acids and/or their salts.[19] For simplicity only the cases of a solution of a pure acid and an acid and its salt will be discussed. In the latter instance, it will be assumed that reaction 15 contributes negligibly to the equilibrium concentration of acid. In both these examples it is derived easily from eq. 10 and $K_f^{H_3O^+X^-}$ that

$$(H_0)_{app.(w)} = (pK_{IH^+})_w - \log K_f^{IHX} - \log (C_{HX})_t + \log (1 + K_f^{IHX} C_{H_2O}) \quad (22)$$

where $(H_0)_{app.(w)}$ is the apparent acidity function in a solution containing an analytical concentration of acid $(C_{HX})_t$ and an equilibrium concentration of water C_{H_2O}. So long as C_{H_2O} is approximately equal to the analytical concentration of water, a plot of $(H_0)_{app.(w)}$ *vs.* log $(C_{HX})_t$ is a straight line of slope minus one. This line will be displaced from the line obtained in anhydrous acetic acid by the value of term, $\log (1 + K_f^{H_3O^+X^-} C_{H_2O})$.

Ludwig and Adams[20] have determined the apparent acidity function of dilute perchloric acid solutions (C_{HClO_4}, 0.1 *M*) in acetic acid containing varying amounts of water. They present a figure with H_0 as the ordinate and $-\log C_{HClO_4}$ as abscissa. As predicted by eq. 22 this figure contains a family of parallel straight lines of unit slope. Using a previously determined value of $K_f^{H_3OClO_4} = 34$,[10] it is calculated from eq. 22 that the displacement in the vertical direction between the lines representing anhydrous and acetic acid containing 1.95% water should be 1.6 H_0 unit. The displacement found from the figure of Ludwig and Adams is about 1.7 to 1.8 units. This agreement is excellent considering that these authors used different indicators in obtaining the acidity function data in anhydrous and wet acetic acid. The results obtained with *p*-naphtholbenzein and perchloric acid[10,19] and *o*-nitroaniline and perchloric acid[12] are also in agreement with eq. 22.

Generally, the effect of water is adequately described by reaction 21 if the concentration of water is less than about 0.4 *M*. At higher concentrations of water the nature of the solvent is changed markedly; specifically the dielectric constant increases. Thus Wiberg and Evans[21] suggest that in the concentration range 3 to 15 *M* water the hydronium ion apparently is hydrated by one molecule of water because they find that in perchloric acid solutions H_0 is proportional to 2 log C_{H_2O}. We[22] find similar behavior for sulfuric acid solutions starting about 1 *M* water.

Acknowledgment.—This work was sponsored by the Office of Ordnance Research, U. S. Army.

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[21] K. B. Wiberg and R. J. Evans, *ibid.*, **80**, 3019 (1958).

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA AND THE WESTINGHOUSE ELECTRIC COMPANY]

Solutions of Metals in Amine Solvents. III. The Conductance of Dilute Solutions of Lithium in Methylamine at −78.3°[1]

BY DONALD S. BERNS,[2] E. CHARLES EVERS AND PAUL W. FRANK, JR.

RECEIVED JULY 23, 1959

The conductance of lithium in methylamine at −78.3° has been measured over the concentration range from 0.22 *N* to 1.8×10^{-4} *N*. The data follow the conductance function proposed earlier[15] and provide further support for the model of metal-amine solutions proposed by Becker, Lindquist and Alder.[7]

Numerous theories have been proposed to account for the physical properties of solutions of metals in amine solvents.[3-10] Of those theories currently in favor, which pertain to dilute metal solutions, we prefer that proposed by Becker, Lindquist and Alder.[7] These authors suggest that "solvated electrons" interact with solvated metal ions to form ion-pairs or "monomers"; the latter then interact to form diamagnetic quadrupoles or "dimers"; the four species are in dynamic equilibrium. This model appears to account well for many of the physical properties of solutions of metals in ammonia, although precise data are lacking in most instances. Recent, direct support for the model may be found in nuclear magnetic resonance studies of McConnell and Holm[11] in conjunction with a theoretical interpretation of their results by Blumberg and Das.[12]

The most precise data relating to dilute solutions of metals are those due to Kraus[13] on the conductance of sodium in liquid ammonia at −34°. Recently Evers and Frank,[14] using the mass action concept of Becker, *et al.*,[7] have derived a conductance function which successfully reproduced the data of Kraus up to concentrations in the neighborhood of 0.04 *N*. Since precise data were not avail-

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[1] (a) Taken in part from a thesis by D. S. Berns, presented in partial fulfillment of the requirements for the Ph.D. degree, June, 1959. (b) Sponsored in part by the Office of Ordnance Research, U. S. Army.

