757	.762	.766	.770	.802	.800	.735	.731	.741	.742
.3	...	...	.778	.778	.811	.809	.744	.748	.756	.759	.804	.801	.710	.707	.719	.720
.5	.757	.758	.789	.789	.839	.838	.739	.741	.753	.759	.824	.824	.681	.679	.697	.698
.7	...	...	.815	.815	.883	.881	.748	.749	.767	.772	.852	.863	.667	.666	.689	.690
1.0	.809	.807	.871	.870	.963	.976	.774	.773	.803	.805			.657	.657	.687	.689
1.5	.896	.895					.838	.838	.895	.890			.656	.659	.703	.703
2.0	1.009	1.018					.921	.926	1.015	1.009			.668	.671	.731	.730
2.5									1.161	1.164			.688	.691	.768	.769
3.0													.714	.716	.812	.810
4.0													.783	.781	.929	.924
5.0													.874	.870		

	NaI		KCl		KBr		KI		RbCl		RbBr		RbI	
	n = 5.05		n = 1.9		n = 2.05		n = 2.45		n = 1.25		n = 0.9		n = 0.6	
	(4.73)		(3.63)		(3.84)		(4.20)		(3.47)		(3.48)		(3.56)	
m	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
0.1	0.787	0.791	0.770	0.767	0.772	.770	0.778	0.777	0.764	0.762	0.763	0.762	0.762	0.762
.2	.751	.755	.718	.716	.722	.721	.733	.731	.709	.708	.706	.707	.705	.708
.3	.735	.738	.688	.686	.693	.692	.707	.708	.675	.676	.673	.674	.671	.674
.5	.723	.725	.649	.649	.657	.658	.676	.675	.634	.635	.632	.632	.629	.632
.7	.724	.725	.626	.626	.636	.638	.660	.659	.608	.609	.605	.606	.602	.605
1.0	.736	.734	.604	.606	.617	.619	.645	.645	.583	.584	.578	.579	.575	.577
1.5	.771	.768	.583	.586	.600	.603	.637	.636	.559	.558	.551	.552	.547	.547
2.0	.820	.819	.573	.576	.593	.596	.637	.636	.546	.542	.536	.531	.533	.526
2.5	.883	.883	.569	.571	.593	.594	.644	.641						
3.0	.963	.962	.569	.571	.595	.596	.652	.650						
4.0			.577	.575	.608	.606	.673	.673						

The $\mathring{a}$ values given in parentheses for comparison with Table I are not parameters but are computed from n and the apparent ionic volumes.

TABLE III

COMPARISON OF EXPERIMENTAL ACTIVITY COEFFICIENTS FOR BI-UNIVALENT HALIDES AT 25° WITH THOSE CALCULATED BY THE ONE-PARAMETER EQUATION (10)

The value of n is given below the formula of each salt. In all cases the "penetration distance" is taken as 1.3 Å.

	$MgCl_2$ (4.99)		$MgBr_2$ (5.48)		MgI_2 (5.96)		$CaCl_2$ (4.75)		$CaBr_2$ (5.17)		CaI_2 (5.68)		$SrCl_2$ (4.60)		$SrBr_2$ (4.99)	
	n = 13.9		n = 17.0		n = 20.0		n = 11.9		n = 14.0		n = 17.0		n = 10.8		n = 12.4	
m	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
0.1	0.529	0.530	0.550	0.552	0.580	0.574	0.518	0.519	0.532	0.536	0.560	0.559	0.511	0.511	0.526	0.528
.2	.489	.489	.518	.523	.558	.555	.472	.472	.492	.497	.531	.531	.462	.461	.483	.485
.3	.477	.477	.517	.519	.567	.562	.455	.454	.482	.486	.531	.530	.442	.441	.468	.469
.5	.481	.481	.545	.546	.614	.613	.448	.448	.491	.494	.561	.560	.430	.430	.467	.469
.7	.506	.506	.599	.599	.698	.703	.460	.460	.522	.521	.614	.614	.434	.436	.484	.486
1.0	.570	.572	.723	.727			.500	.499	.597	.603	.741	.748	.461	.462	.535	.535
1.4	.709	.714					.587	.586					.524	.524	.643	.648
1.8							.712	.720					.614	.619		

