[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MALAYA]

The Diffusion Coefficient of Calcium Chloride in Aqueous Solution at 25°

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By means of the porous diaphragm cell technique the integral diffusion coefficient of calcium chloride has been measured at 25° between 0.05 and 1 molar. The differential diffusion coefficient has been calculated and found to correspond to a hydration number of about 24.

Harned and Levy[1] used the conductance method to determine the diffusion coefficient of calcium chloride in aqueous solution at concentrations up to 0.00501 molar and obtained results which differed widely from the predictions of the Onsager–Fuoss theory,[2] a finding which was not unexpected since it was known that the transference number of this salt is not consistent with the Onsager theory.

Stokes[3] has improved the porous diaphragm cell method and applied[4] his technique to the measurement of the diffusion coefficients of a number of 1:1 electrolytes. We have now used this method to extend the data of Harned and Levy to more concentrated solutions of calcium chloride, supplementing the earlier data of Hollingshead and Gordon.[5]

TABLE I

INTEGRAL DIFFUSION COEFFICIENTS OF CALCIUM CHLORIDE AT 25°

β	t, sec. × 10^6	c_1	c_2	c_3	c_4	$\bar{D}$	$\bar{D}^0(C_m')$
0.10526	1.871	0.05128	....	0.04101	0.01031	1.165	1.171
.07722	1.494	.07564	....	.06563	.00995	1.153	1.158
.10540	1.538	.1153	....	.09544	.01998	1.136	1.142
.07881	1.525	.2155	....	.1866	.02873	1.123	1.128
.07720	1.480	.3152	....	.2747	.04030	1.126	1.129
.08830	1.716	.3453	....	.2891	.05633	1.131	1.134
.08846	1.440	.3807	....	.3276	.05324	1.117	1.121
.09611	2.141	.4897	....	.3891	.1015	1.123	1.126
.07678	0.9072	.6799	0.3040	.6484	.3353	1.140	1.132
.08798	1.800	.8483	....	.7048	.1438	1.134	1.135
.10140	1.279	1.0060	....	.8600	.1466	1.150	1.146
.07750	0.8490	0.9692	.2987	.9155	.3521	1.147	1.139
.10450	0.5463	1.0105	.4943	.9739	.5310	1.167	1.145
.07690	1.481	1.0973	.5067	1.0175	.5860	1.197	1.162
.07863	1.557	1.2016	.4943	1.0992	.5961	1.208	1.169

Experimental Results

The method followed very closely that outlined by Stokes[3] and needs no further description. We shall also use the nomenclature introduced by Stokes.[4] The cell "constant" was determined by allowing approximately decinormal potassium chloride to diffuse into water; for some cells the cell "constant" increased slowly and regularly with time, whilst for others it first decreased to a minimum and then increased slowly. The calcium chloride was prepared by adding calcium carbonate to a solution of "analytically pure" chloride, filtering and crystallizing; a solution of these crystals was brought to pH 6.5 by the addition of very dilute hydrochloric acid in amount determined by titration of an aliquot of the solution. A solution prepared in this way gave reproducible results but difficulty was experienced with solutions which contained an excess of hydrochloric acid and also with solutions to which calcium carbonate had been added unless the pH of the solution was adjusted to 6.5. Some of the runs were made with a dilute solution of calcium chloride in the upper compartment of the cell instead of water and for the calculation of $\bar{D}^0$ from $\bar{D}$ we plotted $\bar{D}$ against $\sqrt{c_1 + c_2}$ instead of against $\sqrt{c_1}$. Our experimental results are given in Table I, the diffusion coefficients being expressed in terms of 10^{-5} cm.^{2} sec.$^{-1}$ as the unit.

In several runs the pH of the solution in each compartment was tested before and after the run but no significant departure from a pH of 6.5 was found. Any error introduced by hydrolysis with formation of more rapidly diffusing hydrochloric acid should, therefore, be negligible.

