no boiling points for these chlorosilanes. The first values reported for these substances have been superseded by better data.[8] After carefully reviewing the literature and considering the evidence available to us here, we have selected the following provisional normal boiling points: DDS, 70.2 ± 0.1°; MTS, 66.1 ± 0.1°. In selecting these values, we have assigned the greatest weight to determinations on both compounds by R. O. Sauer (one of these having been made on Fraction 460–6, Table I) and to the difference (4.0 ± 0.1°) in the boiling points of DDS and MTS, which was established by Experiments 1 and 2, Table I.

We wish to thank our colleagues A. L. Marshall, C. E. Reed, R. O. Sauer, W. J. Scheiber, A. E. Schubert and E. H. Winslow for helping in various ways with the work reported here.

SCHENECTADY, NEW YORK RECEIVED MARCH 15, 1951

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(8) (a) Gilliam and Sauer, THIS JOURNAL, **66**, 1793 (1944); (b) Booth and Martin, *ibid.*, **68**, 2655 (1946); (c) Booth and Suttle, *ibid.*, **68**, 2658 (1946); (d) Lewis and Newkirk, *ibid.*, **69**, 701 (1947); (e) Stull, *Ind. Eng. Chem.*, **39**, 517 (1947); (f) Burkhard, Rochow, Booth and Hartt, *Chem. Revs.*, **41**, 97 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

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

BY HERBERT S. HARNED AND CHARLES A. BLAKE, JR.

The differential diffusion of lanthanum chloride in water at 25° has been determined by the conductometric method through a concentration range of 0.00093 to 0.026 molar. The results are all somewhat lower than those computed by the theory of Onsager and Fuoss but appear to approach the limiting law of the theory in a satisfactory manner.

Accurate measurements of the conductance,[1,2] transference numbers[3] and activity coefficient[4] of lanthanum chloride at 25° in dilute aqueous solutions provide the necessary data for the theoretical computation of the diffusion coefficient according to the theory of Onsager and Fuoss.[5] It is to be noted that the conductance of this salt approaches the limiting law of the Onsager theory normally as its concentration approaches zero. This evidence indicates that it is a strong electrolyte. Shedlovsky's calculation of the thermodynamic data yields 6.8 Å. for the "mean distance of approach" of the Debye and Hückel theory. Although this value indicates high dissociation, it does not exclude the formation of ions such as $LaCl_2^+$, etc.

The 2–1 salt, calcium chloride, shows analogous characteristics. Similar agreement with theory occurs with both the conductance and the activity coefficient. On the other hand, the cation transference members of both calcium and lanthanum chlorides show no tendency to approach the limiting law of the theory at 0.01 molar.[6] Since the diffusion coefficient of calcium chloride[7] exhibits the largest deviation from theory of any of the salts yet investigated, it is a matter of considerable interest to investigate the diffusion coefficient of a salt whose other properties parallel those of calcium chloride.

Experimental Results and Theoretical Calculations

Anhydrous lanthanum chloride of high purity was obtained from the Atomic Energy Commission. Upon dissolving this salt in water at room temperature, heat was evolved and hydrolysis occurred. The *p*H of this solution was 5.0. Accordingly, 20 g. was dissolved slowly in ice-water and the solution was filtered. Crystallization was effected by slow evaporation in a vacuum desiccator over concentrated sulfuric acid. After 48 hours, the crystals were dried by centrifuging. The *p*H of a 0.005 molar solution was found to be 5.6. This process of crystallization was repeated and the crystals dried in air. Assuming the composition to be $LaCl_3 \cdot 7H_2O$, a 0.2 molar stock solution was prepared. A 0.005 molar solution prepared from this stock solution was found to have a *p*H of 5.9.

The technique of measurement and the method of computation of the diffusion coefficient from the observed conductances were essentially the same as those previously employed and described in detail.[8] Examination of the specific conductance of lanthanum chloride showed that, over the concentration ranges employed, the assumption that the differences in conductances between the bottom and top electrodes of the cell are proportional to the differences in concentrations between the bottom and top of the cell is valid within the required limits.