[2] E. I. du Pont de Nemours Teaching Fellow in Chemistry, 1958–1959.

[3] C. A. Kraus, *J. Franklin Inst.*, **212**, 537 (1931).

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[14] E. C. Evers and P. W. Frank, Jr., *J. Chem. Phys.*, **30**, 61 (1959).

able in other solvent media, the present study was undertaken to test the applicability of the *Becker, et al.*, model to solutions of metal in methylamine. We have therefore undertaken a study of the conductance of dilute solutions of lithium in methylamine at $-78°$. It will be seen that the conductance function reproduces the data in methylamine with almost the same degree of success as in ammonia. We feel this is further support of the Becker, *et al.*,[7] model and of the applicability of electrolyte theory to dilute metal solutions.

Experimental

The high chemical metastability and reactivity of the lithium–methylamine system made it necessary to exercise extreme care to guarantee cleanliness of equipment and purity of the materials involved. In an earlier study[15] it was found that at $-23°$ decomposition constituted a major problem even in the more concentrated solutions. Attempts to prepare sufficiently stable dilute solutions at $-23°$ and at $-33.5°$ were unsuccessful; therefore, the present study was carried out at $-78.3°$ where the requisite stability was achieved.

1. **Materials and Apparatus.**—The conductance cell was constructed with bright platinum electrodes sealed into Pyrex glass using the method of Hnizda and Kraus.[16] Only a small portion of the platinum tubing, beaded on the end, was allowed to protrude beyond the glass seal to serve as an electrode.[15] The cell constant was 1.300 cm.$^{-1}$ as determined by methods described previously.[17] Before metal solutions were prepared, the cell was cleaned with hot fuming nitric acid, washed with distilled water and rinsed with absolute alcohol. It was then attached to a vacuum system and evacuated to a pressure of 10^{-5} mm. for approximately 10 hours while being heated to 250°.

The conductance cell had a solution capacity of approximately 1500 ml. Lithium metal, cut in small pieces (<50 mg.), was introduced by means of four "doser" stopcocks. The stopcocks were loaded through 19–22 standard taper joints, bearing caps. The loading assemblies and cell proper were each sealed to the vacuum system by separate lines, so they could be evacuated independently. N-Apiezon grease was used throughout. To permit preparation of solutions of concentrations above 0.01 N, one of the "doser" stopcocks was replaced by a 20–40 standard taper ground-glass assembly so that larger pieces of metal could be added directly to the cell.

Lithium metal was cut under oil saturated with argon, washed free of oil, dried and transferred under argon as described previously.[15] Samples of metal were weighed in argon-filled tubes on a semi-micro balance. The samples then were transferred to the "doser" stopcocks in a stream of argon and the loading system was thoroughly evacuated. To prepare the most dilute solutions (2×10^{-4} N) approximately a 2-mg. sample of metal was required. This could be weighed with a precision of roughly 0.5%. However, as we shall see below, it was not necessary to know precisely the weight of the samples employed for the more dilute solutions, since it was possible to calculate their concentrations using overlapping conductance data from other experiments.

The solvent was a Rohm and Haas product obtained from the Matheson Chemical Co. It was purified in the manner described previously[15] except that one additional treatment with metal and fractionation was employed. The purified solvent was stored in stainless steel weighing cans equipped with packless diaphragm valves. These were attached to the vacuum system, using DeKhotinsky cement. The solvent conductance was beyond the range of measurement with our equipment and was certainly less than 1×10^{-9} mho cm.$^{-1}$; accordingly, a correction for solvent conductance was not necessary.

