[CONTRIBUTION NO. 1206 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Differential Diffusion Coefficients of Magnesium and Barium Chlorides in Dilute Aqueous Solutions at 25°

BY HERBERT S. HARNED AND FRANCESCO M. POLESTRA

RECEIVED DECEMBER 16, 1953

The differential diffusion coefficients of magnesium and barium chlorides at concentrations between 0.0005 and 0.006 M at 25° in water have been determined by the conductometric method. In accord with similar results for strontium chloride, the values of these diffusion coefficients agree well with those predicted by the equations of the Nernst–Onsager and Fuoss theory.

The diffusion coefficients of magnesium and barium chlorides in dilute aqueous solutions recorded in this communication supplement similar results obtained by Harned and Levy[1] and Harned and Polestra[2] for calcium and strontium chlorides.

Theoretical Computations

According to the theory of Onsager and Fuoss[3] the diffusion coefficient, $\mathfrak{D}$, of an electrolyte in dilute solution may be calculated by the equation[4]

$$\mathfrak{D} = (\nu_1 + \nu_2)\, 1000RT\, (\overline{\mathfrak{M}}/c)\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

where the term $(\overline{\mathfrak{M}}/c)$ is given by[4]

$$\begin{aligned} \overline{\mathfrak{M}}/c = {} & 1.0748 \times 10^{-20}\,\frac{\lambda_1^0\lambda_2^0}{\nu_1|z_1|\Lambda^0} \\ & - \frac{(|z_1|\lambda_1^0 - |z_2|\lambda_2^0)^2}{|z_1z_2|(\nu_1 + \nu_2)\Lambda^{02}}\,\frac{3.122 \times 10^{-19}}{\eta_0(DT)^{1/2}}\,\frac{\sqrt{\Gamma}}{(1 + \kappa a)} \\ & + \left(\frac{z_2^2\lambda_1^0 + z_1^2\lambda_2^0}{\Lambda^0}\right)^2 \frac{9.304 \times 10^{-13}}{\eta_0(DT)^2}\, c^2\phi(\kappa a) \end{aligned} \quad (2)$$

In these equations, R is the gas constant, T the absolute temperature, c the concentration in moles per liter, $y_\pm$ the activity coefficient on the molar concentration scale, λ_1^0 and λ_2^0 the limiting equivalent conductances of the ions of the electrolyte, $\Lambda^0 = \lambda_1^0 + \lambda_2^0$, z_1 and z_2 the valences of the ions, Γ the ional concentration, η_0 the viscosity of water, D its dielectric constant, κ the Debye and Hückel reciprocal radius, a the mean distance of approach of the ions and $\phi(\kappa a)$ the exponential integral functions of the theory.

For both magnesium and barium chlorides $\nu_1 = 2$, $\nu_2 = 1$, $z_1 = -1$, $z_2 = 2$, $\eta_0 = 8.949 \times 10^{-3}$,[5] $D = 78.54$[6] and $T = 298.16$. For magnesium chloride, $\lambda_1^0 = 76.34$,[7] $\lambda_2^0 = 53.06$,[7] $A' = 2.804$ and $a = 4.92$. For barium chloride, $\lambda_1^0 = 76.34$,[7] $\lambda_2^0 = 63.64$,[7] $A' = 2.456$ and $a = 4.32$. Substitution of these values in equation 2 yields the following numerical equations. For magnesium chloride

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 16.8222 - \frac{5.5342\sqrt{c}}{1 + 2.804\sqrt{c}} + 18.5001(\kappa a)^2\phi(\kappa a) \quad (3)$$

and for barium chloride

$$(\overline{\mathfrak{M}}/c) \times 10^{20} = 18.6515 - \frac{5.7782\sqrt{c}}{1 + 2.456\sqrt{c}} + 21.8413(\kappa a)^2\phi(\kappa a) \quad (4)$$

The function $(\kappa a)^2\phi(\kappa a)$ was evaluated from tables recorded by Harned and Owen.[8]

The thermodynamic term in equation 1 was evaluated by employing the Debye and Hückel functions in the usual way. For magnesium chloride, results given by Stokes[9] were found to yield the numerical equation

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{2.0304\sqrt{c}}{(1 + 2.804\sqrt{c})^2} + 0.5073c \quad (5)$$

For barium chloride, values of the activity coefficient obtained by Robinson[10] yielded the equation

$$\left(1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{2.0304\sqrt{c}}{(1 + 2.457\sqrt{c})^2} + 0.1830c \quad (6)$$

Experimental and Calculated Diffusion Coefficients

The observed diffusion coefficients for both magnesium and barium chlorides are compiled in Table I. The theoretical values, calculated by equations 1 to 6 at the same designated concentrations are also given in the table. The calculated limiting values, $\mathfrak{D}_0$, are represented by the numbers in parentheses. The quantity $\mathfrak{D}'$, defined by the equation $\mathfrak{D}' = (\mathfrak{D}_0 - \mathfrak{D})_{\text{calcd}} + \mathfrak{D}_{\text{obsd}}$, is also given in the table. This quantity should not be a function of the concentration and should equal the limiting value, $\mathfrak{D}_0$. The fact that the mean value of $\mathfrak{D}'$ differs from the limiting value $\mathfrak{D}_0$ by only 0.2% for both magnesium and barium chlorides is evidence that the theory is valid over this dilute range of concentrations.

The results up to the present time show that the values computed by the complete Onsager–Fuoss equations agree with the observed values for magnesium, strontium and barium chlorides. On the other hand, the calcium chloride diffusion coefficients cannot be computed satisfactorily from the theory and available data. In Table II, the observed diffusion coefficients of these halides at 0.001 and 0.002 M are given. It is to be observed that $\mathfrak{D}$ increases from magnesium to barium chloride but not uniformly since the calcium and strontium values differ by approximately 2% only. This result differs from the order of the limiting equivalent

---

[1] H. S. Harned and A. L. Levy, THIS JOURNAL, **71**, 2781 (1949).

[2] H. S. Harned and F. M. Polestra, *ibid.*, **75**, 4168 (1953).

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

[4] H. S. Harned, *Chem. Revs.*, **40**, 461 (1947).

[5] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 128.

[6] Reference 5, p. 118.

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

[8] Reference 5, p. 130.

[9] R. H. Stokes, *Trans. Faraday Soc.*, **44**, 295 (1948); see also ref. 5, p. 602.

[10] R. A. Robinson, *ibid.*, **36**, 735 (1940); see also ref. 5, p. 567.

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.

NEW HAVEN, CONNECTICUT

---

[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

RECEIVED NOVEMBER 24, 1953

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

---

[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).