TABLE I

OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS OF MAGNESIUM AND BARIUM CHLORIDES AT 25°

$MgCl_2$				$BaCl_2$			
c, mole/l.	$\mathfrak{D} \times 10^5$ Obsd.	$\mathfrak{D} \times 10^5$ Calcd.	$\mathfrak{D}' \times 10^5$	c, mole/l.	$\mathfrak{D} \times 10^5$ Obsd.	$\mathfrak{D} \times 10^5$ Calcd.	$\mathfrak{D}' \times 10^5$
0.00000	...	(1.251)	(1.251)	0.00000	...	(1.387)	(1.387)
.00129	1.187	1.180	1.258	.00068	1.332	1.327	1.392
.00153	1.180	1.176	1.255	.00097	1.319	1.317	1.389
.00205	1.168	1.163	1.256	.00109	1.321	1.314	1.394
.00270	1.164	1.161	1.254	.00139	1.308	1.307	1.388
.00283	1.157	1.160	1.248	.00214	1.302	1.294	1.395
.00309	1.157	1.153	1.247	.00229	1.301	1.291	1.397
.00364	1.155	1.152	1.248	.00287	1.285	1.284	1.388
.00400	1.164	1.159	1.256	.00403	1.265	1.272	1.382
		Mean	1.253	.00452	1.271	1.268	1.390
				.00542	1.261	1.262	1.386
						Mean	1.390

conductances which according to Shedlovsky and Brown[11] are $1/2Ba^{++} = 63.64$, $1/2Sr^{++} = 59.46$, $1/2Ca^{++} = 59.50$, $1/2Mg^{++} = 53.06$. Thus, the limiting conductances of calcium and strontium ions are nearly identical, a situation which is inconsistent with the diffusion data. It is hoped that experiments now being carried out in this Laboratory will clarify this situation.

TABLE II

OBSERVED ALKALINE EARTH CHLORIDE DIFFUSION COEFFICIENTS IN DILUTE SOLUTION

	$\mathfrak{D} \times 10^5$			
c, mole/l.	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
0.001	1.187	1.248	1.267	1.317
.002	1.169	1.223	1.250	1.296

This investigation was supported in part by the Atomic Energy Commission under Contract AT-(30-1)1375.

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[11] T. Shedlovsky and A. S. Brown, THIS JOURNAL, **56**, 1066 (1934).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WESTERN AUSTRALIA]

The Diffusion Coefficients and Conductances of Some Concentrated Electrolyte Solutions at 25°

BY B. F. WISHAW[1] AND R. H. STOKES

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Diffusion coefficients of aqueous ammonium nitrate, lithium nitrate and ammonium sulfate solutions, and conductances of ammonium nitrate and ammonium chloride solutions are reported for high concentrations (0.1–8.0 moles/liter at 25°). Theoretical expressions for the diffusion coefficient and conductance of the 1:1 electrolytes are found to be remarkably successful. In the case of ammonium nitrate there is evidence of marked ion-pair formation, the extent of which is estimated from the conductance data and then used in the interpretation of the diffusion results.

Introduction

Diffusion data for aqueous solutions at 25°, to concentrations of several molar, have previously been obtained by the magnetically-stirred porous diaphragm cell method for eight alkali halides, hydrochloric acid and hydrobromic acid.[2,3] The Goüy diffusiometer has been used for similar studies on potassium chloride,[4] ammonium chloride and calcium chloride.[5] All these electrolytes are of the non-associated type, and while the interpretation of the diffusion data is by no means a simple task it is at least not complicated by the effects of ion-pair formation. There are, however, indications that such effects are present in the diffusion of bivalent metal sulfates, for which data at low concentrations (< 0.01 *M*) are available from the conductometric diffusion cell studies of Harned and collaborators.[6,7]

In the present paper we report diffusion measurements on concentrated solutions of ammonium nitrate, lithium nitrate and ammonium sulfate by the Goüy method, in order to provide further basis for studying the effects of ion-pair formation. These measurements are supplemented by some conductance determinations.

Experimental

Materials.—Ammonium nitrate of analytical reagent quality was recrystallized and made into a concentrated stock solution, the composition of which was found by careful density measurements (reproducible to at least 1 part in 30,000) with the help of recorded density data.[8,9] *Ammonium chloride* of analytical reagent quality was used

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[1] The work reported here is summarized from a thesis presented for the degree of Master of Science of the University of Western Australia by B. F. Wishaw in July, 1953.

[2] R. H. Stokes, THIS JOURNAL, **72**, 2243 (1950).

[3] P. J. Dunlop and R. H. Stokes, *ibid.*, **73**, 5456 (1951).

[4] L. J. Gosting, *ibid.*, **72**, 4418 (1950).

[5] J. R. Hall, B. F. Wishaw and R. H. Stokes, *ibid.*, **75**, 1556 (1953).

[6] H. S. Harned and R. M. Hudson, *ibid.*, **73**, 5880 (1951).

[7] H. S. Harned and C. A. Blake, *ibid.*, **73**, 4255 (1951).

[8] "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 59.

[9] L. H. Adams and R. E. Gibson, THIS JOURNAL, **54**, 4520 (1932).

without further purification, in the form of a concentrated stock solution analyzed gravimetrically for chloride as silver chloride. *Lithium nitrate:* Reagent grade lithium hydroxide was precipitated as carbonate by saturating with carbon dioxide. The washed and dried carbonate was then dissolved in a known weight of previously analyzed nitric acid until the acid was just neutralized. After boiling out carbon dioxide, the solution was made up to a known weight and its concentration was calculated from that of the nitric acid. The *p*H of the stock solution was close to 7.0. *Ammonium sulfate* of analytical reagent quality was made into a stock solution which was analyzed by density and by gravimetric determination of sulfate as barium sulfate.