	SrI_2 (5.55)		$BaCl_2$ (4.29)		$BaBr_2$ (4.77)		BaI_2 (5.51)		$MnCl_2$ (4.65)		$FeCl_2$ (4.75)		$CoCl_2$ (4.83)		$NiCl_2$ (4.83)	
	n = 15.5		n = 8.4		n = 10.3		n = 14.7		n = 11.4		n = 12.1		n = 13.0		n = 13.1	
m	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
0.1	0.553	0.552	0.500	0.496	0.513	0.516	0.542	0.548	0.516	0.514	0.518	0.518	0.522	0.523	0.522	0.523
.2	.520	.519	.444	.440	.465	.468	.509	.515	.469	.466	.473	.472	.479	.479	.479	.479
.3	.517	.514	.419	.415	.446	.448	.502	.508	.450	.446	.454	.454	.463	.464	.463	.464
.5	.536	.534	.397	.393	.435	.437	.523	.524	.440	.438	.450	.449	.462	.463	.464	.463
.7	.578	.577	.391	.388	.442	.443	.562	.561	.448	.447	.463	.462	.479	.481	.482	.482
1.0	.680	.680	.395	.395	.469	.469	.649	.650	.479	.479	.506	.504	.531	.533	.536	.535
1.4			.419	.420	.529	.528			.542	.550	.596	.594	.634	.644	.647	.650
1.8			.449	.458	.609	.615					.719	.731				

As in Table II the $\mathring{a}$ values in parentheses are not parameters but are computed from n and the apparent ionic volumes.

Experimental

Calcium nitrate from British Drug Houses, Limited, was recrystallized twice from water. Solutions, analyzed for calcium as carbonate, were equilibrated against sulfuric acid by the isopiestic method.[16] From the experimental results, given in Table IV, the osmotic and activity coefficients were evaluated (Table V) with the aid of the data

