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ELECTROMOTIVE FORCE MEASUREMENTS ON CELLS CONTAINING ZINC CHLORIDE. THE ACTIVITY COEFFICIENTS OF THE CHLORIDES OF THE BIVALENT METALS

BY GEORGE SCATCHARD AND RALPH F. TEFFT[1]

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The behavior of zinc chloride in solution is of interest as it represents an intermediate step in the transition from typical strong electrolytes, such as the alkaline earth chlorides, to salts like cadmium chloride in which ion association shows an important effect. A few measurements on the cell Zn, $ZnCl_2$ (*m*), AgCl, Ag have been made at 0° by Jahn,[2] and several in very dilute solutions at 25° by Horsch.[3] We have made a series of measurements on the cell ZnHg (2 phase), $ZnCl_2$ (*m*), AgCl, Ag at 25° in which *m* was varied from 0.003 *M* to 1.48 *M*.

Experimental Methods

A solution of C. P. sodium carbonate was added to a solution of C. P. zinc chloride in water. The resulting precipitate was washed free from chlorides and dried at about 300° overnight, leaving a product largely zinc oxide. This was mixed with purified hydrochloric acid and boiled until no more would dissolve. The concentration of this stock solution was determined by a gravimetric chloride analysis, and the solutions used in the cells were prepared from it by weight dilution.

The stock solution was saturated with zinc oxide, and on dilution a small amount of precipitate always formed. According to Driot[4] the solid phase is $4ZnO\cdot ZnCl_2\cdot 6H_2O$ at these concentrations of zinc chloride, and the solubility is given by $m_{ZnO} = 0.005\ m^2_{ZnCl_2}$. This excess concentration affects only the zinc electrode, so that the correction is 0.03 log $(1 + 0.005\ m)$, which is less than 0.1 mv. even for the most concentrated solution studied. All measurements are so corrected, however. The two most concentrated solutions, which were prepared from a more concentrated stock solution than the others so that precipitation was considerable, were each analyzed for chloride.

The zinc amalgam was prepared by the electrolysis of the stock solution, acidified with a small amount of hydrochloric acid, between a C. P. zinc anode and a mercury cathode. After the electrolysis the amalgam was washed, dried and stored in a pyrex

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[1] The experimental work was presented in May, 1928, by Ralph F. Tefft in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Jahn, *Wied. Ann.*, **28**, 21 (1886).

[3] Horsch, THIS JOURNAL, **41**, 1787 (1919).

[4] Driot, *Compt. rend.*, **150**, 1427 (1910).

container under hydrogen. To fill the cells the amalgam was heated until it was practically one phase and withdrawn through a capillary stopcock.

The purification of other materials and the preparation of the silver–silver chloride electrodes, chloridized in the solution in which they were to be used except as noted below, the thermostat and the electrical apparatus were the same as in previous work.[5]

The electrode vessel was triplicate. Each section was shaped like an inverted h. The long arm contained the amalgam and had a platinum wire sealed through the bottom. A tube which delivered hydrogen just above the amalgam surface passed through a rubber stopper at the top. The silver chloride electrode was supported in a rubber stopper in the short arm. The three long arms were connected in a row by two series of tubes, one below and one above the liquid–gas interface. The middle section had a second side arm for the escape of hydrogen.

The nine possible electrode combinations were measured in each case except for the most dilute solutions, where the resistance was too high to permit accurate measurements from one end cell to the other. Each cell was observed for at least six hours after it was placed in the thermostat, with the hydrogen flowing continually, although the electromotive force never changed more than 0.1 mv. after the first half-hour, even in one case which was observed for several days. In the 0.003 and 0.02 *M* solutions one zinc electrode, and in the 0.008 *M* solution one silver chloride electrode, gave results so different from the other two that they were not considered. Excepting these, the average deviations for a given solution were 0.02–0.07 for all but the most dilute solution, where it reached 0.22 mv. from the average for two fillings, for one of which the silver chloride electrodes were chloridized in a more concentrated solution.

The effect of air was studied with the 0.09 *M* solution. The passage of air over the amalgam electrodes for twenty minutes caused a decrease of 3–5 mv. in the electromotive force, but the electromotive force began to increase as soon as the flow was stopped and after seven hours had returned to its initial value, which was not further changed by passing through hydrogen. The passage of air caused a scum to be formed on the amalgam surface. Evidently the oxygen removes zinc from the dilute amalgam to form zinc hydroxide, which is precipitated, so that the net effect is the decrease of the zinc concentration in the amalgam. As the amalgam returns to equilibrium, the electromotive force recovers. This action probably accounts for the fact that Horsch,[3] who did not eliminate oxygen, could not prepare reproducible amalgam electrodes.

