for all cases, but generally becomes smaller for a faster reaction and smaller diffusion coefficient. However, values of μ from 10^{-2} to 10^{-3} cm. will at least predict the order of magnitude of the rate constants for the cases where the reaction involves a reduction product of the electrode, and values closer to 10^{-7} cm. for reactions that precede the electrode reduction.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Properties of Dilute Solutions of Magnesium Halides in Ethanol at 20° from Conductance Measurements[1,2]

BY LYLE R. DAWSON AND MICHAEL GOLBEN

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The electrical conductances of dilute solutions of magnesium chloride, bromide and iodide in ethanol at 20° have shown these halides to be incompletely dissociated electrolytes increasing in strength in the order named. The data gave evidence of second stage dissociation in the dilute range. A mass law expression has been derived for the secondary dissociation of a bi-univalent electrolyte for the special case in which the primary dissociation is substantially complete. An expression has been developed for the secondary dissociation which corrects the mass law expression for ion retardation and deviation from ideality in the manner of Fuoss and Shedlovsky. Limiting equivalent conductances, actual and theoretical slopes, classical and thermodynamic dissociation constants have been computed for the magnesium halides in ethanol at 20°.

Recent conductance work with ethanol solutions of bi-univalent salts has been confined largely to solutions in the mixed solvent ethanol–water of different ratios rather than in ethanol alone.[3–5] An exception is the work of Olmer,[6] who measured the conductance of magnesium chloride in ethanol and obtained an improbably low value of Λ_0, indicating that his measurements were not carried to a dilution necessary to show a rapid change in equivalent conductance in the very dilute range.

Paucity and variability of existing conductance data for ethanol solutions of polyvalent electrolytes are due partly to difficulties of experimentation and interpretation. Solvent and salts must be anhydrous. The true trend of a multi-step dissociation may not be revealed in non-aqueous solutions except at dilutions where experimental error tends to increase rapidly. Sometimes solute–solvent relationships complicate the interpretation of data.

In the studies reported here the magnesium halides in dilute ethanol solution were found to be weak electrolytes undergoing second-stage dissociation. A dilution law has been developed for the secondary dissociation, as well as an equation corrected for interionic effects in a manner similar to that of Fuoss and Kraus[7] and Shedlovsky[8] for weak uni-univalent electrolytes. This equation has been applied to the data by plotting parameters which would show linearity if the assumed relationships were correct.

Experimental

Preparation of Anhydrous Ethanol.—Ethanol of low specific conductance and high purity was prepared from commercial absolute alcohol by azeotropic distillation with small amounts of benzene, adding alkaline silver oxide to remove aldehyde, then refluxing briefly with aluminum amalgam and activated alumina. The mixture was distilled slowly, retaining the middle portion for conductance work. The average specific conductance of the samples used was 3×10^{-8} ohm^{-1}.

Preparation of Solutions.—Anhydrous solutions of the magnesium halides were prepared by dissolving best grade commercial salts in anhydrous ethanol and removing the water by azeotropic distillation, first using dry redistilled benzene, then dry redistilled ether.

Substantially the same conductance results were obtained by an alternate method of preparing anhydrous magnesium chloride, involving careful preparation of a magnesium chloride–pyridine complex and heating under vacuum to remove the pyridine.[9] The ethanol solutions were tested for water by density measurements and a modified Weaver test.[10] The halide concentration of each was determined by potentiometric titration with 0.01 N silver nitrate, using a Fisher titrimeter with silver and calomel electrodes.

A Dike bridge,[11] incorporating features recommended by Jones and Josephs[12] and Shedlovsky,[13] was used. The conductivity cell was held in a kerosene-bath thermostated at 20 ± 0.001°.

Experimental Technique.—The "solution addition" technique[14] was adopted. After calibration the buret was filled through the tip from a stock solution by means of air pressure, 30 to 40 g. of freshly distilled ethanol was transferred to the conductance cell, and the unit assembled. The conductance of the solvent was obtained *in situ* upon reaching temperature equilibrium after several passes between cell and mixing chamber. Each subsequent addition of stock solution from the buret was followed by mixing in the mixing chamber, then several passes between chamber and cell until the resistance readings became constant.

