[CONTRIBUTION NO. 1221 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Cesium Chloride in Dilute Aqueous Solution at 25°

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The differential diffusion coefficient of cesium chloride has been determined by the conductometric method at 25° through the concentration range 0.001 to 0.012 *M*. At these low concentrations, the results are in accord with the Nernst–Onsager and Fuoss theory.

The diffusion coefficients of lithium,[1] sodium,[1] potassium,[2] rubidium[3] chlorides have been determined in dilute aqueous solutions by the conductometric method devised in this Laboratory. The present communication contains the differential diffusion coefficient of cesium chloride in the dilute solution range.

Theoretical Considerations.—The theory of Onsager and Fuoss[4] leads to the equation

$$\mathfrak{D} = 10.629 \times 10^{10}\, T \frac{\overline{\mathfrak{M}}}{c}\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) \quad (1)$$

in which the mobility term, $\overline{\mathfrak{M}}/c$, for 1–1 electrolytes is represented by

$$\overline{\mathfrak{M}}/c \times 10^{20} = 1.0748\left(\frac{\lambda^0{}_1\lambda^0{}_2}{\Lambda^0}\right) - \frac{22.148}{\eta_0(DT)^{1/2}}\left(\frac{\lambda^0{}_1 - \lambda^0{}_2}{\Lambda^0}\right)^2 \frac{\sqrt{c}}{1 + A'\sqrt{c}} + \frac{9.304 \times 10^{-7}}{\eta_0(DT)^2}\, c\phi((A'\sqrt{c}) \quad (2)$$

and the thermodynamic term $(1 + c(\partial \ln y_\pm/\partial c)$ by

$$\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{1.1514\, \mathcal{S}_{(f)}\sqrt{c}}{(1 + A'\sqrt{c})^2} + 4.606\, Bc - c\psi(d) \quad (3)$$

In these equations, $\mathfrak{D}$ is the diffusion coefficient in cm.², sec.⁻¹, T is the absolute temperature, c is the concentration in moles per liter and $y_\pm$ is the activity coefficient on the molar concentration scale. D is the dielectric constant of the water, and η_0 its viscosity. The equivalent conductances of the cation and anion are $\lambda^0{}_1$, and $\lambda^0{}_2$, respectively, and Λ^0 is their sum. $\mathcal{S}_{(f)}$ is the limiting slope of the Debye and Hückel theory. $A^1\sqrt{c} = A\sqrt{\Gamma} = \kappa a$ in which Γ is the ional concentration, κ the reciprocal radius, "a" the mean distance of approach of the ions, and $A = 35.56 \times 10^8/(DT)^{1/2}$. The quantity $\phi(A'\sqrt{c})$ is the exponential integral function of the theory which may be obtained from tables given by Harned and Owen.[5] B is an empirical constant and $c\psi(d)$ the term required to convert the expression from rational to molar activity coefficient.[6] This term is small enough to be neglected in the subsequent calculations.

The limiting law for the diffusion coefficient is

$$\mathfrak{D} = 17.872 \times 10^{-10}\, T\left(\frac{\lambda^0{}_1\lambda^0{}_2}{\Lambda^0}\right) - \mathcal{S}_{(\mathfrak{D})}\sqrt{c} \quad (4)$$

where the limiting slope $\mathcal{S}_{(\mathfrak{D})}$ is given by

$$\mathcal{S}_{(\mathfrak{D})} = \frac{3.754 \times 10^{-3}}{D^{3/2}T^{1/2}}\frac{\lambda^0{}_1\lambda^0{}_2}{\Lambda^0} + \frac{3.683 \times 10^{-8}}{\eta_0 D^{1/2}T^{-1/2}}\left(\frac{\lambda^0{}_1 - \lambda^0{}_2}{\Lambda^0}\right)^2 \quad (5)$$

TABLE I

QUANTITIES USED IN THEORETICAL CALCULATIONS

T	298.16	$\lambda^0{}_1$	77.27[7]
$\mathcal{S}_{(f)}$	0.5091[a]	$\lambda^0{}_2$	76.34[a]
η_0	8.949×10^{-3}[a]	$a \times 10^8$	3.00[a]
D	78.54[a]	B	0.000[a]

[a] Ref. 5.