The constant temperature bath consisted of a five gallon insulated Pyrex glass jar containing a slurry of Dry Ice in isopropyl alcohol. The bath was raised or lowered by means of a hydraulic lift; the cell was attached permanently to the vacuum system and to the source of methylamine. A copper–constantan thermocouple was used for temperature measurements in conjunction with a Leeds and Northrup Portable Precision Potentiometer, Model No. 8662. The potential was checked after each conductance measurement; the readings were reproducible to ±0.03°. The temperature of several Dry Ice baths was measured with a four-lead, platinum, resistance thermometer, calibrated by the National Bureau of Standards; the bath temperatures were in the range $-78.33 \pm 0.01°$.

Resistance measurements were made at 2000 cycles with a Leeds and Northrup Jones Bridge, using earphones as the null detector. Polarization effects were not noted when metal solutions were measured.

The solutions were stirred continuously during preparation and during resistance measurements. Stirring was done with a magnetic stirring bar encased in Pyrex glass. The bar was driven externally by a magnet which was powered by an electric motor through a flexible drive-shaft and a reduction gear assembly. The latter was encased in a metal housing in order to prevent the gears from fouling when the stirring unit and cell were immersed in the cooling bath.

2. **Procedure.**—In preparing solutions, amine was condensed from the weighed storage cylinder into the cell immersed in the Dry Ice bath.[15] The solvent was stirred for an hour or so to ensure temperature equilibrium; then a sample of metal was released. The solution was stirred until a constant resistance reading was obtained, indicating that all metal had dissolved and thermal equilibrium had been reached. Under optimum conditions the resistance of even the most dilute solutions remained constant for several hours; usually we assumed equilibrium had been established if the resistance readings were constant over a period of one-half hour. The other samples were then released successively, following the same procedure. Considerable flexibility was afforded as to the range and magnitude of the metal concentration. Samples weighing up to approximately 50 mg. could be accommodated in the "doser" stopcocks thus furnishing a concentration range of well over a factor of ten in four samples; between 150 ml. and 1500 ml. of solvent could be accommodated in the cell which could likewise furnish a concentration range of a factor of ten by dilution. Thus it was possible at times to determine a series of four points using a small amount of solvent, then to dilute sufficiently to check some point on the specific conductance–concentration curve established at lower concentrations.

In preparing the more concentrated solutions, metal was first added directly to the body of the cell, amine was condensed in and the solution was stirred until equilibrium was reached; then the three smaller pieces were added from the "doser" stopcocks according to the procedure described above.

3. **Very Dilute Solutions.**—To determine accurately the concentration of the very dilute solutions presented somewhat of a problem for two reasons: (1) the atomic weight of lithium is low making it necessary to use very small quantities of metal; errors in weighing and contamination of the metal during handling were increased accordingly. (2) It was not possible to free the solvent completely of impurities, which probably were introduced during manipulation of solvent or remained absorbed on the walls of the cell. Although these reacted with metal, they were used up by the first sample of metal and apparently caused no catalytic effect on the reaction of metal with amine, since a constant resistance reading always was obtained. The effect of impurities usually became apparent only below concentrations of approximately 10^{-3} N. The effect was particularly noticeable on using the dilution technique, where the Λ-$C^{1/2}$ curve commenced to become concave downward with increasing dilution. It was for this reason that the dilution procedure was abandoned in favor of the concentration method described above.

In order to obtain the conductances of the most dilute solutions, between 1000 and 1500 ml. of solvent was employed. The first piece of lithium was added and the solution was stirred until a constant resistance reading was obtained. Other pieces of metal were then added in succession and the resistance recorded after each addition. The final resistance reading was made on a solution of sufficiently high concentration so that one could refer this final reading

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[15] E. C. Evers, A. E. Young, II, and A. J. Panson, THIS JOURNAL, **79**, 5118 (1957).

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[17] E. C. Evers and A. G. Knox, Jr., *ibid.*, 1739 (1951).

(and sometimes the previous reading) to a curve of specific conductance *versus* the square root of concentration, which had been determined using data from previous experiments. In this way one could obtain the concentrations of the final and intermediate points by graphical means with good precision and then extrapolate to obtain the concentration of the most dilute solution. As a check on the method, the calculated weights of metal added after the first sample, namely, for points 2, 3 and 4, were compared with the quantities actually weighed in. Excellent agreement was obtained in all cases, indicating that no measurable loss of metal had occurred after the first sample had been added. The results of a typical experiment are presented in Table I, where point No. 4 represents the most concentrated solution.