An Expression for the Secondary Dissociation of Bi-univalent Salts

Preliminary values for the limiting equivalent conductances of the magnesium halides in ethanol solution as obtained by extrapolation of the Kohlrausch plots gave evidence that secondary dissociation occurred in dilute solution. Treatment of these solutions as electrolytes for which primary and secondary dissociations occur simultaneously,

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[1] Abstracted from a Ph.D. dissertation submitted by Michael Golben.

[2] Support for part of this work was received from a research contract with the U. S. Army Signal Corps.

[3] I. C. Connell, R. T. Hamilton and J. A. V. Butler, *Proc. Roy. Soc. (London)*, **A147**, 418 (1934).

[4] B. Norberg and C. J. Clemedson, *Arkiv Kemi, Mineral. Geol.*, **A16**, No. 4 (1942); ref. *Chem. Zentr.*, **114**, I, 130 (1943).

[5] R. L. Bateman, University Microfilms (Ann Arbor, Mich.), Publication No. 668.

[6] F. Olmer, *Bull. soc. chim. France*, [5] **5**, 1178 (1938).

[7] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 2387 (1933); **57**, 1 (1935).

[8] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938); Fuoss and Shedlovsky, THIS JOURNAL, **71**, 1496 (1949).

[9] H. L. Davidson, M.S. Thesis, University of Kentucky, 1948.

[10] F. L. Schneider, "Qualitative Organic Microanalysis," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 78.

[11] P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[12] G. Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928).

[13] T. Shedlovsky, *ibid.*, **52**, 1793 (1930).

[14] J. E. Frazer and H. Hartley, *Proc. Roy. Soc. (London)*, **A109**, 351 (1925).

with and without postulation of the presence of a significant concentration of intermediate ion, yielded equations which did not represent the experimental data. For the magnesium halides, best agreement with data was obtained when it was assumed, at sufficient dilution of a particular electrolyte, that the primary dissociation was substantially complete and that further increase in the number of ionic carriers with increased dilution resulted from the dissociation of the intermediate ion MgX^+.

In the following treatment for secondary dissociation the general procedure is similar to that of Fuoss and Kraus[7] and Shedlovsky[8] for the dissociation of uni-univalent electrolytes; the dilution law for the secondary dissociation is developed in the Ostwald manner and then corrected for interionic effects. The principal modifications are necessary because of the application of the Onsager–Shedlovsky equation to unsymmetrical valence-type electrolytes and the postulated presence of an intermediate ion whose relative mobility must be estimated.

If c is the original normality of MgX_2, now assumed to be completely dissociated into MgX^+ and X^- ions, and γ' the apparent degree of dissociation of MgX^+, the equilibrium concentrations of the different ion species in dilute solution may be represented as

$$\begin{array}{ccccc} \text{MgX}^+ & \rightleftarrows & \text{Mg}^{++} & + & \text{X}^- \\ \frac{1}{2}c(1-\gamma') & & c\gamma' & & \frac{1}{2}c(1+\gamma') \end{array} \qquad (1)$$

The classical "ionization" function, K', is given by the mass law expression

$$K' = c\gamma'(1+\gamma')/(1-\gamma') \qquad (2)$$

γ' is defined by the Arrhenius conductance ratio Λ'/Λ_0' in which Λ' is the conductance at a finite concentration that is attributable to the ions formed by the dissociation of MgX^+, and Λ_0' is the limiting equivalent conductance of these ions. These quantities are evaluable in terms of the measured conductance Λ, the extrapolated value of Λ_0 (determined by successive approximations), and the limiting equivalent ionic conductances $\lambda^\circ_{\text{Mg}^{++}}$, $\lambda^\circ_{\text{X}^-}$, and $\lambda^\circ_{\text{MgX}^{+}}$. The dilution law for the secondary dissociation is obtained by substituting Λ'/Λ_0' for γ' in equation (2) and rearranging terms

$$\Lambda' = \Lambda_0' - [1/(K'\Lambda_0')][c\Lambda'(\Lambda' + \Lambda_0')] \qquad (3)$$