In Table I the specific quantities used in the theoretical calculations are listed. Substitution of these data in equations 2, 3, 4 and 5 leads to the following numerical expressions

$$\left(\frac{\overline{\mathfrak{M}}}{c}\right) \times 10^{20} = 41.273 - 0.000593\frac{\sqrt{c}}{(1 + 0.958\sqrt{c})} + 18.959c\phi(0.9858\sqrt{c}) \quad (2a)$$

$$\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{0.5862\sqrt{c}}{(1 + 0.9858\sqrt{c})^2} \quad (3a)$$

$$\mathfrak{D} = 2.0463 - 1.1996\sqrt{c} \quad (4a)$$

Experimental Results.—Comparisons of the experimental results with those computed by equa-

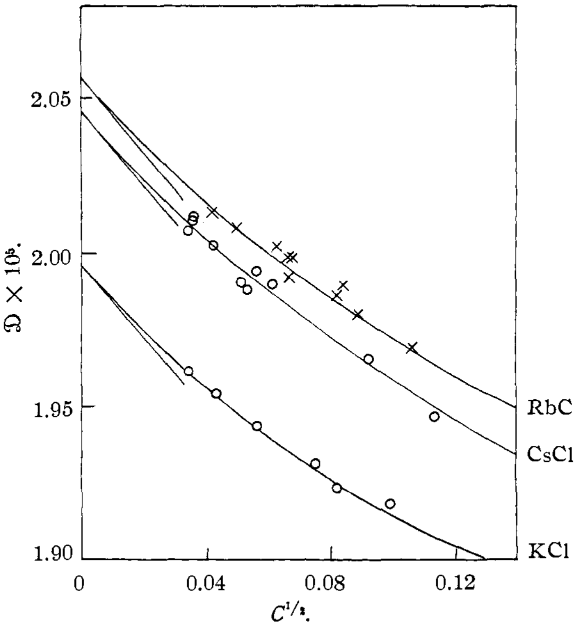

Fig. 1.—Diffusion coefficients of potassium, rubidium and cesium chlorides at 25°. The limiting theoretical equation is represented by the straight lines and the complete theoretical result by the curved lines.

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[1] H. S. Harned and C. L. Hildreth, Jr., THIS JOURNAL, **73**, 650 (1951).

[2] H. S. Harned and R. L. Nuttall, *ibid.*, **69**, 737 (1947); **71**, 1460 (1949). For results at 4°, see H. S. Harned and C. A. Blake, Jr., *ibid.*, **72**, 2265 (1950).

[3] H. S. Harned and M. Blander, *ibid.*, **75**, 2853 (1953).

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

[5] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 130.

[6] Reference 5, p. 179.

[7] W. E. Voisenet, Jr., Dissertation, Yale University, June, 1951.

tions 1, 2a and 3a are given in Table II. In the last column values of $\mathfrak{D} = \mathfrak{D}_{obs} + (\mathfrak{D} - \mathfrak{D}_0)_{calc.}$ are recorded. The mean value of $\mathfrak{D}'$ is equal to the limiting value $\mathfrak{D}_0$ and all the values are within ±0.2% of this mean. This confirmation of the adequacy of the theory at concentrations up to 0.01 molar is in accord with similar agreement found for lithium, sodium, potassium and rubidium chlorides.

TABLE II

CALCULATED AND OBSERVED DIFFUSION COEFFICIENTS OF CESIUM CHLORIDE AT 25

c	$\mathfrak{D} \times 10^6$ (obs.)	$\mathfrak{D} \times 10^5$ (calcd.)	$\mathfrak{D}' \times 10^5$
0.0000	...	(2.046)	(2.046)
.00122	2.007	2.010	2.043
.00131	2.012	2.009	2.049
.00134	2.011	2.008	2.049
.00179	2.002	2.002	2.046
.00266	1.990	1.994	2.042
.00275	1.988	1.993	2.041
.00314	1.994	1.991	2.049
.00368	1.990	1.987	2.049
.00849	1.965	1.963	2.048
.01287	1.946	1.950	2.042
		Mean	2.046

In Fig. 1, the observed and calculated diffusion coefficients of potassium, rubidium and cesium chlorides have been plotted against the square root of the concentration. The straight lines represent the limiting equation 4a and the solid lines the values derived from the theory. It is to be noted that the diffusion coefficient of rubidium chloride is about 0.5% higher than that of cesium chloride. This result is in complete accord with the recent values of the limiting conductances obtained by Dr. Walter E. Voisenet, Jr., in this Laboratory.

