an ion-pair is very interesting, the approximate nature of the calculations involved should not be overlooked. The estimation of the thermodynamic term in equation (1) directly from experimental data should be fairly reliable. On the other hand, the two terms in equation (2) which represent the effect of electrophoresis depends on the value of 3.64 Å. assigned to the mean distance of approach a and of course this may be in error. However, this uncertainty does not invalidate the qualitative nature of the estimate of λ^0_m for if we assumed an extreme value of a of 10.8 Å., we find that λ^0_m is about 50. A further uncertainty resides in the values of α derived from conductance data.

Although these calculations are approximate, the theory of ion-pair formation in the case of zinc sulfate is consistent with our data in diffusion, the theory of electrophoresis of Onsager and Fuoss, the determination of the degree of dissociation by the conductance method and known behavior of the activity coefficient.

NEW HAVEN, CONNECTICUT RECEIVED DECEMBER 20, 1950

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

Conductances of Potassium Iodide, Silver Nitrate and Some Alkaline Earth Halides in Methanol at 20° and 0°[1,1a]

BY LYLE R. DAWSON AND WILLIAM M. KEELY[2]

Conductance studies have shown that for solutions of potassium iodide and silver nitrate in methanol the equivalent conductance is a linear function of the square root of the concentration over the range 1.6×10^{-5} to 2.0×10^{-2} N at 0 and 20°. Linearity was observed also at concentrations below 0.001 N for magnesium, strontium and barium chlorides and strontium bromide and iodide. The experimental slope is less than the theoretical for potassium iodide, but greater for all others with the deviation becoming less with increasing atomic weight of the bivalent cation. Considering the dielectric constant to be the principal variable, the effective dielectric constants have been calculated. The data give evidence that the principal temperature effect is its influence on the viscosity. Indications that solvation and acid–base effects are complicating factors appear also.

Conductance studies of solutions of silver nitrate and the halides of some of the alkali and alkaline earth metals were made for the purpose of testing the applicability of the Onsager equation[3] to solutions of these salts in a non-aqueous medium. Previous studies[4] have shown fair agreement between the observed values of the slopes of plots of equivalent conductance *versus* the square root of the concentration and the values predicted by the Onsager equation for uni-univalent electrolytes in methanol. However, this agreement does not extend to the results for bi-univalent salts, indicating that there is considerable tendency for association of ions which results in values for the equivalent conductance being less than that predicted by theory. It has been reported[5] that the thiocyanates of barium, strontium, calcium and magnesium behave like nearly completely dissociated bi-univalent electrolytes at low concentrations in methanol, but the thiocyanates of zinc and cadmium appear to be weak electrolytes. Data reported by Kanning and coworkers[6] suggest that sulfuric acid is an incompletely dissociate uni-univalent electrolyte in methanol.

Experimental

Apparatus.—The bridge assembly was essentially the same as that described by Shedlovsky.[7]

Four Washburn-type cells, having constants ranging from 0.07292 to 2.166, were used. The cell constants were determined by the method of Jones and Bradshaw.[8] The electrodes were coated lightly with platinum black and errors which might result from adsorption were minimized by agitating the solution in the cell. The cells were held in a thermostated bath which maintained a constant temperature to within ±0.01°.

Salts.—C.P. potassium iodide was recrystallized twice from conductivity water. C.P. silver nitrate was dissolved in hot conductivity water and recrystallized by slowly adding freshly distilled ethanol. Both of these salts used in this research were better than 99.9% pure.

Anhydrous magnesium chloride was prepared by the method described by Davidson[9] in which a pyridine–magnesium chloride complex was formed. The complex was decomposed under vacuum into anhydrous magnesium chloride and pyridine which volatilized. Analyses showed purities greater than 99% for all samples used. Anhydrous barium chloride and anhydrous halides of strontium were obtained from W. D. Mackay Co. In every case, analysis showed the purity to be greater than 99.9%.

Solvent.—Commercial reagent grade methanol was purified by the method described by Kanning, Bobalek and Byrne.[6] Specific conductances of the samples used ranged from 1.5×10^{-7} to 3.0×10^{-7} ohm^{-1} cm.$^{-1}$ at 20°. The Karl Fischer reagent gave no evidence of water in either the solvent or the solutions used in this research.