TABLE I

ANALYSIS OF CONDUCTANCE DATA FOR DILUTE SOLUTIONS

Point no.	Meq. of Li added By wt.	Meq. of Li added Calcd.
2	0.690	0.697
3	.535	.536
4	.629	.626

By employing the method of overlapping data the internal consistence of the results was assured for all but the most dilute solutions recorded in Table II, namely, those below 2.790×10^{-4} N. The concentrations of these solutions, however, were obtained by extrapolation as described above, where the most concentrated points in each series experiment were in the concentration range from 4 to 8×10^{-4} N. The values obtained by extrapolation were internally consistent in that they fell within 1 or 2%, of the specific conductance-concentration curve predicted by the data at the higher concentrations.

TABLE II

CONDUCTANCE OF SOLUTIONS OF LITHIUM IN METHYLAMINE AT −78.3°

	Λ			Λ	
$C \times 10^2$	Exptl.	Calcd.	$C \times 10^2$	Exptl.	Calcd.
0.01798	107.1	107.7	0.3174	41.93	39.72
.02280	100.0	100.1	.3354	41.71	38.91
.02490	94.17	97.32	.3737	38.66	37.37
.02680	92.77	95.05	.3899	37.59	36.78
.02790	90.31	93.82	.4109	35.61	36.03
.03590	84.51	86.37	.4684	37.08	34.33
.04130	75.16	82.41	.5255	35.98	32.88
.05420	72.19	75.13	.5353	34.53	32.65
.05760	73.96	73.67	.6050	32.85	31.18
.06640	65.56	70.02	.6171	32.17	30.95
.08380	61.50	64.52	.9213	27.82	26.64
.08823	60.94	63.35	1.054	25.28	25.35
.09364	59.93	62.03	1.243	23.77	23.87
.09401	60.52	61.94	1.515	21.83	22.26
.1048	59.53	59.58	1.683	21.04	21.47
.1058	59.59	59.38	2.653	18.05	18.66
.1142	56.51	57.78	3.082	16.78	17.99
.1590	50.41	51.26	3.407	16.36	
.1682	50.06	50.21	5.807	13.74	
.1706	50.79	49.95	6.972	13.00	
.2016	48.15	46.99	7.424	12.84	
.2106	47.86	46.24	7.887	12.72	
.2219	46.77	45.36	8.275	12.55	
.2375	45.30	44.23	11.37	11.03	
.2535	44.91	43.18	13.15	10.15	
.2989	42.02	40.62	16.24	11.62	
.2993	41.65	40.59	17.31	11.65	
			22.34	12.35	

4. **Experimental Results.**—The viscosity of methylamine was determined at four temperatures with the following results: −78.3° (Dry Ice), η = 0.009120 poise; −63.3° (melting chloroform), 0.006704; −22.8° (melting carbon tetrachloride), 0.003532; and 0°, 0.002742 poise, respectively. The method of least squares was applied to the data to give the equation $\log \eta = 355.8/T - 3.868$, where T is the absolute temperature.

The dielectric constant of methylamine at −78.3° was found to be 17. This value is in good agreement with the value obtained by extrapolating the data of Ulich and Nespital[18] given at higher temperatures.

The conductivity data are given in Table II. The density of the solvent at −78.3° was computed using the equation of Felsing and Thomas.[19] The density of the solutions were assumed to be that of the solvent. Λ is equivalent conductance and C is concentration in g. atoms per liter; included in the table are calculated values of Λ obtained from equation 1.

