ultraviolet spectra. Such results should provide further useful data for confronting acid–base theories. Also it will be of interest to compare the structures of the neutralization products for bases of different basic strength and steric requirements.

EVANSTON, ILLINOIS

Diffusion Coefficients for Aqueous Solutions of Calcium Chloride and Cesium Chloride at 25°

BY PHILIP A. LYONS AND JOHN F. RILEY

Diffusion coefficients, molal refractive increments and supplementary densities and relative viscosities are reported for calcium chloride solutions from $c = 0.03$ to $c = 6$, and for cesium chloride solutions from $c = 0.06$ to $c = 6$. In agreement with results available from the conductance method diffusion coefficients for cesium chloride approach the values predicted by the Onsager–Fuoss relation at low concentration. At higher concentrations the deviation from theory is positive. Data reported for calcium chloride solutions supplement existing data indicating a negative deviation from the Onsager–Fuoss theory but the values presented are not consistent with the conductometric results which are at present available. Evidence is presented which suggests that Gouy diffusiometry, as currently employed, yields data for very dilute electrolyte solutions which are inaccurate and define an upper bound to the correct values.

Introduction

Diffusion coefficients for dilute aqueous calcium chloride solutions have been of considerable interest because of the large negative deviations from theory which have been observed for this system. These data[1] were obtained using the conductometric method of Harned. It has been shown that under certain conditions the conductance technique and Gouy diffusiometry yield the same values[2,3] within the experimental errors involved. The work here reported supplements existing data[4-6] with which the conductance data can be compared. Results presented for aqueous cesium chloride solutions provide a reasonable confirmation of the conductometric work for this system.[7]

The investigation was extended into regions of high concentrations for several reasons: first, to permit a comparison of concentration diffusion data with existing ionic self-diffusion values[8]; secondly, to provide data for 1–1 and 2–1 salts at high concentrations which should be suitable for the calibration of other diffusion devices for electrolytes in these regions.

Experimental

Preparation of Solutions.—Following the procedure of Shedlovsky and Brown[9] stock solutions of calcium chloride were prepared from C.P. calcium chloride which had been recrystallized three times. These stock solutions were analyzed and used for the preparation of the solutions of low concentration. The more concentrated solutions were prepared by addition of water to the recrystallized salt. Direct analysis of the latter solutions provided the concentration data which are reported.

Cesium chloride solutions were prepared by transferring weighed amounts of dried cesium chloride into calibrated volumetric flasks. The cesium chloride used was, spectrochemically, the purest sample available. The same sample

had been used to establish the limiting equivalent conductance for this salt[10] and also for the conductometric determination of diffusion coefficients at very low concentrations.[7] The salt was recrystallized several times from water and vacuum dried first at room temperature and finally at 50°.

Diffusion Procedure.—Equipment similar to that used for this work has previously been described.[8,11,12] One modification has been made in the design of a cell holder for use with a large Tiselius cell (92 × 5 × 50 mm. channel).[13] Measurements were made with this cell at low concentrations. In the new cell holder appropriate masking devices were inserted into slots immediately in front of the Tiselius cell which placed the cell and masks much closer than was the case for the conventional arrangement.

Boundary formation, movement of the boundary to the optic axis, and sharpening of the boundary by siphoning were accomplished in the usual fashion. During sharpening the positions of fringe minima in the focal plane were observed visually with the aid of a calibrated eye-piece. Following the suggestion of Longsworth[14] these readings were used to estimate a time correction which compensates for a finite boundary thickness at the start of the experiment. If the siphoning operation is interrupted temporarily the Gouy pattern which appears can also be observed visually in the same manner. During the period of interruption the following experiment was performed several times using the large cell holder. After the withdrawal of the siphoning needle and the appearance of the pattern, a fine wire crosshair which was the optic axis reference for this unit was moved slightly with respect to the boundary. By careful positioning, the cross-hair could be arranged so as to just blur the lowest fringe in the pattern while the boundary was still thin. At any other position of the cross-hair a blurring of fringes at higher values of j was observed. If the position of the maximum in the index of refraction gradient were invariant as would be required for ideal diffusion the lowest fringe should remain blurred. If the maximum in the gradient moved with respect to the optic axis during diffusion the blurring of fringes should be noticed at higher values of j.