Values of Λ' and Λ_0' were calculated by means of equations of (6), (7) and (8), using a preliminary value of Λ_0 obtained from the plot of $\Lambda = \Lambda_0 - kc$ (an approximate but simplified form derived from equation (3)). The linearity of plots of Λ' as a function of $c\Lambda'(\Lambda' + \Lambda_0')$ (Fig. 2) showed that equations (2) and (3) best represented the mass law behavior of the magnesium halides as weak electrolytes in ethanol. Extrapolation of the first plot by the method of least squares yielded a value of Λ_0' as intercept. This value was introduced into the term $c\Lambda'(\Lambda' + \Lambda_0')$ and a new extrapolation was made, the process being repeated until Λ_0' remained constant. K' was calculated from the slope of the final plot, $1/K'\Lambda_0'$. Using ionic concentrations shown in equation (1), and neglecting interionic retardation for the moment

$$\Lambda = \frac{1}{2}(1-\gamma')\lambda^\circ_{\text{MgX}^+} + \gamma'\lambda^\circ_{\text{Mg}^{++}} + \frac{1}{2}(1+\gamma')\lambda^\circ_{\text{X}^-} \qquad (4)$$

By definition

$$\Lambda' = \gamma'\lambda^\circ_{\text{Mg}^{++}} + \frac{1}{2}\gamma'\lambda^\circ_{\text{X}^-} \qquad (5)$$

Combining equations (4) and (5)

$$\Lambda' = \Lambda - \frac{1}{2}[\lambda^\circ_{\text{X}^-} + (1-\gamma')\lambda^\circ_{\text{MgX}^+}] \qquad (6)$$

Also, by definition

$$\Lambda_0' = \lambda^\circ_{\text{Mg}^{+-}} + \frac{1}{2}\lambda^\circ_{\text{X}^-} \qquad (7)$$

Dividing (6) by (5) and solving for γ'

$$\gamma' = [2\Lambda - \lambda^\circ_{\text{X}^-} - \lambda^\circ_{\text{MgX}^+}]/[2\lambda^\circ_{\text{Mg}^{++}} + \lambda^\circ_{\text{X}^-} - \lambda^\circ_{\text{MgX}^+}] \qquad (8)$$

For the dilute solutions involved, estimated values for the limiting transference numbers were used. If t_+° and t_-° are the limiting transference numbers of the cation and anion, respectively, of a completely dissociated magnesium halide, and x is the ratio $\lambda^\circ_{\text{MgX}^+}/\lambda^\circ_{\text{X}^-}$, it can be shown that

$$\gamma' = [2\Lambda - t_-^\circ(1+x)\Lambda_0]/[2\Lambda_0 - t_-^\circ(1+x)\Lambda_0] \qquad (9)$$

In equation (8) appear limiting ion conductances as a result of assuming the applicability of the Arrhenius conductance ratio in equations (4), (5) and (6) and of Kohlrausch's additive law in equation (7); these are all converted to Λ_0 in equation (9). Since in the above formulas solutions of definite ionic strength are being considered, the limiting ionic conductances, and therefore Λ_0, should be corrected for the effect of interionic forces. Thus, by replacing Λ_0 with Λ_e, the conductance predicted by the Onsager–Shedlovsky equation,[9] equation (9) becomes

$$\gamma = [2\Lambda - t_-^\circ(1+x)\Lambda_e]/[2\Lambda_e - t_-^\circ(1+x)\Lambda_e] \qquad (10)$$

where γ is the thermodynamic degree of dissociation for the second stage. Equation (11) expresses the ionic strength ω for salts of the magnesium halide type under the assumed manner of dissociation (with c as normality)

$$\omega = \frac{1}{2}c(1+2\gamma) \qquad (11)$$

The Onsager–Shedlovsky equation may be written as

$$1/\Lambda_e = (1/\Lambda_0)\{1 + [(A + B\omega\Lambda_0)/\Lambda_0]\sqrt{(2/3)\omega}\} \qquad (12)$$

in which A, B and w are Onsager constants. A and B as evaluated for ethanol become applicable for any bi-univalent or uni-bivalent salt, while w depends upon transference number. (At 20°, for a bi-univalent salt in ethanol, $A = 148.1$; $B = 2.714$.) For complete dissociation ($\gamma = 1$) it is evident from equation (11) that $(2/3)\omega$ is equal to c.