Calculations

As noted above, the present study was undertaken to test the applicability of the Becker, *et al.*,[7] model to solutions of lithium in methylamine. The solute species number four: (1) the solvated electron e^-, (2) the solvated metal ion M^+, (3) the ion pair or monomer M consisting of an electron circulating about the metal ion among the hydrogen atoms of the solvating amine molecules and (4) the dimer or quadrupole, M_2, consisting of two monomers held together chiefly by exchange forces. Our task then is to evaluate the two equilibrium constants for competing reactions, where bracketed terms represent activities

$$M = M^+ + e^- \qquad k_1 = \frac{[M^+][e^-]}{[M]}$$

$$M = {}^1/_2M_2 \qquad k_2 = \frac{[M_2]^{1/2}}{[M]}$$

On assuming that one may differentiate between activity and mobility effects, and that one may apply methods developed for solutions of normal electrolytes, Evers and Frank[14] have developed the equation for dilute metal solutions

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda_0} + \frac{S(z)Cf^2\Lambda}{\Lambda_0{}^2k_1}\left[1 + \frac{2k_2{}^2\Lambda^2S(z)^2C^2f^2}{k_1\Lambda_0{}^2}\right] \quad (1)$$

Here Λ is equivalent conductance, Λ_0 is the limiting value of equivalent conductance, $S(z)$ includes mobility corrections as defined by Shedlovksy,[20] f is the mean activity coefficient of ionized metal, C is normality and k_1 and k_2 have the significance defined above.

The method of Shedlovsky[20] was used to evaluate Λ_0 using data below approximately 1.5×10^{-3} N and also to approximate k_1. Values obtained for Λ_0 and k_1 were 228.3 and 5.5×10^{-5}, respectively. The value of k_2, as well as a more precise value of k_1, were then obtained from equation 1 using the method of least squares as explained previously.[14] This analysis led to the values $k_1 = (5.79 \pm 0.12) \times 10^{-5}$ and $k_2 = 5.42 \pm 0.33$.

A comparison between the experimental values of Λ and those calculated using equation 1 are recorded in Table II and presented graphically in Fig. 1. The average difference between observed and calculated values of the conductance is ±1.54 Λ units or approximately 3%. It is felt that these results reflect the precision of the data, since the calculated curve represents the functional dependence of Λ upon C as well as any other smooth curve which might be drawn arbitrarily through the data. In

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[18] H. Ulich and W. Nespital, *Z. physik. Chem.*, **B16**, 221 (1932).

[19] W. A. Felsing and A. R. Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

[20] T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

fact we feel that these results lend considerable credence to formula 1 and the assumptions on which it is based.

Discussion

The form of the conductance–concentration curve for solutions of lithium in methylamine is similar to that found for sodium in ammonia. Concentrated solutions in either solvent display metal-like properties.[15,21] As the metal concentration is decreased the conductivity falls off exponentially, passes through a minimum and then increases less rapidly with further dilution.

Conductances are much lower in methylamine than in ammonia. For example, with lithium in methylamine at −78° the minimum occurs at about 0.13 N and a conductance value of approximately 17 Kohlrausch units; at −23°, the values are 0.1 N and 47, respectively.[15] With sodium in ammonia at −34° the minimum is found at 0.04 N and a conductance of 540.[13] The conductances of dilute solutions of sodium in ammonia and lithium in methylamine are compared in Fig. 1. Here the conductance ratio, Λ/Λ_0, is plotted against $C^{1/2}$, where Λ_0 is the respective limiting value in the two cases. In the sodium–ammonia system the increase in equivalent conductance from the minimum to the limiting value is gradual and about twofold. With lithium in methylamine the increase is about twenty-fold. The region of the minimum is broader in methylamine than in ammonia. It is evident that the mobilities, or the concentrations, of the conducting species are lower in methylamine than in ammonia. We are of the opinion that both effects are responsible for the difference in the behavior of the two systems.

The various constants derived from conductance data, which characterize the two systems, are presented in Table III. Also included is the Bjerrum radius, a, for the two metals.

TABLE III

CONSTANTS DERIVED FROM CONDUCTANCE DATA

System	Temp., °C.	$k_1 \times 10^3$	a	k_2	Λ_0	$\Lambda_0\eta$
Li in CH_3NH_2	−78	0.0579	4.0	5.42	228.3	2.1
Na in NH_3	−34	7.23	7.6	27.0	1022.0	2.6