---

[16] R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

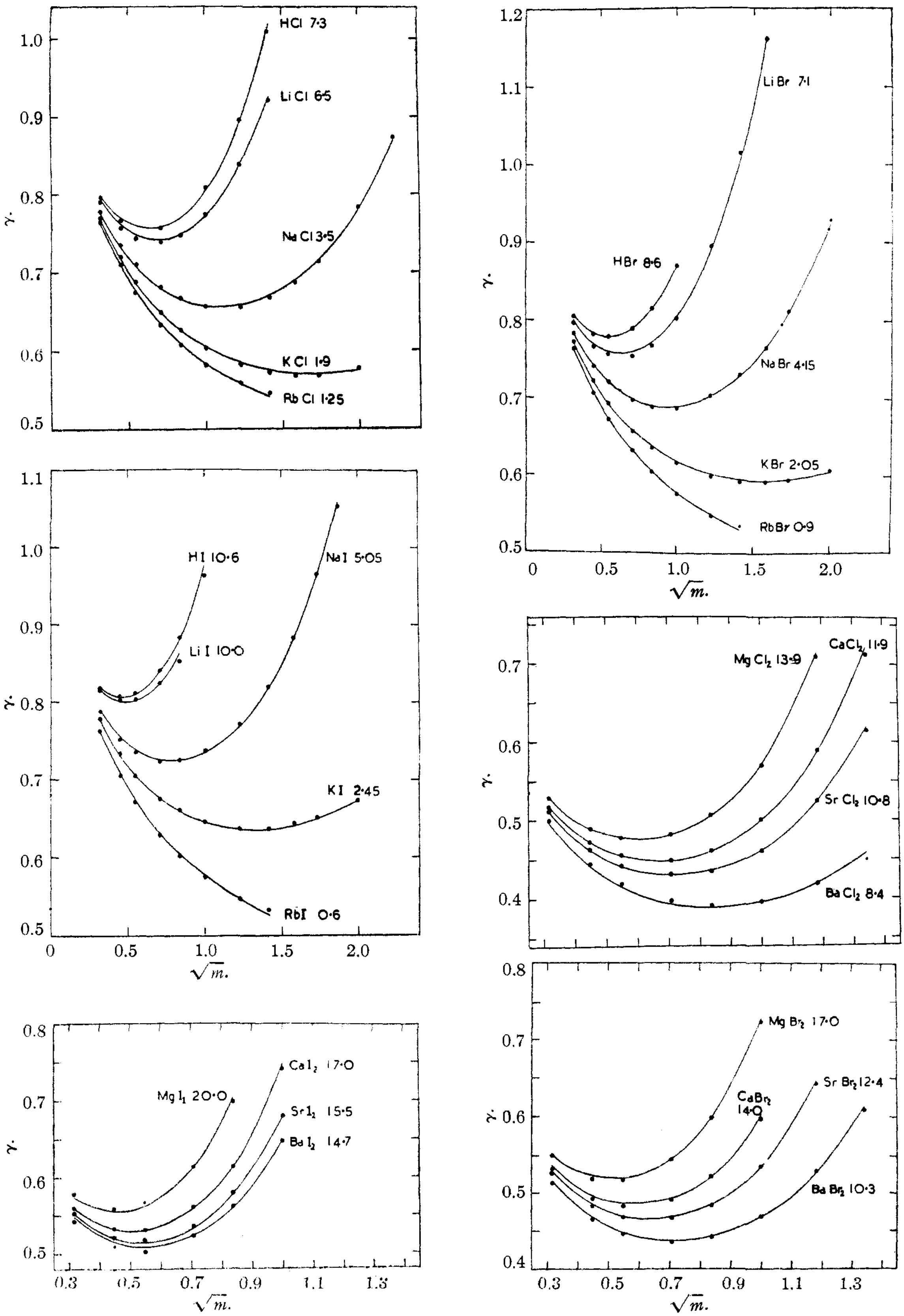

Fig. 1.—Comparison of experimental activity coefficients with those predicted by the one-parameter equation (10). The full curves are calculated from equation (10), using the value for the "hydration parameter" n following the formula of each salt. The circles give the experimental values. Diameter of circles equals 0.004 in γ.

for sulfuric acid.[17,18] Previous values[19] at concentrations up to 3 *M* have been recalculated to conform to more recent standards. Compared with such salts as calcium chloride low γ values are obtained for calcium nitrate over the whole concentration range. Thus at 6 *M* we find $\gamma_{Ca(NO_3)_2} = 0.592$, $\gamma_{CaCl_2} = 11.11$. This is consistent with the general behavior of bivalent metal nitrates, and is probably to be explained in terms of Bjerrum's ideas of ion-pair formation. It seems quite likely that at high concentrations the salt would be better formulated as $(CaNO_3)^+ \cdot NO_3^-$.

TABLE IV

ISOPIESTIC SOLUTIONS OF CALCIUM NITRATE AND SULFURIC ACID AT 25°

$M_{Ca(NO_3)_2}$	$M_{H_2SO_4}$	$M_{Ca(NO_3)_2}$	$M_{H_2SO_4}$	$M_{Ca(NO_3)_2}$	$M_{H_2SO_4}$	$M_{Ca(NO_3)_2}$	$M_{H_2SO_4}$
3.070	3.184	3.784	3.823	4.535	4.494	5.505	5.346
7.038	6.675	7.208	6.815	7.426	7.000	7.860	7.386
8.110	7.615	9.148	8.530	10.44	9.610	11.35	10.31
11.88	10.73	12.07	10.87	14.28	12.50	15.67	13.39
16.34	13.89	17.00	14.35	17.94	14.92	18.96	15.45
19.67	15.79	21.58	16.80				

TABLE V

OSMOTIC AND ACTIVITY COEFFICIENTS OF CALCIUM NITRATE AT 25°

M	φ	γ	*M*	φ	γ
0.1	0.827	0.485	4.0	1.157	0.435
.2	.819	.426	4.5	1.210	.469
.3	.818	.395	5.0	1.263	.507
.4	.821	.376	6.0	1.361	.592
.5	.825	.363	7.0	1.452	.690
.6	.831	.354	8.0	1.535	.801
.7	.837	.347	9.0	1.622	.935
.8	.843	.342	10.0	1.683	1.065
.9	.850	.338	11.0	1.722	1.184
1.0	.859	.336	12.0	1.759	1.311
1.2	.879	.335	13.0	1.780	1.425
1.4	.898	.335	14.0	1.798	1.538
1.6	.917	.337	15.0	1.803	1.633
1.8	.934	.340	16.0	1.805	1.724
2.0	.953	.345	17.0	1.820	1.838
2.5	1.001	.360	18.0	1.815	1.917
3.0	1.051	.380	19.0	1.795	1.961
3.5	1.103	.405	20.0	1.778	2.008