The fractional values of j_m were determined in the usual way[15] by using the equipment as a modified Rayleigh interferometer. With a good cell and careful alignment the δ-values (corrections for displacement of the Rayleigh bundle by the cell in the absence of the gradient of refractive index produced by the boundary) can be made quite small, and equal, for both the open and closed cell positions. A preliminary set of data for calcium chloride assuming that

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

(2) H. S. Harned and R. L. Nuttall, ibid., 71, 1460 (1949).

(3) L. J. Gosting, ibid., 72, 4418 (1950).

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

(5) R. A. Robinson and C. L. Chia, THIS JOURNAL, 74, 2776 (1952).

(6) J. R. Hall, B. F. Wishaw and R. H. Stokes, ibid., 75, 1556 (1953).

(7) H. S. Harned, M. Blander and C. L. Hildreth, Jr., ibid., 76, 4219 (1954).

(8) J. H. Wang, ibid., 75, 1769 (1953).

(9) T. Shedlovsky and A. S. Brown, ibid., 56, 1066 (1934).

(10) W. E. Voisenet, Jr., and B. B. Owen, private communication.

(11) L. G. Longsworth, THIS JOURNAL, 69, 2510 (1947).

(12) L. J. Gosting, E. M. Hansen, G. Kegeles and M. S. Morris, Rev. Sci. Instruments, 20, 209 (1949).

(13) Cell made by Pyrocell Mfg. Co., New York, N. Y.

(14) L. G. Longsworth, private communication.

(15) L. J. Gosting and M. S. Morris, THIS JOURNAL, 71, 1998 (1949).

these corrections were the same, exhibited a systematic error. This was found to be due to the fact that accidental rotation of the achromatic lens about the optic axis between the time of alignment and the time of measurements had caused these two correction values to differ by about 15 μ. All the values of j_m here reported were obtained by applying to the fractional values determined in each position the corrections measured with the cell in the same position. The corrected fractional values from the open and closed positions agreed within several hundredths of a fringe.

Interruption of sharpening[16] was used for all determinations on concentrated solutions. This technique, besides being particularly useful for solutions in limited supply, seemed to result in somewhat sharper boundaries, as evidenced by lower time corrections and the agreement between the observed[11] and computed[16] corrections.

When they were unavailable, relative viscosities and densities of calcium chloride and cesium chloride solutions of the appropriate concentrations were measured. Relative viscosities were determined in Ostwald–Fenske viscometers, the reported values having been corrected for small kinetic energy losses. The supplementary densities were measured in a twin-armed pycnometer of 20-ml. capacity. Densities, viscosities and diffusion coefficients are reported for 25 ± 0.01°.

Results

Diffusion coefficients, molar refractive increments and relative drift in C_t are tabulated for calcium chloride solutions in Table I and for cesium chloride solutions in Table II. The reported diffusion coefficients were computed from C_t values obtained by using the Airy integral approximation.[15] C_t values for the lowest seven minima, excluding the zeroth minimum, were averaged for the actual computation of the reported diffusion coefficients.