The theoretical equations for computing the diffusion coefficients[9,10] may be written

$$\mathfrak{D} = K \times 10^{13} \left(\frac{\overline{\mathfrak{M}}}{c}\right)\left[1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right] \tag{1}$$

$$\left[1 + c\,\frac{\partial \ln y_\pm}{\partial c}\right] = 1 - \frac{E\sqrt{c}}{(1 + A'\sqrt{c})^2} + Fc - c\psi(\mathrm{d}) \tag{2}$$

$$c\psi(\mathrm{d}) = \frac{Gc - Hc^{3/2}}{d_0 + Gc - Jc^{3/2}} \tag{3}$$

$$\left(\frac{\overline{\mathfrak{M}}}{c}\right) \times 10^{20} = P - Q\,\frac{\sqrt{}}{(1 + A'\sqrt{c}} + R'\phi(A'\sqrt{c}) \tag{4}$$

where

$$K = 1000\,RT(\nu_1 + \nu_2) \tag{5}$$

$$E = 1.15148_{(f)} \tag{6}$$

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(1) Jones and Bickford, THIS JOURNAL, **56**, 602 (1934).

(2) MacInnes, *J. Franklin Institute*, **225**, 661 (1938).

(3) Longsworth and MacInnes, THIS JOURNAL, **60**, 3070 (1938).

(4) Shedlovsky, *ibid.*, **72**, 3680 (1950).

(5) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(6) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950, Fig. (6-6-2), p. 164.

(7) Harned and Levy, THIS JOURNAL, **71**, 2781 (1949).

(8) Harned and Nuttall, *ibid.*, **69**, 736 (1947).

(9) Ref. 6, pp. 89, 90; Harned, *Chem. Revs.*, **40**, 461 (1947).

(10) Harned and Blake, Jr., THIS JOURNAL, **73**, 2448 (1951).

$$F = 0.536\ (2.303 \log c + 1) \tag{7}$$

$$P = \frac{1.0748}{\nu_1 z_1}\left(\frac{\lambda_1^0\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right) \tag{8}$$

$$Q = \frac{31.322}{(\nu_1 z_1^2 + \nu_2 z_2^2)^{3/2}\eta_0(DT)^{1/2}}\left[\frac{|z_1|\lambda_1^0 - |z_2|\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right]^2 \tag{9}$$

$$R' = \left(\frac{z_2^2\lambda_1^0 + z_1^2\lambda_2^0}{\lambda_1^0 + \lambda_2^0}\right)^2 \frac{9.304 \times 10^7}{\eta_0(DT)^2} \tag{10}$$

G, H and J are constants obtained by differentiation of the expression for the variation of the density of the solution with respect to the molar concentration. In these equations c is the molar concentration, $y_\pm$ the activity coefficient on the molar scale, and $S_{(f)}$ the limiting Debye and Hückel function for the activity coefficient. $A'\sqrt{c}$ equals κa where κ is the reciprocal radius of the ionic atmosphere and a the mean distance of approach of the ions. R is the gas constant in ergs, T the absolute temperature, z_1 and z_2 are the valences of the ions, $|z_1|$ and $|z_2|$ their magnitudes, ν_1 and ν_2 are the number of kinds of ions obtained from the dissociation of the electrolyte, and λ_1^0, and λ_2^0 are the equivalent conductances of the ions at infinite dilution. D is the dielectric constant of the solvent, η_0 its viscosity and d_0 its density. The exponential integral term of the theory $\phi(A'\sqrt{c})$ for various values of $A'\sqrt{c}$ may be obtained from tables compiled by Harned and Owen.[11]

The required data for the theoretical computation of the diffusion coefficient, $\mathfrak{D}$, are compiled in Table I. The thermodynamic term $[1 + c\partial \ln y_\pm/\partial c]$ was derived from activity coefficients obtained from cells with liquid junctions at concentrations from 0.0006 to 0.033 mole per liter.[4] The mobility term $(\overline{\mathfrak{M}}/c)$ was evaluated from the accurately determined values of λ_1^0 and λ_2^0. These data should assure the preciseness of the theoretical values up to the highest concentration at which the diffusion coefficient was measured.

The observed and calculated results are recorded in Table II. All the observed values are lower than the calculated ones and in this respect are analogous to the behavior of the diffusion coefficient of calcium chloride. The upper curve in Fig. 1 represents the complete theoretical computation corresponding to the calculated values in Table II. In this figure,

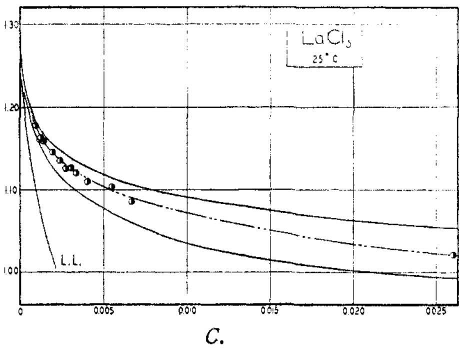

Fig. 1.—The diffusion coefficient of lanthanum chloride at 25°. Upper curve, complete theory by equation (1) to (10): circles, observed results; curve below observed results, mobility term constant; L. L., limiting law.