In each case more dilute solutions were prepared as required by weighing out suitable amounts of stock solution and making up to known volumes at 25° in calibrated standard flasks. Doubly distilled water with a specific conductivity of $\sim 2 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ was used throughout.

Diffusion Measurements.—These were made with the Goüy diffusiometer previously described.[5] The experimental results are given in Table I and those for the 1:1 electrolytes are plotted in Fig. 2.

TABLE I

OBSERVED DIFFUSION COEFFICIENTS OF AQUEOUS AMMONIUM NITRATE, LITHIUM NITRATE AND AMMONIUM SULFATE SOLUTIONS AT 25°

$\bar{c}$[a]	Δc,[b]	$D \times 10^5$[c]
	NH_4NO_3	
0.0507	0.0610	1.791, 1.785
.1011	.1013	1.769
.2024	.2014	1.750, 1.747
.4050	.2037	1.731, 1.731
1.001	.1927	1.695, 1.685
2.026	.2515	1.638, 1.633
3.000	.1920	1.576
4.000	.1897	1.522, 1.522
5.104	.1620	1.469, 1.470
6.004	.1990	1.418, 1.422
7.628	.1813	1.338
	$LiNO_3$	
0.0710	0.1022	1.240, 1.243
.1279	.1551	1.240, 1.240
.2681	.1253	1.247, 1.247
.5989	.1837	1.267, 1.264
1.014	.2617	1.294, 1.293
1.573	.2801	1.320, 1.319
2.529	.2620	1.335, 1.337
3.283	.0947	1.326, 1.323
4.350	.2903	1.276, 1.276
5.127	.3629	1.230, 1.227
6.404	.1518	1.117, 1.117
	$(NH_4)_2SO_4$	
0.0525	.0419	0.800, 0.805
.1002	.0503	.825, .825
.2050	.0660	.869, .869
.3824	.0711	.915, .917
.5621	.1227	.950, .950
1.155	.2002	1.027, 1.025
2.393	.1735	1.086, 1.082
3.594	.2032	1.126, 1.124

[a] $\bar{c}$ = mean concentration of upper and lower parts of diffusion column, moles/liter. [b] Δc = concentration difference between these parts, moles/liter. [c] D = diffusion coefficient, cm.^{2} sec.$^{-1}$. The two results in this column are from duplicate runs with the same solutions.

Conductivity Measurements.—These were made with a conventional a.c. bridge circuit, with Wagner earth, at a frequency of approximately 700 c.p.s. Though the bridge was not of the highest precision, it was believed to be capable of 0.1% accuracy; this estimate is confirmed by the excellent agreement of our data for ammonium nitrate with those of Campbell and Kartzmark,[10] and of our result for 0.1 *N* ammonium chloride with that of Longsworth.[11] This accuracy is quite sufficient for the concentrated solutions studied here. The conductance cell was of a simple tubular design with electrodes 1 cm. square separated by about 25 cm., and was calibrated with potassium chloride solutions at 25° using the Jones and Bradshaw[12] standards. The observed conductivities are given in Table II. Table III presents the diffusion and conductance data interpolated to round molarities. Our values for the conductance of ammonium nitrate solutions agree with those of Campbell and Kartzmark[10] within 0.1% over the entire concentration range studied; and our value for 0.1 *M* ammonium chloride (Λ 128.8) agrees closely with Longsworth's value[11] at this concentration, the highest which he studied (Λ 128.75).

TABLE II

EQUIVALENT CONDUCTANCES OF AQUEOUS AMMONIUM NITRATE AND CHLORIDE SOLUTIONS AT 25°

NH_4NO_3		NH_4Cl	
c[a]	Λ[b]	c	Λ
0.1020	122.6	0.1019	128.6
.1978	117.1	.2015	123.8
.5000	108.6	.5019	116.8
1.021	101.1	1.011	111.2
2.020	91.8	2.005	105.1
3.031	83.9	3.006	100.2
4.048	76.6	4.005	95.1
5.11	69.3	5.252	87.0
6.13	62.5		
7.05	56.6		
7.83	51.5		
7.95	50.7		

[a] c in moles/liter. [b] Λ on Jones and Bradshaw standard.

TABLE III

DIFFUSION COEFFICIENTS AND EQUIVALENT CONDUCTANCES AT ROUND MOLARITIES AT 25°

c[a]	$D_{NH_4NO_3}$	D_{LiNO_3}	$D_{(NH_4)_2SO_4}$	$\Lambda_{NH_4NO_3}$[b]	Λ_{NH_4Cl}
0	1.928	1.337	1.527	144.84	149.7
0.05	. . .	. . .	0.802	. . .	. . .
.1	1.769	1.240	.825	122.7	128.8
.2	1.749	1.243	.867	117.0	123.8
.5	1.724	1.260	.938	108.6	116.8
1.0	1.690	1.293	1.011	101.4	111.3
1.5	1.661	1.317	1.047	. . .	. . .
2.0	1.633	1.332	1.069	91.9	105.1
2.5	1.605	1.336	1.088	. . .	. . .
3.0	1.578	1.332	1.106	84.1	100.2
4.0	1.524	1.292	1.125 (at c 3.6)	77.0	95.1
5.0	1.472	1.238	. . .	70.0	89.4
6.0	1.421	1.157	. . .	63.3	. . .
7.0	1.370	. . .	. . .	56.8	. . .
8.0	1.320	. . .	. . .	50.4	. . .