TABLE I

CaCl$_2$

$\bar{c}^a$	Δc^b	$j_m{}^c$	$D \times 10^5{}^d$	$(\Delta n/ \Delta c)10^{3e}$	$C^*_t/\bar{C}_t{}^f$
0.02813	0.03720	90.60	1.153	26.54	0.996
.0547	.0904	108.52	1.136	26.40	0.998
.1020	.0999	118.38	1.122	26.07	1.001
.1930	.1042	122.03	1.123	25.76	1.000
.3142	.1062	122.81	1.132	25.44	1.001
.4694	.1055	119.81	1.152	24.98	0.999
.6706	.1024	114.41	1.177	24.58	1.001
1.000	.1039	133.33	1.220	23.99	1.001
1.442	.1096	117.32	1.271	23.54	1.001
1.462	.1266	135.11	1.271	23.47	1.000
2.046	.121	132.97	1.310		1.000
2.570	.1023	99.98	1.311	21.50	1.001
3.250	.0961	90.28	1.248	20.44	0.999
4.001	.105	92.46	1.078		1.000
4.486	.058	81.22	0.919		1.000
5.012	.106	52.58	0.716$_3$		0.998
5.424	.079	81.69	0.571$_5$		1.001
6.004		64.24	0.402$_0$		0.999

^{a} $\bar{c}$, average concentration, moles/liter of solution. ^{b} Δc, difference in concentration across boundary. ^{c} j_m, total number of fringes in Gouy pattern. ^{d} D, diffusion coefficient at $\bar{c}$ in cm.^{2}/sec. ^{e} $(\Delta n/\Delta c) = (j_m/\Delta c)(\lambda/a)$ where $a = 2.482_6$ cm. or 5.011_4 cm. and $\lambda = 5460.74$ Å. ^{f} $C^*_t/\bar{C}_t$, ratio of C_t at $j = \frac{1}{2} j_m$ to $\bar{C}_t$, where $\bar{C}_t$ is the average of C_t for $j = 1$ to $j = 6$.

Table III lists values for the densities and relative viscosities of calcium chloride solutions which were needed for this work and in Table IV are listed similar data for the cesium chloride solutions.

(16) L. G. Longsworth, THIS JOURNAL, **74**, 4155 (1952).

TABLE II

CsCl

$\bar{c}$	Δc	j_m	$D \times 10^5$	$(\Delta n/\Delta c)10^3$	$C^*_t/\bar{C}_t$
0.0625	0.1050	63.29	1.887	13.26	0.996
.0900	.1401	84.02	1.874	13.19	1.000
.1600	.2100	125.18	1.859	13.11	0.999
.2500	.2100	124.37	1.855	13.03	0.998
.3600	.2401	141.12	1.855	12.93	0.999
.6400	.2002	115.64	1.868	12.71	1.001
1.000	.2401	136.84	1.902	12.54	1.003
1.960	.2218	121.86	2.023	12.08	1.002
3.060	.2249	120.10	2.183	11.75	1.000
4.000	.2300	120.28	2.291	11.50	1.000
5.000	.234	117.21	2.364		1.000
5.750	.240	118.32	2.354		1.000
6.000	.244	122.56	2.335		1.002

TABLE III

CaCl$_2$

$\bar{c}$	$\eta/\eta_0{}^a$	$\bar{c}$	η/η_0	d^b
0.0953	1.031	2.518	2.263	1.2072
.1918	1.062	3.202	3.035	
.3724	1.119	3.298	3.179	
.6373	1.208	3.949	4.461	1.3166
.7520	1.247	4.054	4.734	1.3239
.7798	1.259	4.467	6.039	1.3531
.8797	1.297	4.536	6.314	1.3582
1.0824	1.377	4.984	8.475	1.3891
1.1155	1.391	5.042	8.905	1.3934
1.398	1.523	5.371	11.01	1.4139
1.525	1.584	5.477	11.91	1.4213
1.917	1.812	5.964	17.01	1.4518
2.016	1.873	6.043	18.27	1.4577

^{a} η/η_0 relative viscosity. ^{b} d measured density in g./ml.^{3}

TABLE IV

CsCl

$\bar{c}$	η/η_0	d	$\bar{c}$	η/η_0	d
0.5002	0.978$_9$	1.0610	3.998	0.982$_1$	1.4966
1.000	.963$_1$	1.1243	5.001	1.036	1.6197
2.269	.946$_4$	1.2829	5.998	1.129	1.7408
2.997	.952$_5$	1.3733			