Measurements

The results of our measurements are given in Table I. The first column

TABLE I

ELECTROMOTIVE FORCE AT 25° OF THE CELL ZnHg (2 PHASE), $ZnCl_2$ (m), AgCl, Ag

m	E	E''_0	(Eq. 2)
0.002941	1.1983	0.9915	−0.00182
.007814	1.16502	.99586	− .00088
.01236	1.14951	.99800	− .00089
.02144	1.13101	1.00070	− .00063
.04242	1.10897	1.00492	− .00004
.09048	1.08435	1.00940	+ .00018
.2211	1.05559	1.01480	+ .00012
.4499	1.03279	1.01893	− .00020
.6404	1.02206	1.02143	− .00003
1.4802	0.99784	1.02789	− .00004

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[5] Scatchard and Tefft, THIS JOURNAL, **52**, 2265 (1930).

gives the molality, the second the measured electromotive force and the third E_0'' defined by the equation

$$\begin{aligned} E_0'' &= E + 0.088725\,[\log m - \log(1 + 0.054\,m)] + 0.01781 \\ &= E_1 - 0.088725 \log f \end{aligned} \tag{1}$$

E_0'' differs from the E_0' of Lewis and Randall only by the addition of the third term, which relates the measurements to Raoult's law rather than to the assumption that the activity is proportional to the molality in an ideal solution. $0.01781 = 0.088725 \log 2^{2/3}$ serves to change from unit concentration of salt to unit mean concentration of ions. The last column gives the deviations of the measured values from those calculated by the Debye–Hückel equation for varying dielectric constant

$$E_0'' = 0.98625 + \frac{0.155\sqrt{c}}{1 + 3.5\sqrt{c}} + 0.0042c \tag{2}$$

The values of c for these computations were determined from the densities in the "International Critical Tables," using the equation

$$\frac{c}{m} = 0.99707 - 0.0134\,m - 0.0129\,m^2 + 0.0288\,m^3$$

From 0.04 to 1.48 M the deviations are not more than 0.2 mv., which is probably as small as could be expected. For the more dilute solutions, however, the deviations become very large, and the value of E_0 obtained by this method, 0.98625 v., is certainly too high.

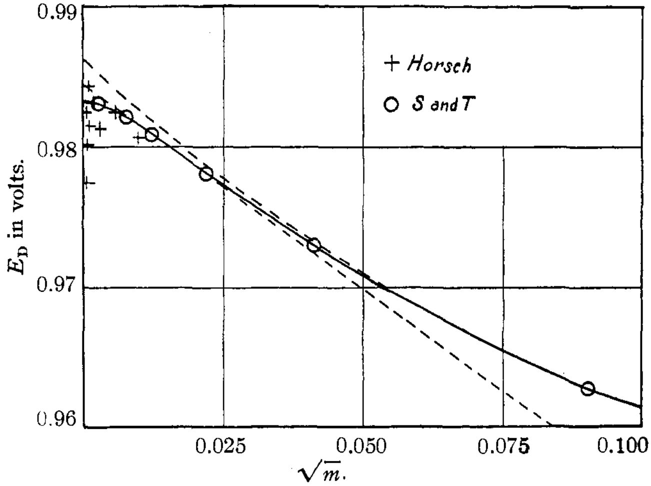

Fig. 1.—Electromotive force of zinc chloride cells.

We have followed the method of Hitchcock[6] in Fig. 1, and plotted

$$E_D = E_0'' - 0.155\sqrt{c} \tag{3}$$

against the concentration. If the Debye–Hückel equation is approached at small concentrations, E_D should approach a straight line asymptotically

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[6] Hitchcock, This Journal, 50, 2076 (1928).

at zero concentration. The upper broken line is that of Equation 2, the lower broken line is a straight one through the points at 0.008, 0.012 and 0.02 M. The point at 0.003 M is well below the line and indicates an inflection in the curve. It would be dangerous to insert an inflection based upon a single measurement, the least accurate of the series, and the measurements of Horsch are too scattered to aid in the extrapolation. However, the points through which the line is drawn fall upon it *too well* in view of the deviation at the next higher concentration, so that these points themselves indicate an inflection. Accurate measurements at lower concentrations, to which our technique is not adapted, are to be desired. We believe that the evidence just given and the theoretical considerations which follow justify the inflection, and make the extrapolation along the full curve the most probable.