[a] c in moles per liter; D in cm.^{2} sec.$^{-1}$ $\times 10^{-5}$; [b] Λ = equivalent conductance. Limiting values at zero concentration are based on the following accepted limiting ionic equivalent conductances: $\lambda^\circ_{NH_4^+} = 73.35$; $\lambda^\circ_{Li^+} = 38.68$; $\lambda^\circ_{NO_3^-} = 71.4_6$; $\lambda^\circ_{Cl^-} = 76.3_5$, $\lambda^\circ_{SO_4^{--}} = 80.0_2$ using equation 2.

Interpretation of the Diffusion Coefficients.—A large part of the variation of diffusion coefficients

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[10] A. N. Campbell and E. M. Kartzmark, *Can. J. Research*, **28B**, 43 (1950). Dr. Campbell has drawn our attention to a misprint in his paper; on p. 49, in Table IB, the equivalent conductivity for 0.100 *M* NH_4NO_3 should be Λ = 122.7 instead of Λ = 112.95.

[11] L. G. Longsworth, THIS JOURNAL, **57**, 1185 (1935).

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

with concentration is known to be attributable to the changing free-energy gradient; interionic effects, hydration and viscosity have also to be considered. A general treatment of diffusion in binary liquid mixtures has been given by Hartley and Crank[13]; its extension to the case of hydrated non-associated electrolyte solutions has been investigated by Agar,[14] who obtained the result

$$D = D'\left(1 + m\frac{\mathrm{d}\ln\gamma\pm}{\mathrm{d}m}\right)(1 - 0.018nm) \times [1 + 0.018m(\nu D^*_{\mathrm{H_2O}}/D° - n)]\frac{\eta°}{\eta} \quad (1)$$

In this equation $D°$ is the Nernst limiting diffusion coefficient given by

$$D° = \frac{RT}{F^2}\frac{|z_1| + |z_2|}{|z_1z_2|}\frac{\lambda_1°\lambda_2°}{\lambda_1° + \lambda_2°} \quad (2)$$

D' is the coefficient corrected for the electrophoretic effect discussed by Onsager and Fuoss.[15] For a 1:1 electrolyte in water a self-consistent and convergent formula[16] is available for this effect, which may be represented by

$$D' = D° + \Delta_1 + \Delta_2$$

Δ_1 and Δ_2 being small concentration-dependent corrections.

$D^*_{\mathrm{H_2O}}$ is the self-diffusion coefficient of water, a quantity as yet known with only poor accuracy in spite of a great amount of work, but for which we shall take $D^*_{\mathrm{H_2O}} = 2.43 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, a reasonable average[17] of existing measurements. m and $\gamma_\pm$ are the molality and the mean molal activity coefficient, respectively. n is the "hydration number," *i.e.*, the number of moles of water transported with the ions of 1 mole of solute as part of the diffusing solute entities. $\eta/\eta°$ is the relative viscosity of the solution. ν is the number of ions formed from one "molecule" of solute.

Though a derivation of Agar's equation 1 has not yet been published, it is obtained in a straightforward manner from equation 65 of Hartley and Crank's paper[13] by treating the components as the solvated electrolyte and the free water, respectively.

In examining the application of equation 1 to 1:1 electrolytes, the known or calculable quantities D_{obsd}, D', $(1 + m\,\mathrm{d}\ln\gamma_\pm/\mathrm{d}m)$ and $\eta/\eta°$ are conveniently combined on the left-hand side of the equation, giving

$$f(D) \equiv \frac{D_{\mathrm{obsd}}}{(D° + \Delta_1 + \Delta_2)(1 + m\mathrm{d}\ln\gamma_\pm/\mathrm{d}m)\eta°/\eta} = (1 - 0.018nm)\left[1 + 0.018m\left(\frac{\nu D^*_{\mathrm{H_2O}}}{D°} - n\right)\right] \quad (3)$$

In Fig. 1 the quantity f(D) is plotted against m for the four electrolytes NH_4Cl,[5] NH_4NO_3, LiCl[2] and $LiNO_3$. The viscosities used were taken from reference 18; the factor $(1 + m(\mathrm{d}\ln\gamma_\pm)/\mathrm{d}m)$ was computed from isopiestic data[19,20] using in some parts of the concentration-range the more convenient equivalent form $\phi + m(\mathrm{d}\phi/\mathrm{d}m)$, ϕ being the osmotic coefficient. The curves in Fig. 1 thus represent the observed diffusion coefficients after correction for the thermodynamic non-ideality of the solution, the viscosity and the electrophoretic effect, but not for the hydration of the ions, for the counter-diffusion of the water, nor for possible ion-association. The broken straight lines I and II represent the right-hand side of equation 3 for two hypothetical *unhydrated* electrolytes obeying equation 1 (with $n = 0$) exactly, and having $D° = 2.00$ and 1.37, respectively (*i.e.*, these values being used in calculating the factor $D^*_{\mathrm{H_2O}}/D°$ in equation 3). Curve I thus corresponds to the behavior of f(D) for a hypothetical unhydrated ammonium chloride or nitrate, and curve II to that of a similar hypothetical lithium salt.

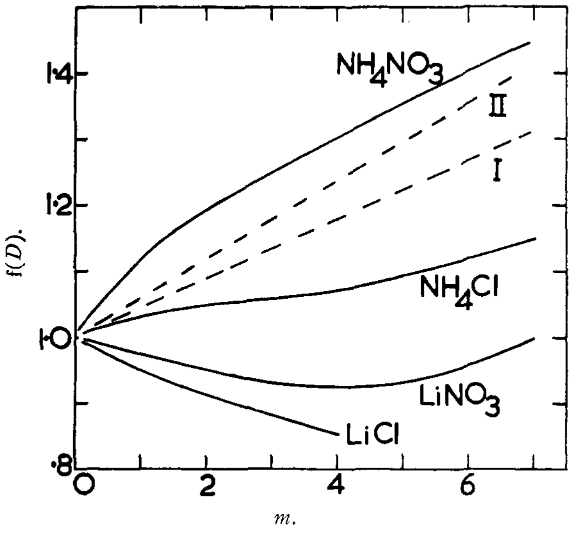

Fig. 1.—The function f(D) defined by equation 3. The broken lines I and II show the behavior of f(D) for two hypothetical non-associated and unhydrated 1:1 electrolytes having $D° = 2.00 \times 10^{-5}$ and $D° = 1.37 \times 10^{-5}$, respectively, *i.e.*, they are plots of $[1 + 0.018m(\nu D^*_{\mathrm{H_2O}}/D°)]$ *vs.* molality for $\nu = 2$.