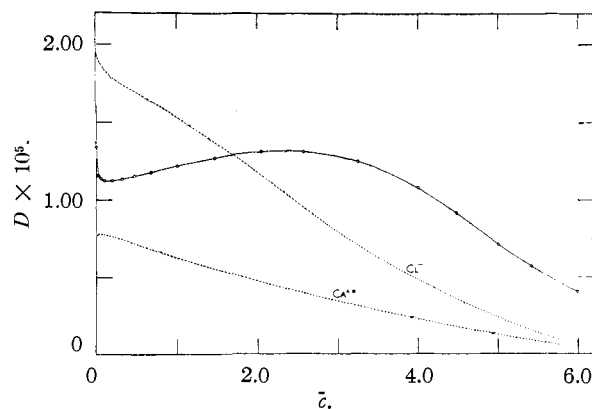In Fig. 1 are plotted the measured values of the diffusion coefficients for calcium chloride solutions

Fig. 1.—Diffusion coefficient of calcium chloride solutions vs. concentration: —O—, salt diffusion; Ca^{++}, self-diffusion coefficient of Ca^{++} ion; Cl$^-$, self-diffusion coefficient of Cl$^-$ ion.
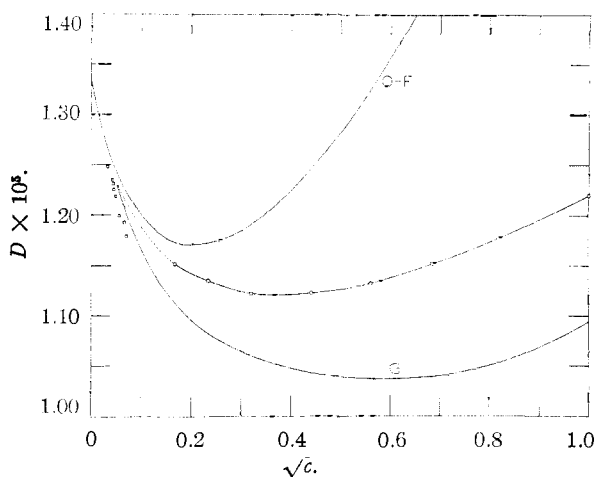
Fig. 2.—D of calcium chloride vs. $\sqrt{c}$: —O—, Gouy results; □, conductometric results; O-F, Onsager–Fuoss theory; G, Gordon relation.

together with self-diffusion data for Ca^{++} and Cl^- ions which have recently been reported.[8] The values for the more dilute solutions are plotted in Fig. 2 against the square root of concentration. In this same figure the data of Harned and Levy have been indicated. The values reported may be compared with the plot of the Onsager–Fuoss expression for this system

$$D = 7.437 \times 10^{13} \left(\frac{\overline{\mathfrak{M}}}{c}\right)\left(1 + c\,\frac{\partial \ln y\pm}{\partial c}\right)$$

The Nernst limiting value for the diffusion coefficient $D_0 = 1.3364 \times 10^{-5}$, is the value calculated from the limiting conductance data of Shedlovsky and Brown.[9] The mobility term, $(\overline{\mathfrak{M}}/c)$, for the Onsager–Fuoss equation was obtained in the usual fashion.[17] The thermodynamic term $(1 + c\,\partial \ln y\pm/\partial c)$ was computed using Robinson's explicit expression for the concentration dependence of the activity coefficient of calcium chloride in aqueous solutions[5]

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

The same thermodynamic term was used for developing the Gordon relation[18] for this system

$$D = D_0 \left(1 + c\,\frac{\partial \ln y\pm}{\partial c}\right) (\eta_0/\eta)$$

which is also plotted in Fig. 2. Relative viscosities required for the Gordon plot were obtained by interpolation of the data in Table III. The densities which were required in connection with these measurements were computed from the equation

$$d = 0.99707 + 0.09279c - 0.00597c^{3/2}$$

up to $c = 4$.[19] At higher concentrations direct interpolation of data from Table III was used.

The diffusion data reported are in reasonable agreement with measurements reported by other workers for the parts of the concentration range

(17) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 89ff.