Solutions.—Solutions were prepared on a weight basis and molarities calculated, assuming the density of the solution to be the same as that of the pure solvent. All transfers were made in a dry atmosphere.

Results

Experimental conductivities were corrected for the conductivity of the solvent, and averages of two

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[1] This work was supported in part by a research contract with the U. S. Army Signal Corps.

[1a] For detailed tables order Document 3239 from 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 $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] Abstracted from a Ph.D. dissertation submitted by William M. Keely.

[3] L. Onsager, *Physik Z.*, **27**, 388 (1926); **28**, 277 (1927).

[4] (a) A. Unmack, E. Bullock, D. A. Murray-Rust and H. Hartley, *Proc. Roy. Soc.* (*London*), **A132**, 427 (1931); (b) J. E. Frazer and H. Hartley, *ibid.*, **A109**, 351 (1925); (c) T. H. Mead, O. L. Hughes and H. Hartley, *J. Chem. Soc.*, 1207 (1933); (d) L. Thomas and E. Marum, *Z. physik. Chem., Abt A*, **143**, 191 (1929).

[5] A. Unmack, D. M. Murray-Rust and H. Hartley, *Proc. Roy. Soc.* (*London*), **A127**, 228 (1928).

[6] E. W. Kanning, E. G. Bobalek and J. B. Byrne, THIS JOURNAL, **65**, 1111 (1943).

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

[8] G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

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

or three separate determinations were used for all computations. Summaries of pertinent data are presented in Tables I and II.

TABLE I

LIMITING EQUIVALENT CONDUCTANCES OF SOLUTIONS OF SALTS IN METHANOL[a,b]

Salt	Temp., °C.	Λ_0	$\Lambda_0\eta$
KI	20	110.5	
$AgNO_3$	20	97.1	0.576
$AgNO_3$	0	71.0	.574
$MgCl_2$	20	101.6	.602
$MgCl_2$	0	74.0	.598
$SrCl_2$	20	102.5	.608
$SrCl_2$	0	75.1	.607
$SrBr_2$	20	106.7	.633
$SrBr_2$	0	77.8	.629
SrI_2	20	112.1	.665
SrI_2	0	81.8	.661
$BaCl_2$	20	104.1	.617
$BaCl_2$	0	76.4	.617

[a] Original data may be obtained from the American Documentation Institute. [b] Properties of methanol: at 20°, density[10] 0.79134, viscosity[11] 0.00593 poise, dielectric constant[12] 33.7; at 0°, density 0.80999, viscosity 0.00808 poise, dielectric constant 37.5.

TABLE II

TEST OF ONSAGER'S EQUATION FOR ELECTROLYTES IN METHANOL

	Slope at 20°		Diel. const. calcd. from exptl. slope	Slope at 0°		Diel. const. calcd. from exptl. slope
	Exptl.	Onsager		Exptl.	Onsager	
KI	218	231	35.9			
$AgNO_3$	309	219	23.2	256	156	21.9
$MgCl_2$	1769	436	9.07	1127	307	10.9
$SrCl_2$	1098	437	13.7	793	310	15.0
$SrBr_2$	765	443	19.4	731	314	16.3
SrI_2	736	451	20.7	690	322	17.7
$BaCl_2$	803	442	18.5	575	314	20.3

Figure 1 shows that the equivalent conductance is a linear function of the square root of the concentration over the entire range studied in solutions of potassium iodide and silver nitrate in methanol.

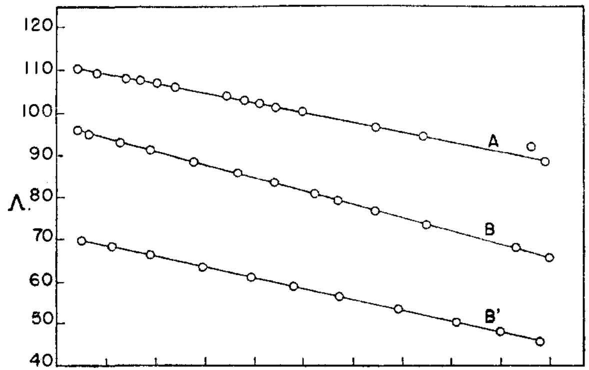

Fig. 1.—Equivalent conductance as a function of the square root of the concentration in methanol of: (A) KI at 20°; (B) $AgNO_3$ at 20°; (B') $AgNO_3$ at 0°.