In the case of calcium nitrate and other highly soluble salts it would be futile to attempt any form of extension of the Debye–Hückel treatment, into the very concentrated solutions. We have only to note that in an 18 molal solution there are only about 3 molecules of water per molecule of solute, to realize the hopelessness of such an approach. Another important point is that at these concentrations there can be little left of the normal coördinated structure of water; for in a solution with say 5 moles of a 2:1 electrolyte per liter, there are $(15 \times 6.023 \times 10^{20})$ ions per cc., so that the average distance between an ion and its nearest neighbors can be only about 5 Å. Clearly there can be in such a solution no water molecules which are not subject to quite large electrical forces from the ionic field. It is in fact rather surprising that the Debye–Hückel treatment as extended in Part I of this paper gives such reasonable results as it does in the case of say 5 *M* sodium chloride. In very dilute solutions the ion–ion forces are dominant, and the simple Debye–Hückel treatment is applicable. In moderate concentrations, the ion–ion and ion–solvent forces become of comparable importance, and the method of Part I provides a satisfactory treatment. We believe that at very high concentrations the ion–solvent forces are the dominant factor, and shall therefore develop as a first approximation a treatment which ignores the ion–ion forces, or rather assumes that they are little affected by concentration in the range to be discussed. There is some justification for this: (a) the Debye–Hückel function $[A\sqrt{c}/(1 + \mathring{a}B\sqrt{c})]$ flattens out with rising concentration, approaching the limit $A/\mathring{a}B$. (b) From an entirely different viewpoint, we might treat the solution as a somewhat irregular ionic lattice with interspersed water molecules, a view supported by the X-ray data of Beck,[20] for example, on concentrated solutions of lithium chloride and bromide and rubidium bromide. The ion–ion energy on this picture might reasonably be expected to be proportional to the inverse cube root of the volume-concentration, so that again it should vary rather slowly with concentration.

The behavior of concentrated calcium nitrate "solutions," described above, raised the question of whether we could obtain a relation between molality and water activity by the application of an adsorption isotherm. Though calcium nitrate is the only electrolyte which we have found to form gels, we have obtained vapor pressure data for a number of other electrolytes at equally high concentrations, and there would seem to be nothing to prevent the application of the same idea to these also. We may picture a concentrated solution as containing ions in various stages of hydration, some with a complete hydration shell forming a monomolecular layer round the ion, others with incomplete shells, and others with more than one layer, the second and higher layers being of course much less strongly bound. All these would be in equilibrium, the relative amounts of each varying with concentration. Now this model bears a strong resemblance to that from which the adsorption isotherm derived by Brunauer, Emmett and Teller[21] was derived. Modifying the notation of these authors to suit the present case, we may write their equation as

$$\frac{m a_w}{55.51(1 - a_w)} = \frac{1}{cr} + \frac{c - 1}{cr} a_w \qquad (11)$$

---

[17] S. Shankman and A. R. Gordon, THIS JOURNAL, **61**, 2370 (1939).

[18] R. H. Stokes, *ibid.*, **69**, 1291 (1947).

[19] R. A. Robinson, *ibid.*, **62**, 3130 (1940).

[20] Beck, *Physik. Z.*, **40**, 474 (1939).

[21] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

where: a_w is the water activity of the solution; m its molality; r is the number of molecules of water in the monomolecular hydration layer *when complete;* and c is a constant related to the heat of adsorption E of the molecules in the layer by the approximate relation $c = \exp (E - E_L)/RT, E_L$ being the heat of liquefaction of pure water. Equation (11) may be tested by plotting the left-hand side (determined from the experimental m and a_w) against a_w. We find that good straight lines are obtained from the following electrolytes in the concentration range where $a_w < 0.3$: calcium nitrate, calcium chloride,[11] calcium bromide,[22] lithium chloride,[23] lithium bromide,[22] zinc chloride,[11] zinc bromide,[11] perchloric acid,[24] hydrochloric acid,[25] and sodium hydroxide.[26] Table VI gives the best values of the parameters c and r for these electrolytes, obtained by a least-squaring process. Also recorded are the average deviations of the water activity observed from that required to reproduce the experimental molality with equation (11) rewritten in the form

$$m = \frac{55.51(1 - a_w)}{a_w} \left\{ \frac{1}{cr} + \frac{c-1}{cr} a_w \right\} \tag{11a}$$