Chlorides of Other Bivalent Metals

The electromotive force measurements with the alkaline earth chlorides extend only to hundredth molal, so they are not useful for the comparison of the behavior in very dilute solutions. The freezing-point measurements of Hall and Harkins[7] on barium chloride up to 0.1 M are fitted within the accuracy with which they are expressed (one unit in the last place) by the Debye–Hückel equation for constant dielectric constant, assuming that at this dilution $c = m$, with $a = 4.81$ Å.

$$\Theta = 1.858\,\nu\,m\left\{1 - \frac{3.445\,z_1z_2}{x^2a}\left[1 + x - \frac{1}{1+x} - 2\ln(1+x)\right]\right\} \qquad (4)$$

ν is the number of ions from one molecule of salt, z_1 and z_2 are their valences, $x = 0.3242\,a\sqrt{\mu}$, μ is the ionic strength, and a the mean effective diameter in Ångström units. This corresponds to

$$-\log\gamma = \frac{0.485\,z_1z_2\sqrt{\mu}}{(1+x)} \qquad (5)$$

The numerical constants are limited, of course, to aqueous solutions.

At 0.01 M this gives $\gamma = 0.737$, which may be compared with the value 0.716 obtained by Lewis and Randall from the same measurements and to the value 0.724 which we compute, in accord with earlier computations,[8] from the electromotive force measurements of Lucasse at 25°.[9] The difference between our values at 0° and at 25° is in the direction to be expected. It appears that there is no inflection for barium chloride. Strontium and calcium chlorides have larger positive deviations from the limiting law above 0.01 M and should have less tendency to irregularities at smaller concentrations.

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[7] Hall and Harkins, THIS JOURNAL, **38,** 2658 (1916).

[8] Harned and Åkerlöf, *Physik. Z.*, **27,** 411 (1926); Jones and Dole, THIS JOURNAL, **51,** 1073 (1929).

[9] Lucasse, *ibid.*, **47,** 743 (1925).

The measurements of Carmody[10] on lead chloride and those of Horsch[3] and of Lucasse[11] on cadmium chloride indicate considerable curvature in dilute solutions when E_D is plotted against the concentration. Figure 2 shows $E_D - E_0$ for these salts and for barium and zinc chlorides plotted against the square root of the concentration. The broken line is the Debye–Hückel limiting law. The values for cadmium and lead chlorides in dilute solutions appear to lie on straight lines. For cadmium chloride the slope of this line is greater than that of the broken line, so that extrapolation along this curve would give a limiting slope more than twice the theoretical; lead chloride would give a value about 30% too high.

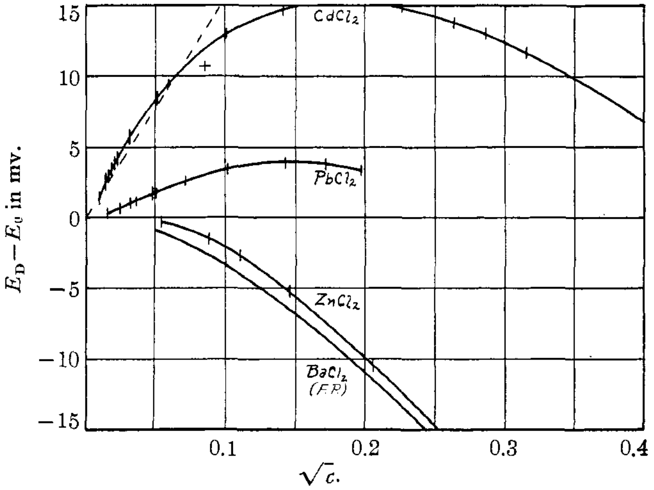

Fig. 2.—Electromotive force of chlorides of bivalent metals.

The Effect of Incomplete Ionization

Since cadmium chloride is certainly not completely ionized and the other salts may not be, the effect of incomplete dissociation on this method of treatment was studied. The effect of the formation of neutral molecules or more complicated ions increases too rapidly with the concentration to resemble the experimentally measured effects, but the formation of the primary ion is capable of explaining the measurements.