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[CONTRIBUTION FROM THE UNIVERSITY OF ARKANSAS]

Basic Salts of Lead Nitrate Formed in Aqueous Media[1]

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Conductometric and potentiometric titrations, analyses and solubility determinations were carried out on the system created by the addition of 1 *N* NaOH to 0.1 *N* $Pb(NO_3)_2$. Precipitates with compositions which correspond to the empirical formula $Pb(NO_3)_2 \cdot Pb(OH)_2$ and $Pb(NO_3)_2 \cdot 5Pb(OH)_2$ were formed. No $Pb(OH)_2$ was found even appreciably past the equivalence point. The results are in opposition to other published data.

Introduction

The addition of a solution of sodium hydroxide to a solution of lead nitrate might be expected to form a precipitate of lead hydroxide followed by dissolution of the precipitate with the formation of sodium plumbite. It has been found that the above system is not as simple as it was believed to be and discrepancies arise which have an important bearing upon the titration of systems containing the Pb^{++}, NO_3^- and OH^- ions as well as the preparation of lead salts in an aqueous medium in the presence of nitrate ions.

An examination of the literature reveals that numerous compounds of Pb, NO_3 and OH groups are proposed.[2-4] The formulas of many of the proposed compounds were deduced by indirect means and considerable confusion exists on certain points. Also, many of the proposed compounds were formed under very special conditions. Britton studied the precipitation of lead salts by hydroxyl ions but made assumptions as to the composition of the precipitates formed. For the compounds formed in aqueous media, Berton's work[3] is of greatest interest. He stated that the titration of $Pb(NO_3)_2$ with NaOH produced compounds with compositions in agreement with the following empirical formulas

$$3Pb(NO_3)_2 \cdot Pb(OH)_2$$
$$Pb(NO_3)_2 \cdot Pb(OH)_2$$
$$Pb(NO_3)_2 \cdot 3Pb(OH)_2$$

The system resulting from the addition of 1 *N* NaOH to an aqueous solution of 0.1 *N* $Pb(NO_3)_2$ was studied conductometrically, potentiometrically and analytically by the authors in an attempt to verify Berton's data.

Experimental

The conductance of the above system was measured as a function of the addition of carbonate-free sodium hydroxide to the lead nitrate at 25°. Sufficient time elapsed between the additions of sodium hydroxide and the conductance measurement to ensure equilibrium. The results of this investigation are presented in Fig. 1, in which the conductivity has been corrected for the dilution effect produced by the addition of the NaOH solution.

The graph shows a gradual decrease in conductivity until the region of the $^5/_6$ fraction of the equivalence point is reached, where a very sharp minimum is encountered. This minimum suggests the formation of a compound whose composition corresponds to the $^5/_6$ fraction of the equivalence point. Further, a white precipitate forms upon the addition of the first drop of NaOH solution and remains throughout the course of the titration. This fact, coupled with the gradually decreasing conductivity of the solution during the initial additions of sodium hydroxide, suggests the precipitation of some other compound, whose solubility is greater than that of the $^5/_6$ compound.

These results are in disagreement with the data published by Berton[3] in that he reports three breaks in the conductance *vs.* ml. of NaOH curve which occur at the $^1/_4$, $^1/_2$ and $^3/_4$ fractions of the equivalence point.

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[1] Presented before the Southwest-Southeast Regional Meeting of the American Chemical Society, New Orleans, La., 1953.

[2] V. J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 7, Longmans and Co., New York, N. Y., 867ff.

[3] A. Berton, *Compt. rend.*, **220**, 693 (1945).

[4] H. T. S. Britton and F. H. Meek, *J. Chem. Soc.*, 183 (1932).