(18) A. R. Gordon, J. Chem. Phys., 6, 522 (1937).

(19) H. S. Harned and B. B. Owen, ref. 17, pp. 250–253.

which have previously been covered. Insofar as they do agree with previous data the values reported here substantiate the negative deviations from the Onsager–Fuoss theory which had been indicated by Harned and Levy. The new aspect of these latest optical measurements is that they indicate that the conductometric values themselves may be somewhat low. As is seen in Fig. 2, the conductometric values are below the Gordon plot whereas the optical data are above that curve. Assuming that the Gordon relation should be a reasonable interpolation function over such a small concentration interval, the results from the two experiments are not completely consistent.

Figure 3 indicates, as might be expected for this 1–1 salt, that the diffusion data smoothly approach the Onsager–Fuoss theory at moderately high concentration. The relative viscosities of aqueous cesium chloride solutions are known to be anomalous. As is indicated by the relevant data in Table IV, η/η_0 decreases from its limiting value of 1, goes through a minimum at $c \approx 2.5$, and then increases slowly with increasing concentration in the more normal fashion. In view of this apparent lowering of frictional forces between solvent molecules which occurs with the use of cesium chloride as a solute, it is not too surprising that the diffusion coefficients are higher than would be normally expected and that the data approach the Onsager–Fuoss theory from above.
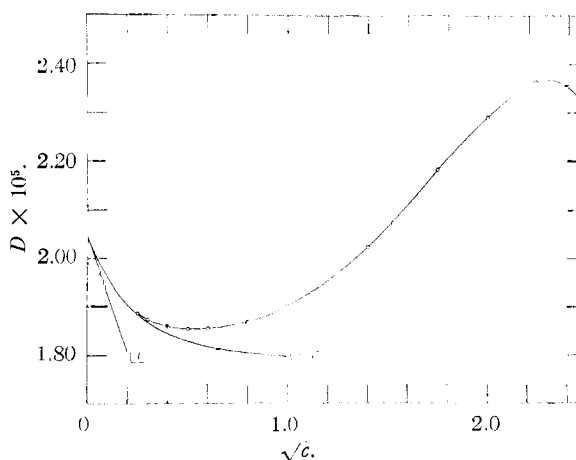

Fig. 3.—D of cesium chloride vs. $\sqrt{c}$: —O—, Gouy results; O-F, Onsager–Fuoss theory; LL, limiting law.

Figure 3 includes a plot of the Onsager–Fuoss equation for this system

$$D = 4.958 \times 10^{13} \left(\frac{\overline{\mathfrak{M}}}{c}\right)\left(1 + c\,\frac{\partial \ln y\pm}{\partial c}\right)$$

The Nernst limiting value for the diffusion coefficient, $D_0 = 2.046_2 \times 10^{-5}$, is the value calculated using the limiting equivalent conductance value, $\Lambda^0 = 153.60$, of Voisenet and Owen.[10] The computation of the thermodynamic term for cesium chloride was performed by appropriate differentiation of an empirical fit of Robinson's isopiestic data.[20] Densities were estimated from the expression[18]

$$d = 0.99707 + 0.12933c - 0.002166c^{3/2}$$

(20) R. A. Robinson, This Journal, 74, 6035 (1952).

The additional density data listed in Table IV show that the above expression is valid to $c = 6$. Viscosities were obtained by direct interpolation of the data from Table IV.

As has been shown for other electrolyte systems[6,21] including calcium chloride, at sufficiently high concentrations the diffusion coefficients for aqueous cesium chloride solutions go through a maximum.