It is necessary to distinguish between those quantities computed from the true concentration of the ions, and those computed in the customary way by assuming complete ionization. To the latter we will give the ordinary symbols, while the former will be distinguished by primes. Thus f'_{21} is the true mean activity coefficient of a bi-univalent electrolyte. In calculating the activity coefficients we have assumed that all ions have the size found for barium chloride from the freezing points, that the terms

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[10] Carmody, This Journal, 51, 2905 (1929).

[11] Lucasse, *ibid.*, 51, 2597 (1929).

linear in the concentration are zero, and that the concentration of each species in moles per liter is 55.5 times its mole fraction, a quantity which is designated by the chemical symbol in parentheses. If μ is the ionic strength in these units

$$-\log f'_{21} = \frac{\sqrt{\mu'}}{1 + 1.56\sqrt{\mu'}} \quad \text{and} \tag{6}$$

$$-\log f'_{11} = \frac{0.5\sqrt{\mu'}}{1 + 1.56\sqrt{\mu'}} \tag{7}$$

Given the reaction $MX^{++} \rightleftharpoons M^{+} + X^{-}$

$$K = \frac{(M^{++})\,(X^{-})}{(MX^{+})}\,\frac{f'^{3}_{21}}{f'^{2}_{11}} \tag{8}$$

Combining (6), (7) and (8)

$$\log \frac{(M^{++})\,(X^{-})}{(MX^{+})} = \log K + \frac{2\sqrt{\mu'}}{1 + 1.56\sqrt{\mu'}} \tag{9}$$

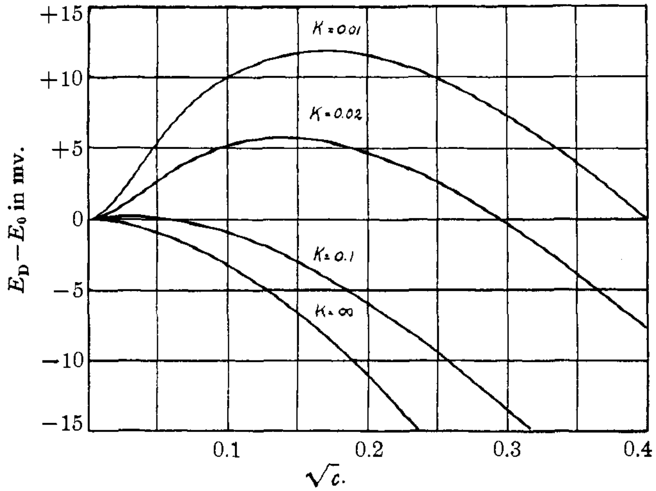

Fig. 3.—Effect of incomplete dissociation on electromotive force of 2−1 salts.

We also have the equations

$$\mu' = 3(M^{++}) + (MX)^{+} \tag{10}$$

$$(X^{-}) = 2(M^{++}) + (MX^{+}) = \mu' - (M^{++}) \tag{11}$$

For a given value of K these equations can be solved without much difficulty if μ' be taken as the independent variable, and

$$\mu = 3[(M^{++}) + (MX^{+})]\,\frac{1 + 0.054\left[(M^{++}) + \frac{2}{3}(MX^{+})\right]}{1 + 0.054\,[(M^{++}) + (MX^{+})]^{3}}, \quad \text{and} \tag{12}$$

$$f_{21} = \frac{\mu' f'_{21}}{\mu} \tag{13}$$

In Fig. 3 is plotted

$$E_D - E_0 = 0.088725\,[\sqrt{\mu} - \log f] \tag{14}$$

for four values of the ionization constant, including complete dissociation.[12] The fraction of the salt in the form of the primary ion at 0.1 *M* is approximately 0.0, 0.3, 0.7 and 0.8. For extremely dilute solutions the limiting law still holds, but the effect of association increases very rapidly, yet soon becomes nearly constant (curves nearly parallel) because of the rapid decrease in the activity coefficients. This leads to an inflection in very dilute solutions with a considerable range through which the curves are nearly rectilinear.

The curves of Fig. 3 have the same general shape as those of Fig. 2; by proper choice of ionic size and ionization constant they might be made to fit very closely. This hardly seems worth while, but the curves of Fig. 3 were used as guides in the extrapolation of those of Fig. 2 to zero concentration. The figure shows that, even with a theory which assumes the Debye–Hückel limiting law at zero concentration, that law can be used as a guide only in extremely dilute solutions if there is a large amount of ion association. The assumption that the activity coefficient is the same as that of a typical strong electrolyte is even more dangerous, and the assumption that the logarithm of the activity coefficient is proportional to $\sqrt{\bar{c}}$ and determination of the proportionality constant from the measurements themselves is still worse.