The curves of f(D) *vs.* m for the chlorides and lithium nitrate lie *below* those of these hypothetical unhydrated salts; this behavior finds an obvious explanation in equations 1 or 3, since some hydration is to be expected, especially with the lithium salt. Giving the values $n = 0.6$ to ammonium chloride and $n = 2.8$ to lithium chloride, we obtain curves lying within 1 or 2% of the experimental ones shown in the figure, even at the highest concentrations studied: considering that the "experimental" f(D) values contain the combined experimental errors of the determinations of D, η and the factor $(1 + m\,\mathrm{d}\ln\gamma_\pm/\mathrm{d}m)$, this must be considered excellent agreement. It means that equation 1 with $n = 0.6$ for NH_4Cl and $n = 2.8$ for LiCl will reproduce the observed D values within 1–2% up to 4 molal for LiCl and 7 molal for NH_4Cl; this is illustrated in Fig. 2.

The curve for lithium nitrate is consistent with the value $n = 2.5$ up to about 2–3 M, but thereafter lies too high: this corresponds to the diffusion

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(13) G. S. Hartley and J. Crank, *Trans. Faraday Soc.*, **45**, 801 (1949).

(14) J. N. Agar, University of Cambridge, unpublished work, 1950.

(15) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(16) R. H. Stokes, THIS JOURNAL, **75**, 4563 (1953).

(17) B. R. Hammond and R. H. Stokes, *Trans. Faraday Soc.*, **49**, 890 (1953).

(18) Reference 8, Vol. V, p. 13.

(19) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

(20) B. F. Wishaw and R. H. Stokes, *ibid.*, **49**, 27 (1953).

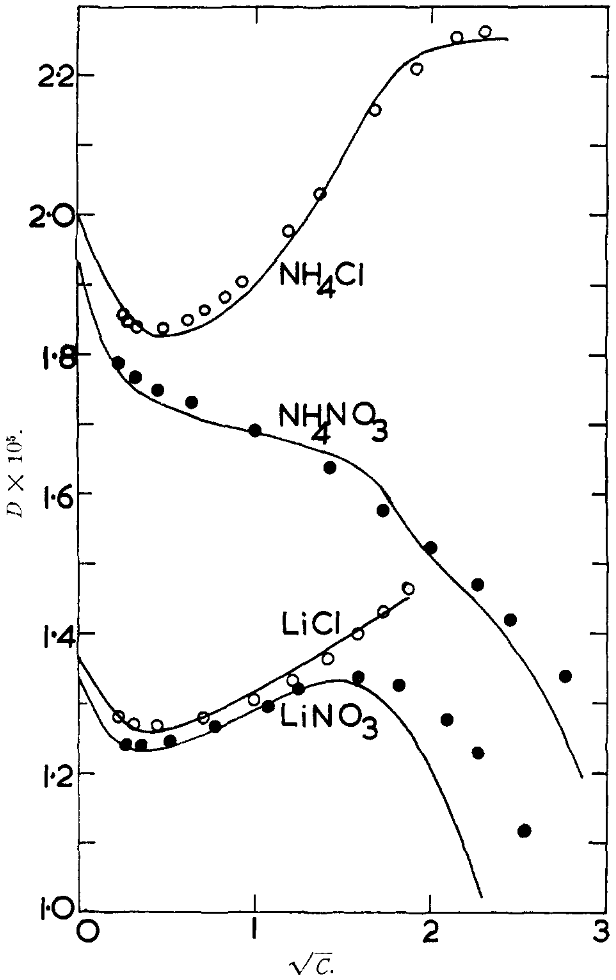

Fig. 2.—Comparison of observed diffusion coefficients (circles) with those calculated from equation 4 (full lines). Ammonium chloride, lithium chloride and lithium nitrate are treated as non-associated (α = 1); for ammonium nitrate, values of α derived from the conductivity data (Table VI) are used. Values of the hydration parameter n: NH_4Cl, 0.6; NH_4NO_3, 0; LiCl, 2.8; $LiNO_3$, 2.5; c in moles/liter.

coefficient above 3 M being higher than that predicted by equation 1 with $n = 2.5$ (see Fig. 2). The values thus obtained for the hydration numbers n are rather low, especially for the lithium salts, but it must be remembered that the hydration number here represents only the average number of water molecules which actually move with the electrolyte as part of the kinetic unit; many other water molecules no doubt interact with the ions, though not strongly enough to stay with them during their motion. The curve for ammonium nitrate is most interesting: it lies well *above* the broken line (I) corresponding to $n = 0$. Since negative hydration numbers are physically inadmissible, this behavior must be accounted for in another way. We believe that the explanation lies in the formation of ion-pairs, the solute in this form offering less resistance to motion through the liquid than it would in the form of two separate ions. Harned and Hudson[6] have already accounted with fair success for the diffusion of zinc sulfate in very dilute solution by invoking the concept of ion-pair formation, which is very marked in 2:2 electrolytes. In their treatment, the mobility of the ion-pair appears as a quantity λ_m, which has the dimensions of an equivalent conductance, though it refers to an uncharged particle. In order to avoid this concept, we give here an essentially similar treatment in terms of the absolute c.g.s. mobilities of the ions and ion-pairs; this also makes possible a direct estimate of the mobility of the ion-pairs without appeal to the diffusion data themselves.