The calculation of the differential diffusion coefficient, D, from the integral coefficient presents some difficulty. Figure 1 is a plot of the integral diffusion coefficient, $\bar{D}^0$, against $\sqrt{(c_1 + c_3)/2}$; values at round concentrations, read from this plot, are given in the second column of Table II. The full line on the left of Fig. 1 is calculated from the data of Harned and Levy[1]; the full line to the right is drawn through our experimental points: it is very difficult to draw a curve through the two points corresponding to our most dilute solutions which will join smoothly with the Harned and Levy curve. These two points, are, however, suspect because Stokes found that the diaphragm cell gave high results at concentrations of 1:1 salts below 0.05 molar as a result of some form of

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

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

(3) R. H. Stokes, THIS JOURNAL, **72**, 763 (1950).

(4) R. H. Stokes, *ibid.*, **72**, 2243 (1950).

(5) E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **9** 152 (1941).

surface effect; at the present stage of the subject we cannot be certain that, for a polyvalent salt, this effect may not be even more pronounced and appreciable to even higher concentrations. There is, therefore, good reason to believe that the first two points are too high and the third point at $c = 0.1$ may also be high. We have, therefore, drawn the broken curve below these points to join smoothly with the Harned and Levy curve; the broken curve is not defined accurately but is the best that can be obtained until we know more about these surface effects with polyvalent salts. If we are prepared to accept this curve, then the differential diffusion coefficient can be calculated; values are given in the third column of Table II.

TABLE II

INTEGRAL AND DIFFERENTIAL DIFFUSION COEFFICIENTS OF CALCIUM CHLORIDE AT 25°

c	D°	D (obsd.)	D (calcd.)	n
0.05	(1.154)	(1.129)	1.172	(40)
.1	1.139	1.120	1.189	32
.2	1.128	1.117	1.247	28
.3	1.124	1.119	1.316	28
.4	1.124	1.124	1.382	23
.5	1.125	1.132	1.458	24
.6	1.127	1.148	1.532	23
.7	1.132	1.167	1.621	22
.8	1.138	1.189	1.706	23
.9	1.145	1.215	1.780	19
1.0	1.153	1.243	1.890	18

The fourth column of Table II gives the values of D calculated by the Onsager–Fuoss equation.[6] The term in this equation containing the variation of the activity coefficient with concentration was calculated from the equation

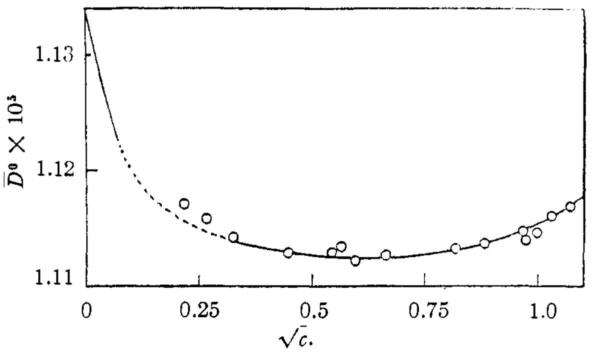

Fig. 1.—Integral diffusion coefficient of calcium chloride

$$\log \gamma = -1.764\sqrt{c}/(1 + 2.704\sqrt{c}) + 0.165c + 0.04c^2 - \log(1 + 0.054\, m)$$

It will be seen from Table II that theory predicts much higher values than those observed, a difference which Stokes[4] has suggested is due to a diffusion of water of hydration along with the ionic hydration, the effect being given by

$$D_{\text{obsd}} = D_{\text{calcd}}(1 - 0.018n)$$

The last column of Table II gives the values of the hydration number, n, so calculated. The value of approximately 24 found seems very high and is not consistent with $n = 11.9$ found by another method.[7] It should, however, be treated with considerable caution because it is based on a theory which assumes the validity of the Onsager–Fuoss equation, an assumption which is very suspect in its application to calcium chloride in view of the results of Harned and Levy.

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(6) See equations 4-4-19, 20 and 21 of H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1950.

(7) R. H. Stokes and R. A. Robinson, THIS JOURNAL, **70**, 1870 (1948).