Discussion

These inflections at very low concentrations were first noted by Bjerrum.[13] They are discussed more specifically for a salt with high valence cation dissolved in one with high valence anion by LaMer and Mason,[14] and for ions of equal valences by Gronwall, LaMer and Sandved.[15] These authors attribute the inflections to the effect of higher terms in the power series expansion of the electrical density, which are neglected in the Debye–Hückel treatment.

The computations which these latter authors have promised for unsymmetrical salt are not yet published. An examination of their Equations 34 and 64 for $\log f\pm$ shows that the ratio of the higher-order odd terms to the first, which is the Debye–Hückel approximation, for a 2–1 salt with no foreign ions is from $^9/_{16}$ to $^4/_9$ the ratio for a 2–2 salt, and that the leading terms in the expansion of all the even terms, which are zero for a symmetrical salt, have the sign opposite to that of the odd terms, so that they tend to compensate. A closer examination of the first even term shows that it must remain positive to a considerable concentration.

Bjerrum's approximate method makes $\log f\pm$ for a 2–1 salt very nearly

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[12] The lowest value is nearly equal to that found for sulfuric acid (0.0115) by Sherrill and Noyes, THIS JOURNAL, **48,** 1861 (1926).

[13] Bjerrum, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.* VII, 9 (1926).

[14] LaMer and Mason, THIS JOURNAL, **49,** 410 (1927).

[15] Gronwall, LaMer and Sandved, *Physik. Z.*, **29,** 358 (1928).

the same as that for two ions with valence $\sqrt{2}$ at the same molal concentration, which is qualitatively consistent with the results of the other method. He treats the solutions as though they were incompletely dissociated with the constant for the *formation* of the binary compound depending on the size and valence in the following way

$$K' = 0.004\,\pi\,N\,(ab)^3 \int_2^b e^y y^{-4} dy$$

$$b = \frac{\epsilon^2 z_1 z_2}{DkT}\,\frac{1}{a}$$

N is Avogadro's number, k the Boltzmann constant, ϵ the charge on the electron, D the dielectric constant, T the absolute temperature, z_1 and z_2 are the valences of the ions, and a is their effective mean diameter. The remainder of his computation differs only in details from that described in this article. The curves of Fig. 2 can be fitted approximately by attributing the sizes: $CdCl_2$ about 1.3 Å., $PbCl_2$ about 1.9 and $ZnCl_2$ from 3.5 to 6.

The properties of an electrolyte solution must depend on those of the solvent and of the individual ions, whether or not dissociation is complete. The original Debye–Hückel treatment, including the extensions to the higher terms cited above, considers only the dielectric constant of the solvent, and the valence and mean collision diameter of the ions. Hückel[16] has included the effect of the ions on the dielectric constant of the solutions, and the general equations of Gronwall, LaMer and Sandved include this effect for the higher terms. These treatments all consider the ions as having spherical symmetry.

There is no question but that a general treatment must consider two kinds of dissymmetry: first, that of the isolated ions, as illustrated by the nitrate and acetate ions; and second, that induced by an electrical field because of the deformability of the ion. The second effect is probably responsible for a large part of what Brönsted terms "specific interaction of ions" and in extreme cases for chemical association. Since it depends upon a very close approach of the ions, it may be expressed to a good approximation by the law of mass action.[17]

The effect of higher terms and that of deformability may each be approximated by assuming chemical combination, and the only difference is that the first makes the association constant a function of the size while the second makes it an independent parameter. Since the further effect of the size is of a smaller order, it would require great confidence in the accuracy of the experimental measurements and in the validity of the Debye method to differentiate between the two effects from measurements on a single salt.

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[16] Hückel, *Physik. Z.*, **26**, 93 (1925).

[17] The authors make no claim of originality for this treatment. It has been discussed more or less specifically in many places. See especially Fajans, *Trans. Faraday Soc.*, **23**, 357 (1927).

The correlation of measurements on a large series of salts, when they are available, may give interesting information.