For partly dissociated electrolytes, the conductance ratio γ^* is defined

$$\gamma^* = \Lambda^*/\Lambda_e = \frac{1}{3}(1+2\gamma) \qquad (13)$$

If a constant k is given the value $[t_-^\circ(1+x) - 2/3]/[2 - t_-^\circ(1+x)]$, it can be shown, by means of equations (10) and (13), that the parameter Λ^* is given by the expression

$$\Lambda^* = (k+1)\Lambda - K\Lambda_e \qquad (14)$$

Multiplying equation (12) by Λ^*, and incorporating equations (11) and (13), we obtain

$$\gamma^* = \Lambda^*/\Lambda_e = (\Lambda^*/\Lambda_0)\{(1 + [(A + Bw\Lambda_0)/\Lambda_0]\sqrt{c(\Lambda^*/V_e}\} \quad (15)$$

Following exactly the procedure of Fuoss and Shedlovsky, a quantity z is defined, equal to $(A + B\omega\Lambda_0)/\Lambda_0^{3/2}\ \sqrt{c\Lambda^*}$ as well as a function F, which is approximated by $(1 + z)$. Thus

$$\gamma^* = (\Lambda^*/\Lambda_0)F \quad (16)$$

From (13) and (16)

$$\gamma = \frac{3}{2}(\Lambda^*/\Lambda_0)F - \frac{1}{2} \quad (17)$$

The thermodynamic dissociation constant, K, is derived from the equilibrium expression (1), using the true degree of dissociation γ, ion activities in place of concentrations, and making the assumption that the activity coefficients of the univalent ions are equal and cancel each other

$$K = [cf_{\mathrm{Mg}^{++}}\,\gamma(1 + \gamma)]/(1 - \gamma) \quad (18)$$

By inserting the value of γ from equation (17) in equation (18), and rearranging terms, we obtain

$$F\Lambda^* = \Lambda_0 - (1.5/K\,\Lambda_0)cf_{\mathrm{Mg}^{++}}[(F\Lambda^*)^2 - 0.1111\Lambda_0^2] \quad (19)$$

This equation represents a correction of equation (3) for interionic effects, its application under the assumed conditions of secondary dissociation (with primary dissociation complete) can be tested from experimental data by plotting $F\Lambda^*$ as a function of $cf_{\mathrm{Mg}^{++}}[(F\Lambda^*)^2 - 0.1111\ \Lambda_0^2]$ and observing whether or not the plot is linear over the proper concentration range. In practice, repeated computations were necessary, beginning with approximate values of Λ_0 and Λ_e, then inserting better values of Λ_0 and $\Lambda_e(\Lambda_e = \Lambda_0/F)$ and recomputing until Λ_0 became constant. Extrapolations for Λ_0 were made by the method of least squares, and K was calculated from the slope of the final plot.

A difficulty in applying equation (19) to uni-bivalent or bi-univalent salts, particularly in non-aqueous solutions, is the lack of reliable transference data that are required for computing the Onsager coefficients and evaluating γ by equation (10). By using available literature values[15] and unpublished conductance data the limiting transference numbers for the chloride, bromide and iodide ions in ethanol at 20° were estimated to be 0.534, 0.561 and 0.584, respectively.