For electrolyte solutions the interpretation of diffusion results is complicated by a number of factors, one of which is the ambiguity of the thermodynamic term which is to be used.[22] Robinson[5] and Stokes[6] have properly drawn attention to this point with particular emphasis on the fact that the mobile solute is hydrated. They have pointed out that if the frictional coefficient for the mobile species is assumed to be known as a function of concentration the value of the hydration number can be estimated, if the driving force for the diffusion process is identified with the gradient of the chemical potential of the hydrated solute. In this way, as an example, assuming the validity of a modification of the Hartley–Crank diffusion equation

$$D = D_0 \left(1 + m \frac{\partial \ln \gamma}{\partial m}\right) (1 - 0.018nm)$$
$$\left(1 + 0.018m\left(\nu \frac{D^*}{D_0} - n\right)\right)$$

Stokes[6] has computed the most appropriate value for the hydration number of calcium chloride to be four. Using the same equation the most acceptable value for cesium chloride is 0.6.

It is agreed that values obtained in this way for the hydration parameter are at best approximate. Some of the reasons why this must be so are well known. First, the assumption that the frictional coefficient is directly proportional to the macroscopic relative viscosity is only approximate. Even for simple non-electrolyte systems the use of the macroscopic relative viscosity is usually in error by an amount roughly proportional to the difference between solution and solvent viscosity. Secondly, for complex electrolyte systems the frictional coefficients of the individual ionic species in the same solutions are not influenced in the same way by changing the relative viscosity. The self-diffusion data for Ca^{++} and Cl^- in aqueous calcium chloride solutions are plotted in Fig. 1. The curves illustrate the point under consideration. As has been stressed by Wang,[8] "the ratio of the self-diffusion coefficient at infinite dilution to that in 5.36 formula wt. per liter calcium chloride solution is approximately 13 for Cl^- and 8 for Ca^{++}. The ratio of viscosity of 5.36 formula wt. per liter calcium chloride solution to that of pure water at 25° is about 11." If the mobility for salt diffusion is computed by dividing the diffusion coefficient by the thermodynamic term it will be found that the ratio of diffusion coefficient at infinite dilution to the corrected quantity at $c = 5.36$ is 15.

Despite the limitations of the above technique as a method of directly measuring the hydration number, the experimental evidence[5,6] leaves little doubt that the correction of the chemical potential

of the solute for solvation effects is in the right direction. If n is considered simply as an arbitrary parameter it takes on values of from about -1 to $+0.7$ to fit the observed diffusion data for cesium chloride over the entire concentration range. Identifying the most satisfactory value of n, $+0.6$, with an approximate estimate of the hydration number for cesium chloride is not unreasonable in the light of the known properties of this solute.

An untreated sample of cesium chloride from the A. D. McKay Co. was used for one unreported diffusion experiment and gave a value only 0.1% higher than the datum obtained with the purer sample. This represents agreement within the estimated experimental error.

Since it might not be immediately apparent why this optical work was not carried to lower concentrations a brief comment will be made on the nature of the results obtained by the Gouy method for electrolytes at low concentrations. Using the normal averaging methods for the Gouy experiment which assume the validity of Fick's second law in the form $(\partial c/\partial t) = D(\partial^2 c/\partial x^2)$, and that the refractive index is a linear function of concentration, values for the diffusion coefficient at low concentrations are obtained which are apparently higher than the correct values. Although the evidence for this statement is not overwhelming it is still fairly convincing.

In the first place it is generally agreed that for electrolyte solutions, the values of D obtained are not absolutely correct since D is not a constant, the flow of solute is not governed by the gradient of concentration, and Δn is not directly proportional to Δc. It is well known that these assumptions which are made in the usual application of the Gouy method are particularly inappropriate for dilute aqueous electrolyte solutions.

Gosting[3] has pointed out that the Gouy value for the diffusion coefficient of potassium chloride at $\bar{c} = 0.1$ is about 0.2% high. In this present work it was found that for concentrations lower than those for which data are reported higher values of D were obtained than would be predicted by appropriate extrapolation of the more reliable data. For just these rejected data the drift in C_t was greater than was acceptable. Typical values of the ratio $C_t^*/\bar{C}_t$ are plotted in Fig. 4. C_t^* is the value of C_t at $j = 1/2 j_m$ and $\bar{C}_t$ is the average value of C_t for the lower fringes $(j = 1$ to $j = 6)$. At high concentrations this ratio is negligibly greater than unity. At progressively lower concentrations this ratio decreases alarmingly. Consequently the values of D which were inconsistently high for very dilute solutions would be even higher if $\bar{C}_t$ for these determinations had been computed using data from a larger range of values of j.