We can say with assurance that for higher valence ions part, at least, of the association constants must be attributed to the higher terms. This effect seems sufficient for the rare gas type ions, though deviations might be expected with the larger anions and high valence cations, and for some polyatomic ions. The authors believe that, whenever the assumption of spherical symmetry leads to a value of a less than two Ångström units, some other explanation should be sought, and that deformation often plays an important part in other cases. Certainly, unless the values in Table II are considerably in error two, and probably three, specific parameters (which might be the size, deformability, and effect on the dielectric constant) are required to fit both barium chloride and zinc chloride. No theory assuming spherical non-deformable ions can account for the transference number of the cadmium ion becoming negative,[18] or for the behavior of a weak electrolyte like acetic acid. It should be noted that we have no definition of association precise enough to determine the extent of it exactly or even to recognize its existence in small quantities.

Results

For the cell ZnHg (2 phase), $ZnCl_2$, AgCl, Ag we obtain $E_0 = 0.9834$ v. Combining this with Cohen's[19] value of 0.0006 v. for the difference in potential between zinc and the two-phase amalgam, and -0.2224 v. for the silver chloride electrode,[20] we obtain

$$\text{Zn, ZnCl}_2\text{, AgCl} \quad E_0 = 0.9840 \text{ v.}$$
$$\text{Zn, Zn}^{++} \quad E_0 = 0.7616 \text{ v.}$$

Lewis and Randall give the values 0.9839 and 0.7581. The close agreement of the first is somewhat of a coincidence; the difference in the second is due to the high value attributed to Horsch's silver chloride electrodes.

For the cell PbHg (2 phase), $PbCl_2$, AgCl, Ag we obtain $E_0 = 0.3430$ v. Carmody, extrapolating as a linear function of $\sqrt{m}$, obtained 0.3426.

For the cell Cd, $CdCl_2$, AgCl, Ag (Horsch) we obtain $E_0 = 0.5678$ v. Lewis and Randall give 0.5700 v.

In Table II are given values of the activity coefficient for several of the bivalent metal chlorides at rounded concentrations. The values for zinc, lead and cadmium chlorides are computed from the data discussed in this paper. The computations for calcium chloride are made from Equation 1 of the preceding paper[5] with the constants there given. For barium chloride a similar equation was used with $\alpha = 2.3$, $\beta = 0.0136$ volt, and $c/m = 0.99707 - 0.0286\,m - 0.00139\,m^2$.

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[18] See McBain and Van Rysselberge, This Journal, **50**, 3009 (1928).

[19] Cohen, *Z. physik. Chem.*, **34**, 612 (1900).

[20] Scatchard, This Journal, **47**, 2098 (1925).

TABLE II

ACTIVITY COEFFICIENTS ($\gamma = a/m$) AT 25° OF CHLORIDES OF BIVALENT METALS

m	$CaCl_2$	$BaCl_2$	$ZnCl_2$	$PbCl_2$	$CdCl_2$
0.0001	0.961	0.961	0.960	0.958	0.923
.0002	.947	.947	.945	.939	.885
.0005	.918	.918	.913	.902	.818
.001	.888	.889	.881	.859	.755
.002	.850	.850	.838	.803	.684
.005	.785	.784	.767	.704	.569
.01	.725	.724	.708	.612	.475
.02	.658	.655	.642	.497	.384
.05	.570	.561	.556	..[a]	.277
.1	.515	.494	.502		.206
.2	.481	.438	.448		.149
.3	.482	.413	.415		.121
.4	.496	.400	.393		.104
.5	.519	.393	.376		.093
.6	.548	.390	.364		.083
.8	.622	.391	.343		.070
1.0	.715	.397	.325		.061
1.25	.863	.409	.306		.054
1.5	1.047	.425	.290		.048

[a] In a saturated solution, m = 0.03905, γ = 0.413.

Summary

The electromotive force of the cell $ZnHg_x$ (2 phase), $ZnCl_2$, AgCl, Ag has been measured at 25° from 0.003 to 1.5 *M*.

Measurements on barium chloride agree with the Debye–Hückel equation, assuming complete ionization. Those on zinc chloride, lead chloride and cadmium chloride do not, but they may be fitted by assuming incomplete dissociation of the primary ion. The effect of incomplete dissociation is calculated and values of the standard cell potentials and activity coefficients are computed. The relation of the apparent association to the "higher terms" and to the deformability of the ions is discussed.

CAMBRIDGE, MASSACHUSETTS