Activity coefficients were computed by means of the Debye–Hückel equation

$$-\log f_{\mathrm{i}} = (z_{\mathrm{i}}^2\alpha\sqrt{\omega})/(1 + \beta a_{\mathrm{i}}\sqrt{\omega}) \quad (20)$$

It was necessary to estimate a_{i}, the minimum distance of approach for the magnesium ions, but it was believed that a better value of f_{i} could be obtained, especially for polyvalent electrolytes, than if the quantity $\beta a_{\mathrm{i}}\sqrt{\omega}$ were neglected entirely (at 20°, $\alpha = 2.9072$; $\beta = 5.874 \times 10^7$). An average value of 7.2 Å. was obtained for a_{i}, making use of calculated values[16] of the radii of the solvated magnesium ion in water and methanol solutions and of the solvated lithium ion in water, methanol and ethanol solutions.

Results and Discussion

The accumulated results of confirmatory determinations at each concentration were used in computations to obtain values for constructing the plots shown in Figs. 1, 2 and 3. In each case extrapolation to zero concentration was made by the method of least squares. The values which were obtained are collected in Table I.

TABLE I

CONSTANTS FROM CONDUCTANCE DATA FOR MAGNESIUM HALIDES[a]

	$MgCl_2$	$MgBr_2$	MgI_2
Λ_0 (from $\Lambda - \sqrt{c}$ plot)	43.45	46.18	48.79
Λ_0 (equation 3)	41.08	42.90	45.70
Λ_0 (equation 19)	41.75	44.57	47.18
Actual slope (Fig. 1)	−1510	−961.3	−913.3
Theoretical (Onsager) slope	−266.9	−272.9	−278.8
Ionization function, K'	1.709×10^{-4}	5.391×10^{-4}	6.208×10^{-4}
Dissociation constant, K	1.659×10^{-4}	4.650×10^{-4}	5.515×10^{-4}

[a] Detailed tables of original data and summaries may be obtained as Document 3606 from the American Documentation Institute, 1719 N Street, N.W., Washington 6, D.C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.20 for photocopies (6 × 8 inches) readable without optical aid.

From a comparison of the limiting equivalent conductances, it is apparent that the limiting ionic conductances of the chloride, bromide and iodide ions increase in the order named. The iodine atom has the largest radius; therefore, the ion would have the smallest charge per unit surface area, the lowest degree of solvation, the smallest *ionic* radius, and consequently, the greatest mobility, of the three halide ions. It is interesting to note that data for the cadmium halides, not included in this paper, showed a reverse order of ionic conductances, indicating the probability of complex ion formation.

The considerable discrepancy between the actual and theoretical slopes for the magnesium halides indicates that these salts are incompletely dissociated electrolytes, with the chloride being the weakest. The latter conclusion is also indicated by the lower dissociation constant of 1.659×10^{-4} for magnesium chloride, as compared to 5.515×10^{-4} for magnesium iodide. The ionization function, K', is not a true constant. When K' was calculated at various concentrations, rather than from the slope of equation (3), using a value of Λ_0 as obtained by equation (19), a trend of increasing values of K' with increasing concentration was obtained, whereas no such trend occurred for values of K in the same concentration range (over the range of linearity of the plot of equation (19)). The stronger dissociation shown by magnesium iodide might be expected as a result of the smaller surface charge density of the unsolvated iodide ion, requiring less energy for dissociation to occur.

The two most potent factors in equation (19) are the Shedlovsky function, F, and the activity coefficient of the magnesium ion, $f_{\mathrm{Mg}^{++}}$. F is a factor correcting the measured conductance for the

(15) J. W. Woolcock, H. Hartley and O. L. Hughes, *Phil. Mag.*, **11**, 222 (1931).

(16) G. Sutra, *J. chim. phys.*, **43**, 279 (1946).