In Figs. 2 and 3 it may be observed that a linear relationship between Λ and $\sqrt{C}$ appears to exist for solutions of alkaline earth halides at concentrations below 0.001 *N*, but at higher concentrations the curves become concave upward.

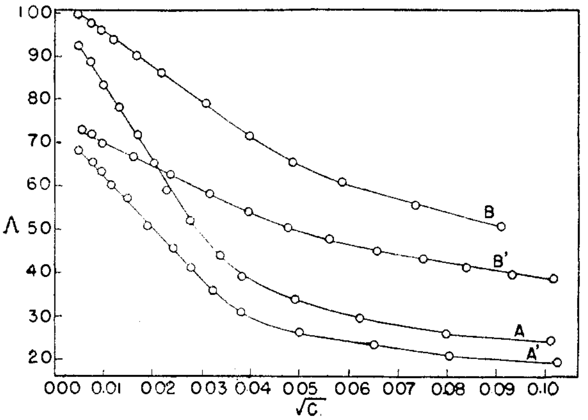

Fig. 2.—Equivalent conductance as a function of the square root of the concentration in methanol of: (A) $MgCl_2$ at 20°; (A') $MgCl_2$ at 0°; (B) $BaCl_2$ at 20°; (B') $BaCl_2$ at 0°.

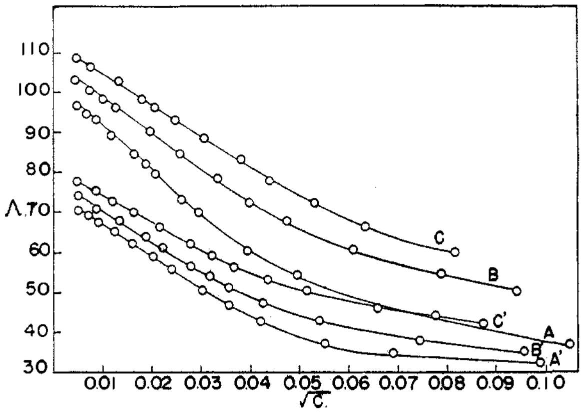

Fig. 3.—Equivalent conductance as a function of the square root of the concentration in methanol of: (A) $SrCl_2$ at 20°; (A') $SrCl_2$ at 0°; (B) $SrBr_2$ at 20°; (B') $SrBr_2$ at 0°; (C) SrI_2 at 20°; (C') SrI_2 at 0°.

The limiting equivalent conductances were obtained by extrapolating the Kohlrausch plot constructed by least squaring the data and with these values the Onsager slopes were calculated. For a bi-univalent electrolyte, the Onsager equation becomes

$$\Lambda = \Lambda_0 - \left[\left(\frac{2.622 \times 10^6}{(DT)^{3/2}}\right) \frac{\Lambda_0/(\lambda_0^- + \Lambda_0)}{1 + \sqrt{\frac{3}{2}\frac{\Lambda_0}{\lambda_0^- + \Lambda_0}}}\Lambda_0 + \frac{86.82}{(DT)^{1/2}\eta}\right]\sqrt{3C}$$

In the absence of transference data in methanol, transference numbers in aqueous solutions were used in calculating Onsager slopes for the unsymmetrical halides. Had it been possible to attain concentrations below approximately 10^{-5} *N*, extrapolation might have produced somewhat smaller values for Λ_0. It is recognized that the Onsager ex-

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(10) "Int. Critical Tables," Vol. III, p. 27.
(11) *Ibid.*, Vol, V, p. 11.
(12) *Ibid.*, Vol. VI, p. 83.

pression is a limiting equation and that a straight line Kohlrausch plot is not proof of complete dissociation. However, such a linear relationship may be considered to be evidence that the solute behaves like a relatively strong electrolyte.

Since there was wide disagreement between the experimental and observed slopes for bi-univalent salts, the theoretical expressions for the slopes of these plots as a function of the dielectric constant were equated to the observed slopes and the equations solved for the effective dielectric constants. These are reported in Table II.

Discussion

Greater conductance than predicted by theory, as shown by solutions of potassium iodide, seems to point to the presence of an additional force tending to counteract interionic attraction. This may be the result of the acidic nature, in the Lewis sense, of both the cation and the iodide ion toward methanol. Conductance and transference data in aqueous solutions have shown that the behavior of the iodide ion frequently is abnormal. Closer agreement between predicted and observed values was obtained for uni-univalent than for bi-univalent salts.