The "Intrinsic Diffusion Coefficients" of an Associated Electrolyte.—Consider a 1:1 electrolyte at concentration c, in the form of free ions at concentration αc in equilibrium with ion-pairs at concentration $(1 - \alpha)c$. Let u_1 and u_2 denote the absolute c.g.s. mobilities (in cm. sec.$^{-1}$ per dyne) of the cation and anion, and u_{12} the mobility of the ion-pairs. Let the velocities of diffusion be $v = v_1 = v_2$ (these being equal because of the condition of electrical neutrality) and v_{12}, respectively. Then the free energy gradients acting on the respective kinds of particles are

$$\frac{1}{N}\frac{\mathrm{d}\bar{G}_1}{\mathrm{d}x},\ \frac{1}{N}\frac{\mathrm{d}\bar{G}_2}{\mathrm{d}x} \text{ and } \frac{1}{N}\frac{\mathrm{d}\bar{G}_{12}}{\mathrm{d}x}$$

respectively. Since the ions and ion pairs are in equilibrium, we have also $\bar{G}_{12} = \bar{G}_1 + \bar{G}_2 = \bar{G}$, $\bar{G}$ denoting the measured chemical potential of the solute. Hence, introducing and then eliminating the diffusion potential in the usual way we obtain, for the ions

$$v = \frac{1}{N}\frac{\mathrm{d}\bar{G}}{\mathrm{d}x}\,\frac{u_1u_2}{u_1 + u_2}$$

and

$$v_{12} = \frac{1}{N}\frac{\mathrm{d}\bar{G}}{\mathrm{d}x}\,u_{12}$$

for the ion-pairs. The total flux of solute J is therefore

$$\begin{aligned} J &= -\alpha c v - (1 - \alpha)c v_{12} \\ &= -D''\frac{dc}{\mathrm{d}x} \end{aligned}$$

where D'' is the intrinsic diffusion coefficient[13] of the solute as a whole. These equations reduce to

$$D'' = \left(1 + \frac{c\,\mathrm{d}\ln y_{\pm}}{dc}\right)\left[\alpha\, 2kT\,\frac{u_1u_2}{u_1 + u_2} + (1 - \alpha)2kT\,u_{12}\right]$$

where $k = R/N$ is Boltzmann's constant. Allowing for the electrophoretic effect in the ionic motion, we can express this as

$$D'' = \left(1 + c\,\frac{\mathrm{d}\ln y_{\pm}}{\mathrm{d}c}\right)\left[\alpha(D^\circ + \Delta_1 + \Delta_2) + 2(1 - \alpha)D_{12}\right]$$

where D_{12} is the diffusion coefficient of an isolated ion-pair, defined by $D_{12} = kTu_{12}$. When this intrinsic diffusion coefficient is introduced into the Hartley–Crank[13] treatment one obtains finally for a hydrated and associated 1:1 electrolyte

$$\begin{aligned} D = {} & \left(1 + m\,\frac{\mathrm{d}\ln\gamma_{\pm}}{\mathrm{d}m}\right)(1 - 0.018nm) \\ & \times\left[1 + 0.018m\left(\frac{2D^*_{\mathrm{H_2O}}}{D^\circ} - n\right)\right] \\ & \times\left[\alpha(D^\circ + \Delta_1 + \Delta_2) + 2\,(1 - \alpha)D_{12}\right]\eta^\circ/\eta \qquad (4) \end{aligned}$$

In the case of ammonium nitrate, both the parameters n and D_{12} may be estimated without recourse to the diffusion results themselves, as follows: First, the hydration number n can very reasonably be taken as zero, since both the ions are polyatomic but only monovalent. Secondly, the mobility of the ion-pair may be approximately calculated in terms of those of the constituent ions: the ions have nearly equal mobilities ($\lambda_{NH_4^+} = 73.4$, $\lambda_{NO_3^-} = 71.46$) so that we shall consider them as spheres of equal radius r. When two such spheres merge into a single entity, it would have, if spherical, a radius $r\sqrt[3]{2} = 1.26r$. Actually it would be effectively a prolate spheroid of axial ratio 2; for this axial ratio the frictional shape-factor is 1.043,[21] so that the mobility of the ion-pair should be approximately $1/(1.26 \times 1.043)$ of that of a single ion. Since the harmonic mean diffusion coefficient of the ammonium and nitrate ions is $D^\circ = 1.928 \times 10^{-5}$ this gives $D_{12} = 1.47 \times 10^{-5}$ for the ion-pairs. In view of the approximate nature of this estimate, we shall take the round value $D_{12} = 1.5 \times 10^{-5}$ cm.^{2} sec.$^{-1}$. It now remains to obtain values for the degree of dissociation α in ammonium nitrate solutions; this may be done with the aid of the conductivity results and recent extensions of the Onsager theory of conductivity to concentrated solutions.