The accuracy of fit is on the whole surprisingly good; it should be remembered that the experimental accuracy of vapor pressure measurements at these high concentrations is in the majority of cases not much better than 0.0010 in a_w. It is immediately noticeable that the r values for the 1:1 electrolytes are between 3 and 4, while those of calcium chloride and calcium bromide are about twice as large. Zinc chloride and bromide have r values similar to those of 1:1 electrolytes, which is to be explained on the grounds that concentrated solutions of these salts should really be formulated as Zn ($ZnCl_4$) and Zn ($ZnBr_4$)[27] so that only half the zinc is in the form of ions free to undergo hydration. The free zinc ions then have r values similar to those of calcium in calcium chloride and bromide. In the case of calcium nitrate if we adopt the formulation $CaNO_3^+ \cdot NO_3^-$ it is reasonable that the r value should be in the range characteristic of 1:1 electrolytes. The values of the parameter c are also reasonable, corresponding to $E - E_L$ = 1 to 3 kcal. per mole of water adsorbed. An unsatisfactory feature of equation (11) is that it demands the non-integral r values of Table VI. These can scarcely correspond to any physical reality, and have more likely arisen as a result of approximations in the B–E–T. theory and its application to this case. The most drastic of these approximations is that of treating all water molecules beyond the first layer as held by ordinary liquid forces, with a heat of liquefaction E_L. Anderson[28] has deduced a modification of the B–E–T equation in which the subsequent layers (up to about the tenth) have a heat of adsorption less than that of water by d. This has the effect of multiplying a_w, wherever it occurs in (11), by a factor $K = e^{-d/RT}$ leading to the equation

$$\frac{ma_w}{55.51(1 - Ka_w)} = \frac{1}{cKr} + \frac{c-1}{cr} a_w \tag{12}$$

We shall now investigate whether this equation, with r fixed at 4.000 or 8.000 according to the salt considered, will represent the observed relation between m and a_w by an appropriate choice of the two constants c and K. To make the test we rewrite (12) in the form

$$c = \left\{ \frac{1}{K} - a_w \right\} \Big/ \left\{ \frac{rma_w}{55.51(1 - Ka_w)} - a_w \right\}$$

and find by trial a value of K which lends to a reasonably constant c over the widest possible range of molality. The c and K values found for the nine electrolytes are listed in Table VII. The range of validity of equation (12) is somewhat wider than that of equation (11), extending in most cases up to $a_w = 0.5$. The average deviations are on the whole slightly greater, though there would be little difference if equation (12) were restricted to the same range of water activities as equation (11).

TABLE VI

CONSTANTS OF EQUATION (11)

Electrolyte	r	c	Range fitted	Average deviation in a_w
LiCl	3.64	17.2	12*M*–29*M*	0.0008
LiBr	3.82	43.0	11*M*–20*M*	.0015
HCl	3.50	19.1	12*M*–16*M*	.0009
$HClO_4$	3.93	59.0	10*M*–16*M*	.0017
$Ca(NO_3)_2$	3.86	9.40	12*M*–20*M*	.0007
$ZnCl_2$	3.69	22.6	12*M*–22*M*	.0017
$ZnBr_2$	4.01	19.8	11*M*–20*M*	.0008
$CaCl_2$	6.73	9.50	7*M*–10.5*M*	.0004
$CaBr_2$	7.06	42.6	6*M*–9*M*	.0031
NaOH	3.20	19.3	14*M*–29*M*	.0011

The c parameter of equation (12) ranges from 9.0_4 to 58.2, corresponding to values of $E - E_L$ of 1.3 to 2.4 kilocalories per mole of water. These magnitudes seem reasonable enough. The K parameter range corresponds to d = 0 to 150 cal./mole of water in the second and subsequent layers. This relatively small energy might easily correspond to a weak ordering effect on the water molecules concerned. It would however clearly be unwise to go too far in attempting to attach an exact physical meaning to K in terms of the model. It is sufficient to have shown that with an integral r value of 4 or 8, and a c corresponding to a reasonable "energy of adsorption," equation (12) is applicable over the remarkably wide ranges of con-

---

[22] R. A. Robinson and H. J. McCoach, THIS JOURNAL, **69**, 2244 (1947).

[23] R. A. Robinson, *Trans. Faraday Soc.*, **41**, 756 (1945).

[24] R. A. Robinson and O. J. Baker, *Trans. Roy. Soc. New Zealand*, **76**, 250 (1946).

[25] G. Åkerlöf and J. W. Teare, THIS JOURNAL, **59**, 1855 (1937).

[26] R. H. Stokes, *ibid.*, **67**, 1689 (1945).

[27] R. H. Stokes, *Trans. Faraday Soc.*, **44**, in press (1948).

[28] R. B. Anderson, THIS JOURNAL, **68**, 686 (1946).

centration given in Table VII. The K parameter can then be regarded as a convenient carry-all for such effects as ordering in the second and higher layers and the otherwise neglected variation in the ion–ion energy with concentration. In view of the approximate nature of the treatment, the accuracy with which the molality can be related to the water activity by equations (11) and (12) is more than satisfactory.