TABLE I

CONSTANTS, DATA AND PARAMETERS EMPLOYED IN THEORETICAL COMPUTATIONS OF THE DIFFUSION COEFFICIENT OF LANTHANUM CHLORIDE AT 25°

$\|z_1\|$	3	K	9.916
$\|z_2\|$	1	E	4.3059
ν_1	1	F	0.536 (2.303 log c + 1)[14]
ν_2	3	d_0	0.997
λ_1^0	69.6[12]	G	0.05616
λ_2^0	76.34[13]	H	0.01775
A'	5.5[14]	J	0.01182
a (Å.)	6.83[14]	P	13.047
$S_{(f)}$	3.7397[14]	Q	7.8825
		R'	509.94

$R = 8.314 \times 10^7$; $T = 298.16$; $D = 78.54$; $\eta_0 = 8.949 \times 10^{-3}$

TABLE II

OBSERVED AND CALCULATED DIFFUSION COEFFICIENTS OF LANTHANUM CHLORIDE AT 25°

c	$\mathfrak{D} \times 10^5$ obsd.	$\mathfrak{D} \times 10^5$ calcd.
0.0000	...	(1.294)
.00093	1.178	1.183
.00116	1.162	1.175
.00127	1.163	1.170
.00140	1.159	1.167
.00195	1.146	1.155
.00240	1.135	1.147
.00272	1.126	1.142
.00307	1.127	1.137
.00338	1.120	1.134
.00401	1.110	1.127
.00552	1.104	1.113
.00668	1.087	1.106
.026	1.021	1.053

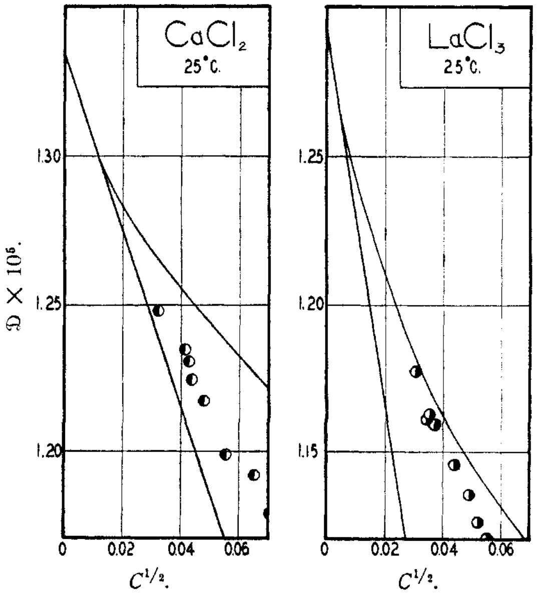

Fig. 2.—The diffusion coefficients of calcium and lanthanum chlorides *versus* $c^{1/2}$ at 25°: upper curve, complete theory; circles, observed results; lower straight lines, limiting law.

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[11] Ref. 6, p. 180.

[12] MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y. 1939, p. 342.

[13] Ref. 6, p. 172.

[14] Shedlovsky, THIS JOURNAL, 72, 3680 (1950).

the circles represent the observed results. The curve below the graph of the observed results was obtained by assuming the mobility, term, $(\overline{\mathfrak{M}}/c)$, to be constant and equal to P, its value at zero concentration. The difference between this curve and the upper curve represents the calculated effect of electrophoresis. The lowest curve was obtained from the limiting law of the theory which for lanthanum chloride becomes

$$\mathfrak{D} = \mathfrak{D}_0 - \mathcal{S}_{(\mathfrak{D})}\sqrt{c} = 1.2937 - 6.354\sqrt{c} \quad (11)$$

It is clear from these graphs that fair agreement with theory is obtained as the concentration of the salt approaches zero. On the other hand, the difference between the calculated and observed results is considerably greater than the estimated error in the determination of the diffusion coefficient. This fact we believe to be significant.