For all of the other salts studied the experimental slopes were greater than the values predicted by the Onsager equation, the deviation for a given halide decreasing with increasing atomic weight of the cation. This same order has been observed for the bivalent thiocyanates, while the reverse order is shown by uni-univalent salts in methanol. From the relative Λ_0 values it may be concluded that the lighter bivalent ions possess larger effective radii because of being more strongly solvated, which might be expected to result in a greater degree of dissociation. If such is not the case, it must be that although there is a larger solvent envelope around the lighter bivalent ion, the residual electrostatic forces available for attracting the anion are greater than around the heavier bivalent cations in the series. Conformity to Walden's rule connecting the limiting equivalent conductance and the viscosity of the solvent is evidence that a change in temperature of 20° has little influence on the extent of solvation but that its principal effect is on the viscosity of the solvent.

Probably the actual dielectric constant of the solvent between the ions in the solution differs considerably from that of the pure solvent. However, in view of the calculated values listed in Table II, it seems unlikely that this factor alone accounts for the disparity. Solvation and acid–base effects may be complicating factors also.

Comparison of the limiting equivalent conductances of the unsymmetrical halides studied with values obtained in this work and those reported in the literature[4] for uni-univalent salts in the same solvent indicates that magnesium and barium chlorides and the halides of strontium behave like relatively strong bi-univalent electrolytes in methanol at concentrations below 0.001 normal.

LEXINGTON, KY. RECEIVED JANUARY 17, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

A Study of Some Complex Chlorides and Oxalates by Solubility Measurements[1]

BY JAMES E. BARNEY, II,[2] WILLIAM J. ARGERSINGER, JR., AND C. A. REYNOLDS

Solubility measurements have been made as a function of added anion concentration for AgCl, $Ag_2C_2O_4$, MgC_2O_4, NiC_2O_4, CdC_2O_4 and CoC_2O_4. A shallow minimum in the solubility of $Ag_2C_2O_4$ is shown to be due entirely to common ion effects and change of activity coefficient with increasing ionic strength. In all other cases, deep minima are observed. The position of the minimum and the solubility in pure water are used to determine the nature and instability constant of the predominant complex ion in the corresponding concentration range in each case. In these dilute solutions complex ions with two coördinated anions are observed, with the following instability constants: $AgCl_2^-$, 2.2×10^{-6}; $Mg(C_2O_4)_2^{=}$, 4.2×10^{-5}; $Ni(C_2O_4)_2^{=}$, 3.1×10^{-7}; $Cd(C_2O_4)_2^{=}$, 2.2×10^{-6}; $Co(C_2O_4)_2^{=}$, 2.0×10^{-7}. In at least two cases, MgC_2O_4 and CdC_2O_4, appreciable amounts of un-ionized electrolyte are present and must be corrected for. Modifications of standard analytical techniques for low concentrations of metal ions are presented.

Introduction

Solubility data for sparingly soluble salts in solutions containing a common anion have been used to determine the nature and stability of the complex ions so formed. Standard methods of calculation have been developed,[3,4] which usually depend on the evaluation of the slope of the nearly linear ascending portion of the solubility curve. An alternative method of calculation has been suggested[5] which depends on the accurate location of the point of minimum solubility; the minimum solubility and the corresponding anion concentration suffice in many cases to determine the composition and the instability constant of the complex ion.

Very reliable solubility measurements for sparingly soluble salts have been reported in the literature, but only a few of these measurements indicate accurately the position of the minimum solubility point when the solubility of such a salt is measured as a function of the added concentration of the common anion. Therefore, in order to provide additional verification and application of the

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[1] Abstracted from a thesis presented by James E. Barney, II, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Kansas, September, 1950.

[2] Standard Oil Company of Indiana, Whiting, Indiana.

[3] A. B. Garrett, M. V. Noble and S. Miller, *J. Chem. Education*, **19**, 485 (1942).

[4] A. J. Fry, J. E. Barney, II, and R. W. Stoughton, AECD-249 (ORNL-63), Publication of the Atomic Energy Commission.

[5] C. A. Reynolds and William J. Argersinger, Jr., *Journal Phys. Colloid Chem.*, in press.