The Conductivity of Concentrated Solutions of Non-associated 1:1 Electrolytes.—In previous articles[22,23] it has been shown that recent theoretical extensions of the theory of Onsager to include the effect of finite ionic size lead to the following equation for the equivalent conductivity of a 1:1 electrolyte

$$\Lambda = \left(\Lambda^\circ - \frac{82.5}{(\epsilon T)^{1/2}}\frac{\sqrt{c}}{1+\kappa a}\right)\left(1 + \frac{\Delta X}{X}\right) \qquad (5)$$

In this expression, the term $-82.5\sqrt{c}/(\epsilon T)^{1/2}(1 + \kappa a)$ gives the electrophoretic effect, and the term $\Delta X/X$ the relaxation effect. The latter has recently been evaluated by Falkenhagen[24] as

$$\frac{\Delta X}{X} = -\frac{\mathrm{e}^2}{3\epsilon kT}\frac{0.2929\kappa}{1+\kappa a} \times \frac{e^{0.2929\kappa a} - 1}{0.2929\kappa a} \qquad (6)$$

In Falkenhagen's derivation the quantity κ is given a slightly different meaning from its usual one: for a 1:1 electrolyte, instead of

$$\kappa = \left(\frac{8\pi N\mathrm{e}^2}{1000\ \epsilon kT}\right)^{1/2}\sqrt{c} \qquad (7)$$

Falkenhagen uses the value

$$\kappa = \left(\frac{8\pi N\mathrm{e}^2}{1000\ \epsilon kT}\right)^{1/2}\sqrt{c}\left(1 - \frac{1}{2}n_1/N_1 - \frac{1}{2}n_2/N_2\right)^{1/2} \qquad (8)$$

The final factor in (8) arises from the use of the Eigen–Wicke distribution function instead of the usual Boltzmann distribution; in this case, n_1 and n_2 denote the concentrations of cations and anions per cc., and N_1 and N_2 the numbers of "sites" available to these ions per cc. The factor thus represents a kind of excluded-volume correction. We are by no means convinced of the validity of this correction nor of that of the distribution function on which it is based, and shall therefore use Falkenhagen's expression (6) for the relaxation effect, but giving κ its ordinary meaning (7).

The validity of equations 5 and 6 for dilute solutions has been demonstrated in a previous paper[23]; the concentrations there considered were such that the final factor $\dfrac{e^{0.2929\kappa a} - 1}{0.2929\kappa a}$ in equation 6, which we here denote by F, approximates closely to unity. For the higher concentrations considered here it is desirable to avoid this approximation; Table IV shows the value of the factor F for a range of (κa) values, from which it is clear that the factor is quite important at high concentrations.

TABLE IV

VALUES OF THE FUNCTION $F = (e^{0.2929\kappa a} - 1)/(0.2929\kappa a)$

κa	F	κa	F
0.00	1.000	1.0	1.162
.05	1.007	1.5	1.256
.1	1.015	2.0	1.360
.2	1.030	3.0	1.602
.3	1.045	4.0	1.901
.5	1.077	5.0	2.271
.7	1.110	6.0	2.730

Equations 5, 6 and 7 may be combined to give

$$\Lambda = \left(\Lambda^\circ - \frac{B_2\sqrt{c}}{1 + B\mathring{a}\sqrt{c}}\right)\left(1 - \frac{B_1\sqrt{c}}{1 + B\mathring{a}\sqrt{c}} \times F\right) \qquad (9)$$

where the coefficients

$$B_1 = 8.20 \times 10^5/(\epsilon T)^{3/2}$$

and

$$B_2 = 82.5/[\eta(\epsilon T)^{1/2}]$$

are those appearing in Onsager's limiting formula and

$$B\mathring{a}\sqrt{c} = 50.29\mathring{a}\sqrt{c}/(\epsilon T)^{1/2} = \kappa a$$

is the dimensionless quantity familiar in the Debye–Hückel formula for the activity coefficient; F is the factor given in Table IV. The only adjustable parameter in equation 9 is the ionic diameter $\mathring{a}$ (in ångströms), apart of course from Λ°, which we shall here regard as already determined from measurements on more dilute solutions or from sums of limiting ionic conductances. It should be noted that the values of the parameter $\mathring{a}$ in equation 9 need not be quite the same as those used in the simplified equation for dilute solutions,[23] since the approximations made in obtaining the latter were of a nature which could largely be compensated by slight adjustments to the $\mathring{a}$ value. They should, however, be about the same as those used in the interpretation of the transport number data,[22] the theory for which was based essentially on equation 9.

There remains the vexed question of whether a viscosity correction is required and, if so, of the form which it should take. The viscosity of aqueous salt solutions, as measured in an ordinary viscometer, is essentially a measure of the shearing force required to move one layer of solution with respect to another. This shearing is resisted by the intermolecular attractions which in an electrolyte solution are of two kinds: (a) the short-range solvent–solvent and ion–solvent forces, and (b) the long-range Coulomb forces between ions.

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[21] A. E. Alexander and P. Johnson, "Colloid Science," Oxford University Press, 1949, p. 261.

[22] R. H. Stokes, THIS JOURNAL, **76**, 1988 (1954).

[23] R. A. Robinson and R. H. Stokes, *ibid.*, **76**, 1991 (1954).

[24] H. Falkenhagen, M. Leist and G. Kelbg, *Ann. Physik*, **6** [11], 51 (1952).

The theoretical evaluation of the latter has been carried out[25-27] and leads to the conclusion that the interionic contribution to the viscosity will be dependent on the square root of the concentration (in the limit of high dilutions). The theory can scarcely be called quantitatively successful, probably because the effect (b) is difficult to disentangle experimentally from the much larger effects which arise from the modification of the short-range interactions (a) by the presence of the ions. These effects are strongly specific for different ions of the same valence-type; thus lithium salts, for example, cause a great increase in viscosity as compared with potassium salts. This specific effect can be interpreted as due to the interference of the ions with the normal loosely coördinated water structure, and as might be expected it is approximately proportional to the first power of the concentration. On this basis, molar fluidity elevations for various ions have in fact been worked out.[28] Now, when we turn from consideration of the measurable bulk viscosity to that of the "viscosity" experienced by a moving ion, as in conductivity or diffusion, it can fairly be argued that the interionic contribution (b) to the bulk viscosity need not be considered, since the forces responsible for it have already been allowed for in the theory leading to equation 9. The short-range contributions (a) to the bulk viscosity are, however, still relevant to the motion of the ion through the solution. In practice, the small interionic effect on the viscosity is virtually completely swamped by the specific effects at concentrations above a few tenths molar. For the concentrated solutions of interest here, therefore, there would seem to be some justification for the introduction of the relative bulk viscosity into the theoretical formulas. It must then be expected that formulas so modified will show small deviations from experiment at lower concentrations, for the measured bulk viscosity contains an unwanted interionic contribution which, since it involves the square-root of the concentration, may predominate over the specific effect in dilute solutions.