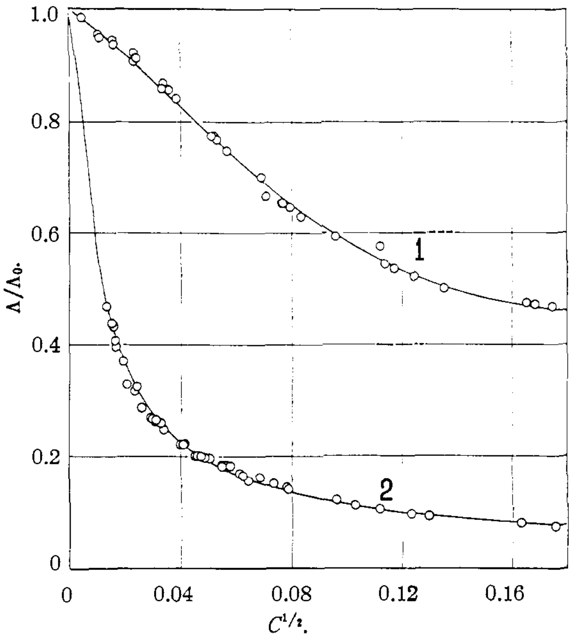

Fig. 1.—Conductance of metals in amine solvents, solid lines computed according to equation 1; circles, experimental; curve 1, sodium in ammonia at −34° (ref. 14); curve 2, lithium in methylamine at −78°.

It will be noted that the constant for "ion-pair" or monomer dissociation k_1 is two factors of ten lower in methylamine than in ammonia. Since the dielectric constants of the two solvents are not too different (22 for ammonia and 17 for methylamine), a difference of this order of magnitude must reflect constitutional differences and probably the effect of temperature. Intuitively the constants seem reasonable and in the right order. The smaller lithium ion should exert a stronger influence on the solvated electron, leading to greater association. While we have no direct measure of the effect of temperature on k_1, the enthalpy change most likely is positive in the temperature range from −78 to −34°; hence k_1 should become smaller with decreasing temperature. Recently we have determined the mass action constant for tetra-n-butylammonium picrate in methylamine[22] at −78° and obtained a value of about $8 \times 10^{-}.^{5}$ This value is only slightly greater than that obtained for lithium. It may be noted further that the mass action constant for sodium bromide in ammonia[16] at −34° is 2.9×10^{-3} which compares well in order of magnitude with that computed for sodium. The values of k_1 for metal solutions, therefore, appear to be substantially the same as those obtained with normal electrolytes. Of further interest are the values of a, the Bjerrum distances, although their physical significance is questionable. The value for sodium is fairly well in accord with previous estimates of size[5] if we concur with the cavitation model and assume the metal ion and solvated electron associate to form an ion pair in the normal sense. The value for lithium in methylamine is smaller, indicating tighter bonding.

The relative values of k_2 are more difficult to justify. If the dimerization reaction is exothermic as suggested by Becker, *et al.*,[7] and others[5,23] who favor the cavitation model, then k_2 must increase with decreasing temperature. This interpretation seems correct on the basis of existing data. Therefore, in view of the values quoted in Table III, it would appear that k_2 must be strongly influenced by either the nature of the solvent medium or the nature of the positive ion. Qualitative data would seem to indicate that the nature of the positive ion is very important. For example, solutions of lithium in methylamine are strongly paramagnetic[23]; this behavior would be predicted as a result of our conductance measurements. Solutions of potassium,[23] on the other hand, are only weakly paramagnetic, suggesting that a substantial fraction of the metal exists as dimers. More data are needed before further correlations are attempted.

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(21) C. A. Kraus and W. W. Lucasse, THIS JOURNAL, **43**, 2529 (1921).

(22) A. M. Filbert, unpublished observations, this Laboratory.

(23) G. W. A. Fowles, W. R. McGregor and M. C. R. Symons, *J. Chem. Soc.*, 3329 (1957).