In a recent publication Gosting and Onsager[23] have provided a method for the computation of diffusion coefficients from Gouy experiments involving only a small total number of fringes. Using their method the value of the diffusion coefficient for cesium chloride was estimated from an eleven fringe experiment at $\bar{c} = 0.00466$. The value of D obtained was 2.02×10^{-5} which is

(21) J. H. Wang, THIS JOURNAL, **74**, 1182 (1952); **74**, 1611 (1952).

(22) O. Lamm, J. Phys. Colloid Chem.. **51**, 1063 (1947).

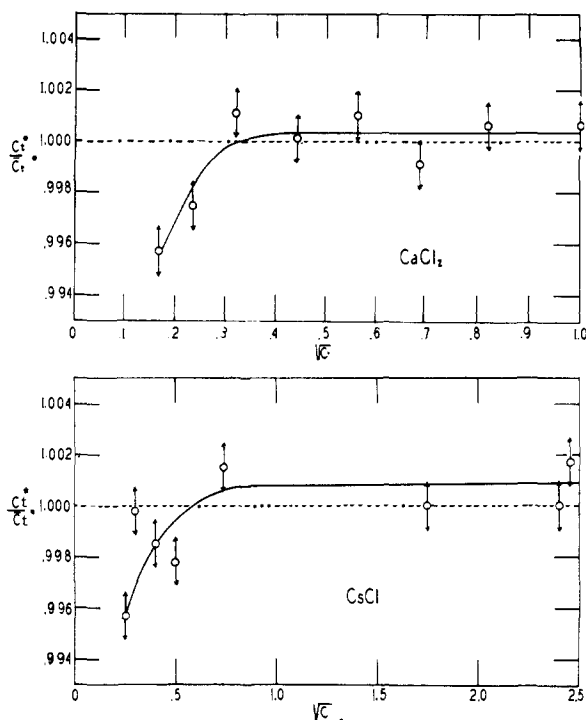(23) L. J. Gosting and L. Onsager, THIS JOURNAL, **74**, 6066 (1952).

Fig. 4.—Drift of C_t vs. $\sqrt{c}$.

about 1.8% above the Onsager–Fuoss prediction. At this concentration the results from the Harned experiment[7] and the extrapolation of the optical data would indicate that agreement with the theory is required. The best estimate of experimental error in the trial, which was large because of the small value of j_m, was about $\pm 0.6\%$. Once again the method as used appears to be giving high results.

Reference has been made earlier to experiments performed with a marker placed on the optic axis in such a way as to initially blur the lowest fringe. If the diffusion were normal and the maximum in the gradient of refractive index did not change with respect to the optic axis the lowest fringe should remain blurred. This was found to be the case for Gouy experiments using aqueous sucrose solutions. This observation is compatible with other information for this system.[15] For potassium chloride solutions at moderately high concentrations the movement was not too marked. However, at low concentrations of both potassium chloride and calcium chloride in water, the blurring of fringes was observed to move rapidly to higher values of j indicating a skewing of the gradient with time.

In summary both theory and experiment suggest that the Gouy technique employing the usual methods of computation will give incorrect results at low concentrations of electrolyte solutions. Experiments indicate that if the data so obtained have any utility they serve merely as an upper bound to the correct values.

The data which have been reported should be satisfactory for the calibration of other equipment to be used for diffusion measurements in concentrated solutions of 1–1 and 2–1 electrolytes. The values of $\Delta n/\Delta c$ available from this work are fairly reliable for calcium chloride up to $\bar{c} = 3.25$ and for cesium chloride up to $\bar{c} = 4.0$. At higher concentrations, the values are quite approximate since for these data Δc was obtained by subtraction of two large values of c which were determined by direct analysis.

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