We shall therefore test the formula

$$\Lambda = \left(\Lambda^\circ - \frac{B_2\sqrt{c}}{1 + B\mathring{a}\sqrt{c}}\right)\left(1 - \frac{B_1\sqrt{c}}{1 + B\mathring{a}\sqrt{c}}F\right)\frac{\eta^\circ}{\eta} \quad (10)$$

for the ammonium chloride data. Using the value $\mathring{a} = 4.35$ for the ion-size parameter, and with viscosities from reference 18, we obtain fairly satisfactory agreement with the experimental values, as shown in Table V.

TABLE V

COMPARISON OF OBSERVED CONDUCTANCES OF AMMONIUM CHLORIDE SOLUTIONS AT 25° WITH THOSE GIVEN BY EQUATION 10, USING $\mathring{a} = 4.35$

c	Λ_{obsd}	Λ_{calcd}	c	Λ_{obsd}	Λ_{calcd}
0.1	128.8	129.4	2.0	105.1	105.0
.2	123.8	124.3	3.0	100.2	99.6
.5	116.8	117.4	4.0	95.1	95.2
1.0	111.3	111.3	5.0	89.4	90.4

It thus appears that equation 10 may be used to give a reasonably close estimate of the conductivity of a non-associated electrolyte at quite high concentrations. More comprehensive tests are obviously desirable, but it is surprisingly difficult to find suitable conductivity data for these high concentrations. It is interesting to note, however, that the data for lithium chloride solutions at 25° given in the "International Critical Tables" are reproduced within about 2 units in Λ by equation 10 with $\mathring{a} = 5.6$, up to the astonishingly high concentration of 9 molar.

The extent of ion-pair formation in the ammonium nitrate solutions may now be estimated as follows: If α be the fraction of free ions in a solution of stoichiometric concentration c moles/liter, the ion-concentration is αc. The equivalent conductivity $\Lambda'(\alpha c)$ of the free ions at this concentration is assumed to be given by equation 9, with the parameter $\mathring{a}$ given a suitable value. The necessity for arbitrary choice of this parameter is unfortunately a weak link in the present argument. It might be argued that ion-pairing will only occur when the sum of the effective radii of the ions is less than the Bjerrum critical distance of 3.57 Å., and that $\mathring{a}$ for the free ions should therefore be set equal to 3.57. However, it seems doubtful whether the effective size of the nitrate ion is really much different from that of the chloride ion, since both have very similar mobilities; hence we propose to use for ammonium nitrate the $\mathring{a}$ value of 4.35 found for ammonium chloride, and to attribute the formation of ion-pairs in this salt to the polarization of the nitrate ion or to its lack of spherical symmetry, rather than to small size. Then if Λ be the observed equivalent conductance of an ammonium nitrate solution of concentration c and relative viscosity η/η°, we have

$$\Lambda\eta/\eta^\circ = \alpha\Lambda'_{(\alpha c)} \quad (11)$$

where

$$\Lambda'_{(\alpha c)} = \left(\Lambda^\circ - \frac{60.3\sqrt{\alpha c}}{1 + 4.35 \times 0.3286\sqrt{\alpha c}}\right) \times \left(1 - \frac{0.2289F\sqrt{\alpha c}}{1 + 4.35 \times 0.3286\sqrt{\alpha c}}\right) \quad (12)$$

Then α can be found by a series of approximations with the help of a graph of the right-hand side of (12) against $\sqrt{\alpha c}$. The α values found in this way (Table VI) seem fairly reasonable, except perhaps at the highest concentrations, where the theory is of course on extremely shaky ground. With the aid of previously reported activity coefficients for ammonium nitrate,[20] a dissociation constant for the ion-pairs may be estimated. Between 0.1 and 6 *M*, it is reasonably constant, lying between $K_c = 2.9$ and $K_c = 3.5$ without marked trend; but at 7 and 8 *M* it rises to 3.9 and 4.5, respectively. This failure at the extreme concentrations is naturally attributable to the breakdown of the conductivity theory, which is necessarily suspect in this region since it leads to values of α which *increase* at 7 and 8 *M* as compared with 6 *M*. It must also be admitted that the degrees of dissociation obtained from the conductivity data are not easily reconciled with the vapor-results for ammonium nitrate; the latter, however, present in many respects a more complex theoretical problem.

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(25) H. Falkenhagen and M. Dole, *Z. physik. Chem.*, [B] **6**, 159 (1929).

(26) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(27) H. Falkenhagen and G. Kelbg, *Z. Elektrochem.*, **56**, 834 (1953).

(28) E. C. Bingham, *J. Phys. Chem.*, **45**, 885 (1941).

