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

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The differential diffusion coefficient of strontium chloride between 0.001 and 0.008 *M* concentrations at 25° has been determined by the conductometric method. Good agreement with calculations by the Nernst–Onsager and Fuoss theoretical equations has been obtained. This result differs from the behavior of the diffusion coefficient of calcium chloride which appears to deviate widely from the theoretical prediction in solutions of the same concentrations.

Measurements of the diffusion coefficient of calcium chloride in dilute aqueous solution determined by the conductometric method by Harned and Levy[2,3] differ considerably from the values computed by the Onsager and Fuoss theory.[4] These experimental results agree closely with the diffusion coefficient computed by Hollingshead and Gordon[5] from diaphragm cell measurements. More recently, Hall, Wishaw and Stokes[6] and Lyons and Reilly[7] have determined the diffusion coefficient of this salt at higher concentrations by the Goüy interference method and have shown that their results are consistent with those obtained in the dilute solution range.

Since the discrepancy between the theoretically computed values and the experimental results is so large for calcium chloride solutions of high dilution, we have extended our conductometric studies to include determinations of the diffusion coefficients of other alkaline earth chlorides. The determination of the diffusion coefficient of strontium chloride at 25° from 0.001 to 0.008 *M* concentration and its theoretical calculation is the subject of the present communication.

Theoretical Considerations

The diffusion coefficient as a function of the concentration according to the Onsager and Fuoss[4] theory is given by the equation

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

in which the mobility term $(\bar{M}/c)$ may be evaluated by the expression

$$\bar{M}/c = 1.0748 \times 10^{-20}\,\frac{\lambda_1^0\lambda_2^0}{\nu_1|z_1|\Lambda^0} - \frac{(|z_1|\lambda_1^0 - |z_2|\lambda_2^0)^2}{|z_1z_2|(\nu_1 + \nu_2)\Lambda^{02}}\,\frac{3.122 \times 10^{-8}}{\eta_0(DT)^{1/2}}\,\frac{\sqrt{\Gamma}}{(1 + \kappa a)} + \left(\frac{z_2^2\lambda_1^0 - z_1^2\lambda_2^0}{\Lambda^0}\right)^2\frac{9.304 \times 10^{-13}}{\eta_0(DT)^{1/2}}\,\frac{\sqrt{\Gamma}}{(1 + \kappa a)} \quad (2)$$

In these equations, $\mathfrak{D}$ is the differential diffusion coefficient in cm.^{2} sec.$^{-1}$, 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 equivalent conductances of the ions at infinite dilution, $\Lambda^0 = \lambda_1^0 + \lambda_2^0$, z_1 and z_2 are the valences of the ions, Γ is 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 function of the theory.

For strontium chloride at 25°, $\nu_1 = 2$, $\nu_2 = 1$, $z_1 = -1$, $z_2 = 2$, $\lambda_1^0 = 76.34$, $\lambda_2^0 = 59.46$,[8] $\eta_0 = 8.949 \times 10^{-3}$,[9] $D = 78.54$,[10] $T = 298.16$ and $a = 4.89$ Å. Upon substituting these values, equation (2) reduces to

$$\left(\frac{\bar{M}}{c}\right) \times 10^{20} = 17.9628 - \frac{4.3995\sqrt{c}}{1 + 2.789\sqrt{c}} + 17.5904(\kappa a)^2\phi(\kappa a) \quad (3)$$

The function $(\kappa a)^2\phi(\kappa a)$ is available from tables.[11]

The thermodynamic term in equation (1) was obtained in the usual manner by use of the Debye and Hückel functions. To this end, the results of Robinson[12] were employed to yield the formula

$$\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) = 1 - \frac{2.0304\sqrt{c}}{1. + 2.789\sqrt{c}} + 0.1559c - c\psi(d) \quad (4)$$

At low concentrations the density term $c\psi(d)$ is negligible. The theoretical values of $\mathfrak{D}$ for both calcium and strontium chlorides are plotted in Fig. 1. It is to be noted that they differ little from each other. Indeed, the mobility term for the two salts is nearly identical and the small difference between the curves is to be accounted for by the somewhat lower activity coefficient of the strontium chloride.

Experimental Results and Comparison with Theory

The observed and calculated diffusion coefficients at the designated concentrations are recorded in the second and third columns of Table I, respectively, and it is apparent that the agreement between the two sets of values is good. In the last column of the Table, values of the quantity $\mathfrak{D}' = (\mathfrak{D}_0 - \mathfrak{D})_{\text{calcd}} + \mathfrak{D}_{\text{obsd}}$ are given. This quantity should be constant and equal to the limiting value, 1.336. We note that the mean value of this quantity differs by less than 0.2% from the limiting

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[1] Toscanini Fellow, Yale University, 1950–1952.