Included in column 7 of Table III are the Walden products, $\Lambda_0\eta$, for the two systems. From these results it would appear that the viscosity of the solvent media largely determines the mobilities of the species present at infinite dilution. While a direct comparison between the two solvent systems using one metal is not possible, it would be expected that the product would be somewhat smaller for lithium than for sodium in any case, since the former would probably be heavily solvated.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Transference Numbers and Conductances of Multivalent Salts in Aqueous Solution: Zinc Sulfate and Zinc Perchlorate[1]

BY JAMES L. DYE, M. PATRICIA FABER AND DAVID J. KARL

RECEIVED JULY 23, 1959

The transference number of $ZnSO_4$ in water as a function of concentration was measured by the moving boundary method at 25°. The equivalent conductance of aqueous $Zn(ClO_4)_2$ also was measured and found to deviate markedly from the Onsager equation even in dilute solutions. Attempts to explain this behavior on the basis of ion-pairing, hydrolysis and purely electrostatic interactions were unsatisfactory. The conductance data for $ZnSO_4$ taken alone can be adequately fit by either the Fuoss–Onsager theory including ion-association or including instead higher terms of the electrophoretic equation. The former treatment also fits the transference data. However, when λ_0 for Zn^{++} from measurements on $Zn(ClO_4)_2$ is used, neither theory alone describes the behavior adequately. It is postulated that the covalent-bonding tendencies of Zn^{++} give deviations from any theory which is based upon the assumption of non-polarizable ions.

Introduction

With the recent publication of excellent theoretical papers by Fuoss and Onsager[2] dealing with the time-of-relaxation effect in conductance, and the application to ion-pairing systems by Fuoss,[3] the theoretical treatment of dilute solutions of 1–1 electrolytes in solvents of dielectric constant greater than about 20 is on firm ground. Unfortunately this cannot be said of unsymmetrical electrolytes even for dilute solutions in water. It has been shown[4] that extended terms in the electrophoretic effect are significant for 2–1 and 3–1 electrolytes and it is reasonable to assume that these non-linear terms in the distribution function also are important in the time-of-relaxation expression. We are currently studying the conductances, transference numbers and activity coefficients of a variety of multivalent electrolytes as tests of the various theoretical expressions. Since the Fuoss–Onsager Theory is capable of handling symmetrical electrolytes, it appeared to be of interest to apply the extended theories to the conductance of zinc sulfate, a 2–2 electrolyte for which accurate conductances are available.[5]

An attempt to fit conductance data alone would require three parameters, (1) the limiting equivalent conductance of zinc sulfate, (2) the ion-size parameter $\mathring{a}$ and (3) the ion-association constant A. It would be an unusual equation which could *not* fit a single smooth curve with the aid of three adjustable parameters. In order to reduce the arbitrariness of fit, it was decided to determine the limiting equivalent conductance of zinc ion by measuring the equivalent conductance of zinc perchlorate as a function of concentration. To test further the theoretical expressions, the transference number of zinc sulfate was determined as a function of concentration. The only reasonable data available for transference numbers are those of Purser and Stokes[6] based upon the e.m.f. method and Gold[7] based upon the Hittorf method. These methods are subject to rather large errors and we employed the more accurate moving boundary method. The present paper gives the experimental results obtained and the comparison of theory and experiment.

Experimental

Transference numbers were determined by the moving boundary method. All measurements were made with descending boundaries. The cell employed was the hollow barrel stopcock type with an added stopcock at the bottom of the graduated portion for use with rising boundaries. The transference tube was calibrated with mercury as recommended by Longsworth.[8] Constant currents were obtained with an electronic controller and balancing motor. Current was determined from the potential drop across a standard resistor in series with the cell. Compensation for minor fluctuations not eliminated by the electronic apparatus was made by feeding the unbalance from the Leeds and Northrup type K-1 potentiometer to a Brown "Electronik" 356358-1 amplifier which was used to drive a Brown 76750-3 balancing motor. A cadmium plug anode and silver–silver chloride cathode were utilized. An aquarium type water bath was maintained at 25.00 ± 0.05°. Stopwatches were calibrated using the standard WWV signal. The entire apparatus was checked at intervals by measuring the transference number of potassium chloride followed by lithium chloride. These results agreed with published values to within 0.05%.

Conductivity measurements were carried out in two Leeds and Northrup "Type A" cells, which were modified by sealing them to 500-ml. erlenmeyer flasks. This permitted measurement of the water conductance and the addition of solute without exposure to atmospheric CO_2. Similar cells were used by Kraus and co-workers.[9] The cells, whose electrodes were very lightly platinized (40 seconds)

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[1] Presented in part at the 133rd meeting of the American Chemical Society, April, 1958, San Francisco, Calif.

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