TABLE VI

TEST OF EQUATION 4 FOR AQUEOUS AMMONIUM NITRATE SOLUTIONS

c^a	m^b	$\eta/\eta^{\circ c}$	α^d	$K_c{}^e$	$1 + m\frac{d\ln\gamma_\pm}{dm}$	$D_{\text{calcd}} \times 10^{5f}$	$D_{\text{obsd}} \times 10^5$
0.1	0.1007	0.998	0.981	2.9	0.879	1.750	1.769
.2	.2025	.994	.970	3.1	.856	1.733	1.749
.5	.5139	.985	.950	3.5	.810	1.700	1.724
1	1.055	.972	.923	3.5	.766	1.691	1.690
1.5	1.623	.960	.896	3.3	.720	1.674	1.661
2	2.224	.955	.870	3.1	.686	1.662	1.633
2.5	2.859	.958	.853	3.1	.662	1.642	1.605
3	3.533	.970	.841	3.1	.631	1.608	1.578
4	5.008	1.009	.824	3.2	.573	1.496	1.524
5	6.687	1.065	.807	3.3	.549	1.452	1.472
6	8.617	1.147	.803	3.5	.531	1.393	1.421
7	10.86	1.255	(.806)	(3.9)	.511	(1.312)	1.370
8	13.50	1.396	(.813)	(4.5)	.484	(1.202)	1.320

[a] c = moles/liter. [b] m = molality. [c] η/η° = relative viscosity. [d] α = degree of dissociation of ion-pairs (from conductivities). [e] K_c = molar scale dissociation constant of ion pairs. [f] D = diffusion coefficient.

The Diffusion of Ammonium Nitrate.—In equation 4 we now insert the values $n = 0$, $D^\circ = 1.928 \times 10^{-5}$, $D_{12} = 1.5 \times 10^{-5}$, $D_{H_2O}{}^* = 2.43 \times 10^{-5}$, and use the estimates of α obtained from the conductance data. The resulting calculated diffusion coefficients of ammonium nitrate agree with observation within 2% up to 6 M (8.6 molal) as shown in Fig. 2.

Considering the extremely high concentrations involved, this attempt at correlating the diffusion coefficients and conductances must be considered highly successful.

The lithium nitrate diffusion coefficients indicate only a small amount of ion-pair formation; this is consistent with the activity coefficient data and with some preliminary conductance measurements made in this Laboratory. In Fig. 2 the observed diffusion coefficients are compared with the predictions of theory for lithium and ammonium nitrates and chlorides. The ammonium sulfate data have not yet been analyzed in detail; until an adequate theory of the electrophoretic effect in unsymmetrical salts is available, it is of doubtful value to attempt this.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

Polarographic Diffusion Coefficients

BY CHARLES L. RULFS

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A modified diaphragm-cell technique for the determination of the diffusion coefficients of polarographically-active substances in mM concentrations and in the presence of high concentrations of supporting electrolyte is described. The diffusion coefficients of cadmium, lead and thallous ions in three common supporting electrolytes have been determined within an estimated ±2%. The importance of the *actual vs.* the *infinite dilution* diffusion data in polarographic theory is discussed. A new technique for the evaluation of polarographic n values is described.

In connection with the exact relation between i_d and D it is generally recognized by polarographic workers that independent determinations of D are very essential. This paper describes the determination of the polarographic diffusion coefficients for cadmium, lead and thallous ions in three media. Unstirred diaphragm cells and a polarographic measuring technique have been employed as briefly described elsewhere.[1]

Experimental

All runs were conducted at 25.00 ± 0.05° in unstirred diaphragm cells which are bisected in a vertical plane into two 50-ml. compartments by 2-cm. diam. medium-porosity (10–15 μ nom. max. pore size) fritted glass discs. Each cell compartment has a small mercury-pool reservoir at the bottom with provision for external electrical contact. Each compartment is closed with a 2-hole rubber stopper carrying a nitrogen inlet tube and a bunsen valve. The valve may be opened to permit the insertion or withdrawal of a pipet or of a dropping mercury electrode tip. The cells are thermostated by immersion in an externally-controlled bath at 25 ± 0.05°.

Fifty ml. of nitrogen-saturated and temperature-equilibrated supporting electrolyte solution are pipetted through the bunsen valve into compartment II of a clean cell *simultaneously* with the filling of compartment I with a 2 mM solution of the ion under study in the identical supporting electrolyte. The cell is "pretreated" by standing filled for 2 to 3 hours, after which a glass probe is inserted and the *free* liquid is aspirated out of each compartment (making no attempt, however, to *dry* the frit). The compartments are carefully refilled and the time of filling is noted. The hydrostatic head of liquid in the two compartments must now be checked for equality; the surface of liquid in the bath is a convenient reference point for levelling. Minor adjustment may be made by the addition of more mercury in one of the pools. Each cell is immersed in the bath below the internal level of liquid, of course, but its exact depth is most conveniently fixed at whatever point will afford an equal distance from the mercury reservoir to the tip of the inserted dropping electrode for all cells. After 20 to 24 hours, the dropping electrode is inserted in the II compartment and a polarographic measurement is made of the concentration of diffused metal ion. The polarographic readings may well be repeated at 6- or 8-hour intervals up to about 72 hours.

For a diaphragm cell with compartments of equal volume, McBain and Liu[2] derive the relation

$$KDt = \log C_0 - \log (C_0 - 2C_t) \qquad (1)$$

where C_0 is the initial concentration of transportable material in compartment I, C_t is its concentration in compartment II after an elapsed time, t (and $C_t = 0$ when $t = 0$), D is the diffusion coefficient, and K is a cell constant. Potassium chloride solutions afford the best-characterized reference material for the calibration of such a cell. For the present purposes, a value of $1.87_0 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ will be used for 0.1 M KCl into water at 25° until C_t is *ca.* 0.006 M. A 25-ml. aliquot was withdrawn from the II

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[1] D. F. Boltz (ed.), "Selected Topics in Modern Instrumental Analysis," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 57-58.

[2] J. W. McBain and T. H. Liu, THIS JOURNAL, **53**, 59 (1931).