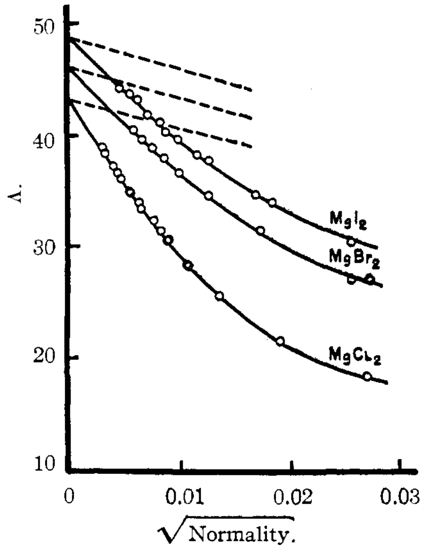

Fig. 1.—Equivalent conductance of $MgCl_2$, $MgBr_2$ and MgI_2 at 20° as a function of $\sqrt{C}$. Broken lines are theoretical Onsager slopes.

retarding effect of interionic forces upon ion mobility, and $f_{\mathrm{Mg}^{++}}$ is a measure of the extent to which the true magnesium ion concentration is effective. The two factors are counter-active; F increases while $f_{\mathrm{Mg}^{++}}$ decreases with increasing concentration. A significant conclusion to be drawn from the constancy of K in the dilute range is the correctness of the assumption that the magnesium ion activity is predominant in the computation of K (by equation (18)), *i.e.*, that dissociation takes place as described. The estimation of deviation from ideality by the Debye–Hückel equation is quite sensitive to ion valence; if a univalent ion or some combination of ions were involved, the numerical value of the activity coefficient would be quite different, since log f depends upon the square of the ion valence.

A comparison of values of the limiting equivalent conductance for magnesium chloride as obtained by extrapolation of various plots illustrates the importance of using those parameters for extrapolation which best represent the data in the measured range and are most likely to maintain linearity (or some known functional relationship) over the extrapolated region. In addition to the values given in Table I for magnesium chloride, the following were obtained: (1) 40.64, from a plot of $1/\Lambda$ *vs.* $c\Lambda$ (mass law plot assuming single dissociation, concentration as normality), and (2) 39.57, from a plot of $1/\Lambda$ *vs.* $(c\Lambda)^2$ (mass law plot assuming simultaneous dissociations of both stages). The Kohlrausch plot probably is inapplicable because of the great discrepancy between theoretical and actual slopes. Of the mass law plots, that of equation (3) showed linearity over a wider concentration range, thus establishing the assumption that the first stage dissociation was substantially complete in the range considered. Equation (19) was based on the same assumption, but incorporated corrections for electrostatic effects.

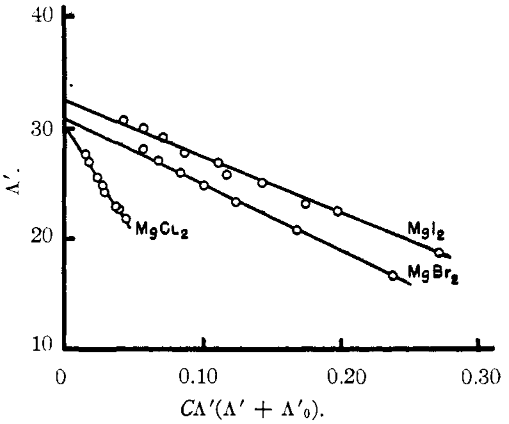

Fig. 2.—Mass law plots (eq. 3) for second dissociations of $MgCl_2$, $MgBr_2$ and MgI_2 in ethanol at 20°.

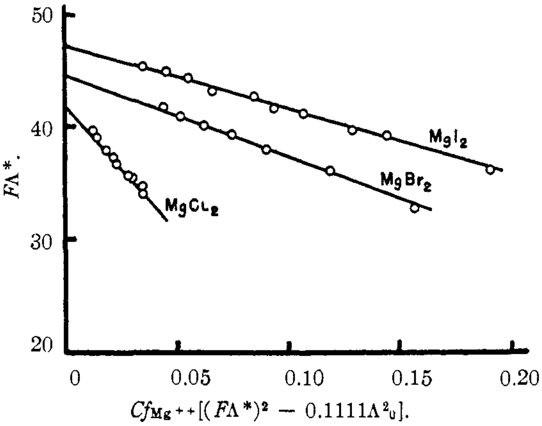

Fig. 3.—Plots of equation (19) for solutions of $MgCl_2$, $MgBr_2$ and MgI_2 in ethanol at 20°.

LEXINGTON, KENTUCKY