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

[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 595.

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

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

[6] J. R. Hall, B. F. Wishaw and R. H. Stokes, THIS JOURNAL, **75**, 1556 (1953).

[7] P. A. Lyons and J. F. Riley, unpublished results, Yale University.

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

[9] Reference 3, p. 128.

[10] Reference 3, p. 118.

[11] Reference 3, p. 130.

[12] R. A. Robinson, *Trans. Faraday Soc.*, **36**, 735 (1940).

value, a fact which indicates that the theory is satisfactory for this case.

TABLE I

OBSERVED AND CALCULATED VALUES OF THE DIFFUSION COEFFICIENT OF STRONTIUM CHLORIDE AT 25°

c, mole/l.	$\mathfrak{D} \times 10^5$ (obsd.)	$\mathfrak{D} \times 10^5$ (calcd.)	$\mathfrak{D}' \times 10^5$
0.00000	...	(1.336)	(1,336)
.00108	1.270	1.265	1.341
.00150	1.256	1.256	1.336
.00250	1.243	1.241	1.338
.00272	1.244	1.238	1.342
.00300	1.233	1.235	1.334
.00300	1.237	1.235	1.338
.00445	1.222	1.223	1.335
.00549	1.212	1.216	1.332
.00611	1.217	1.212	1.341
.00774	1.208	1.205	1.339
		Mean	1.3376

The diffusion characteristics of calcium and strontium chlorides are clearly demonstrated in Fig. 1. Calcium chloride deviates over 1% from theory at a concentration of 0.001 *M* and 4% at 0.005 *M* whereas strontium chloride shows no marked deviation. Incompleted investigations of barium and magnesium chloride solutions also agree with the prediction of the theory. Obviously, the neglect of the higher order terms of the theory for electrolytes of higher valence types cannot account for this result. Of course, one should never exclude the possibility of experimental error but in the case of calcium chloride the agreement between the optical and conductometric results seems to exclude this possibility.

The limiting equivalent conductances of the alkaline earth metal ions and magnesium ion according to Shedlovsky and Brown[7] are $^1/_2\text{Ba}^{++} = 63.64$, $^1/_2\text{Sr}^{++} = 59.46$, $^1/_2\text{Ca}^{++} = 59.50$, $^1/_2\text{Mg}^{++} = 53.06$. This result is peculiar since the calcium and strontium ion conductances are so nearly alike and the order reverses in passing from the barium to magnesium. If the limiting conductance of the calcium ion was 2 to 3% lower than that observed, the theoretical and observed values of the diffusion coefficient of salt would be brought into fairly close agreement. It is certainly unlikely that an error of such a magnitude could occur with the conductance measurements and calculations.

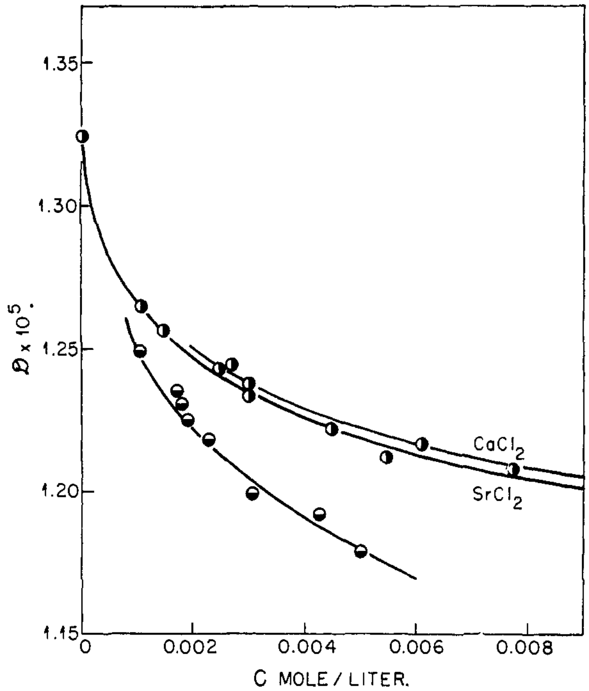

Fig. 1.—Calculated and observed diffusion coefficients: Upper curve represents the diffusion coefficient of calcium chloride as calculated by Harned and Levy. Middle curve represents the diffusion coefficient of strontium chloride calculated by equations (1) to (4). ◑ represent observed diffusion coefficients of strontium chloride. ◒ and lower curve represent the observed diffusion coefficient of calcium chloride.

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