TABLE VII

CONSTANTS OF EQUATION (12)

Electrolyte	r	c	K	Range fitted	Average deviation in a_w.
LiCl	4.00	15.84	0.860	8M–20M	0.0006
LiBr	4.00	42.0	0.890	8M–20M	.0018
HCl	4.00	14.38	0.850	7M–16M	.0019
$HClO_4$	4.00	58.2	0.950	9M–16M	.0024
$Ca(NO_3)_2$	4.00	9.04	0.960	9M–20M	.0010
$ZnCl_2$	4.00	20.5	0.880	10M–22M	.0025
$ZnBr_2$	4.00	20.0	1.000	11M–20M	.0009
$CaCl_2$	8.00	9.24	0.775	4M–10.5M	.0016
$CaBr_2$	8.00	34.1	0.770	4.5M–9M	.0007

In the case of hydrochloric acid, the data available[24] cover the temperature range 0–50°, so that an interesting test of these ideas is possible. Table VIII gives the values of the K and C parameters, taking $r = 4$, for hydrochloric acid at various temperatures. The variation in C is considerable, but corresponds to a practically constant value of $E - E_L$ in the equation

$$C = \exp (E - E_L)/RT$$

This is consistent with the idea of strong electrostatic forces causing the "adsorption." The K values on the other hand do not correspond to a constant value of d; but the various effects covered by the introduction of K are not clearly enough defined to justify the expectation that it would be constant.

TABLE VIII

CONSTANTS OF EQUATION (12) FOR HYDROCHLORIC ACID AT VARIOUS TEMPERATURES

$r = 4.00$ in each case. $c = \exp (E - E_L)/RT$. Range fitted 10 M–16 M at each temperature

Temp., °C.	K	c	$(E - E_L)$, kcal.	Average deviation in a_w.
0	0.870	18.28	1.58	0.0010
10	.861	16.52	1.58	.0020
20	.852	14.98	1.58	.0020
25	.850	14.38	1.58	.0019
30	.843	13.68	1.58	.0016
40	.834	12.45	1.57	.0016
50	.825	11.29	1.56	.0013

We consider that the ideas put forward in this section are worth developing further, perhaps by an attempt to evaluate the ion–ion energies in the quasi-lattice of the concentrated solution. If these energies could be included the treatment should find a firmer theoretical basis. The ideas put forward in the two sections of this paper are not self-contradictory. In Part I we have shown that the introduction into the Debye–Hückel equation of the concept of ion–solvent molecule interaction will account for observed activity coefficients up to a total ionic strength of about 4. In part II we have accounted for vapor pressure data at concentrations above about 12 M by assuming that ion–solvent molecule interaction occurs by a mechanism similar to that of the Brunauer–Emmett–Teller theory. Between these concentrations the hydration number, n, is diminishing and the ions are tending to a quasi-crystalline structure with some of the water molecules imbedded in the remnants of the crystal lattice (adsorbed water) and some present as "free" solvent. There is nothing contradictory in these two methods of approach; rather do we regard them as limiting cases of a more general theory which would cover the entire concentration range.

Summary

Part I: By superimposing on the Debye–Hückel treatment an allowance for the ion–solvent interaction in terms of a hydration model, a two parameter equation for activity coefficients is obtained. This has a range of validity greater than that of the usual Hückel equation. When dealing with the class of the chlorides, bromides and iodides of hydrogen and the alkali metals, the two-parameter form can be reduced to a one-parameter equation by the assumption that the anion can penetrate a distance of 0.7 Å. into the hydration sheath of the cation. A closely similar one-parameter equation holds for the alkaline-earth halides and other normally dissociated bivalent metal halides, the "penetration distance" for this class being 1.3 Å. Within each class only the single parameter n, the effective hydration number of the cation, is required to represent the observed activity coefficients, usually up to an ionic strength of about 4.

Part II: An approximate treatment of the water activity of very concentrated electrolyte solutions is based on the application of the adsorption isotherms of Brunauer, Emmett and Teller and of Anderson. The resulting equations apply with surprising accuracy to nine electrolytes which have recently been studied at very high concentrations. The parameters of the equations are listed and their physical significance discussed.

NEDLANDS, WESTERN AUSTRALIA
NEW HAVEN, CONN.
RECEIVED JUNE 24, 1947