A comparison of the diffusion coefficients of calcium and lanthanum chloride is illustrated by Fig. 2 in which these quantities are plotted against the square root of the concentration. The upper curves represents the complete theory and the lower straight lines the limiting law. These results show that the deviation from theory of the diffusion coefficient of calcium chloride is about twice the magnitude of the deviation for lanthanum chloride. In both cases, the observed results approach the theoretical values as the concentration decreases.

For lanthanum chloride, very close conformity with theory at molar concentrations below 0.0005 molar or 0.003 ionic strength is indicated. For calcium chloride, it appears that agreement between theory and observed results will only occur in extremely dilute solutions.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. VI. The Effect of Ionic Strength on the Diffusion Current Constant in the Absence of Gelatin

BY LOUIS MEITES

Data are presented on the effect of acid concentration on the diffusion current constant of thallium(I) in 0.01–4.1 *F* hydrochloric acid and in 0.01–0.4 *F* perchloric acid, and of iodate in 0.01–4.2 *F* hydrochloric acid. At ionic strengths between about 0.1 and 0.8, I is equal within 1% to the value calculated from the Ilkovič equation using the appropriate values of D^0. At lower ionic strengths, however, I increases, so that the diffusion current constant at infinite dilution is much higher than that predicted. This is considered to represent a failure of the diffusion coefficient dependence expressed by the Ilkovič equation.

Introduction

For want of any convenient and precise method for the determination of ionic diffusion coefficients under polarographic conditions, the values of D^0 calculated from the Nernst equation have commonly been applied to diffusion current data secured in the presence of a large excess of supporting electrolyte. Lingane and Kolthoff[1] compared the diffusion currents of a number of ions with the values calculated from the Ilkovič equation on the basis of this assumption. Although no large systematic discrepancy was apparent, the differences were occasionally as large as 8%.

The work here described was intended to make possible a more direct test of the Ilkovič equation by extrapolating diffusion current constant values to infinite dilution for comparison with the predicted values.

Experimental

Hydrochloric and perchloric acid solutions were prepared by volume dilution of solutions standardized against carefully purified sodium tetraborate decahydrate. A known volume of an acid solution of the desired concentration was placed in a modified H-cell[2] and deaerated. When the residual current had become constant, a weighed portion of a solution of thallium(I) chloride or potassium iodate was added, the solution was deaerated again, and the total current was measured. These measurements were made at four or five potentials between −0.8 and −1.0 v. *vs.* S.C.E. (except with 2 or 4 *F* acid, where slightly more positive potentials were used to obviate interference from the discharge of hydrogen ion), using three or four concentrations of the reducible ion between 0.1 and 0.35 m*M*. Consequently each diffusion current constant is the mean of twelve to twenty individual values: the mean deviation of each such series was about ±0.25%.

All measurements were made with the manual polarograph previously described,[3] with the cell in a water thermostat at 25.00 ± 0.01°. One capillary was used throughout this work: at −0.9 v. *vs.* S.C.E. it gave a drop time of 3.0 sec., which is well within the range in which the diffusion current constant is independent of drop time in the absence of gelatin.[4]

Thallous chloride was twice recrystallized from water and dried at 140°. The preparation of the potassium iodate has been described elsewhere.[5] Stock solutions of these materials were prepared by weight.

It has recently been shown[3,6] that the diffusion current of an ion at very low concentrations may be affected by a phenomenon related to maximum formation, especially if the measurement is made at a potential not very far removed from the half-wave potential. In this work it was always found that the diffusion current constants at the most negative and most positive potentials used agreed within the limits of experimental error, so that any contribution from the above effect must have been negligibly small.

Because the concentration of supporting electrolyte was always at least 35 times that of the reducible ion, and because of the high mobility of the hydrogen ion, no interference from the migration current was expected, and the diffusion current constants always appeared to be independent of the concentration of reducible ion.

Data and Discussion

Table I summarizes the values of I of thallium(I) and iodate found at various ionic strengths. At

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[1] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

[2] L. Meites and T. Meites, *Anal. Chem.*, in press.

[3] L. Meites and T. Meites, THIS JOURNAL, **72**, 3686 (1950).

[4] L. Meites, *ibid.*, **73**, 1581 (1951).

[5] L. Meites and T. Meites, *ibid.*, **73**, 395 (1951).

[6] F. Buckley and J. K. Taylor, *J. Research Natl. Bur. Standards*, **34**, 97 (1945).