[CONTRIBUTION NO. 1190 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

On the Theory of the Polarographic Diffusion Current. I. Diffusion of Small Amounts of Lead and Zinc Ions in Solutions of Various Supporting Electrolytes

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The tracer-diffusion coefficients[1] of Pb(II) ion in aqueous potassium chloride solutions of concentration from 0.02 to 4.0 F and in 0.1 F potassium chloride + 0.1 F hydrochloric acid solution were determined. Preliminary examination of the effect of gelatin on the tracer-diffusion coefficient of Pb(II) ion was made. Similar results were obtained on the diffusion of small amounts of Zn(II) ion in aqueous potassium chloride and nitrate solutions of different concentrations and in 1.0 F NH_4OH + 1.0 F NH_4Cl solution. The variation of the tracer-diffusion coefficient of Zn(II) ion with concentration of the supporting electrolyte in dilute solutions was compared with that predicted from the Onsager theory. The rapid increase of the tracer-diffusion coefficient of Zn(II) ion in potassium chloride solution with increasing salt concentration was interpreted on the basis of complex ion formation. The effect of gelatin on the tracer-diffusion coefficient of Zn(II) ion in 1 F NH_4OH + 1 F NH_4Cl solution was investigated. Finally, theoretical values of the "diffusion current constant" were calculated from the Ilkovič, Strehlow-von Stackelberg and Lingane–Loveridge equations, and compared with experimental data.

During the last decade considerable amount of evidences has been accumulated to show that at least in solutions containing gelatin the "diffusion current constant", $I = i_d/(cm^{2/3}t^{1/6})$, increases with $t^{1/6}m^{-1/3}$ when the latter is above a certain "critical value.[2]" By taking into account the curvature of the electrode surface, Lingane and Loveridge,[2] and independently, Strehlow and von Stackelberg[2] both arrived at the following modified Ilkovič equation

$$i_d = 607nD^{1/2}\,cm^{2/3}\,t^{1/6}\left(1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}}\right) \qquad (1)$$

Lingane and Loveridge assigned to the constant A the value of 39, whereas Strehlow and von Stackelberg estimated it to be 17. Both groups of investigators claimed that their own polarographic data agreed with their own value of the constant A better than the value estimated by the other group. Actually since the tracer-diffusion coefficient of the depolarizer ion is unknown in most cases, the agreement or disagreement found between the calculated and experimental values of $i_d/(cm^{2/3}t^{1/6})$ is quite uncertain. The purpose of the present research program is to determine the tracer-diffusion coefficient of several depolarizer ions in different solutions of supporting electrolytes, and to compare the values of $i_d/(cm^{2/3}t^{1/6})$ computed from them by means of different theories with the experimental values. It is the hope of this investigator that the tracer-diffusion coefficients reported in the present and subsequent articles of this series will be found useful in future studies on the theory of the polarographic diffusion current.

Apparently the theory of the polarographic diffusion current is still in its early stage of development. For example, Koutecký has recently[3] derived the new diffusion current equation

$$i_d = 607nD^{1/2}cm^{2/3}t^{1/6}\,(1 + 34x + 100x^2) \qquad (2)$$

where $x = D^{1/2}t^{1/6}m^{-1/3}$. But according to von Stackelberg,[4] the term $100x^2$ in equation 2 is negligible, the constant 34 should be changed to 17 because of what he called a "depletion effect," and the constant 607 should be changed to 619 because of an "enrichment effect." More definite evidences for the validity or invalidity of von Stackelberg's arguments are yet to be established. Furthermore since equation 1 was obtained by taking into consideration the effect of curvature of the dropping electrode surface, its validity should not be affected by the presence or absence of gelatin. Contrary to this expectation, Meites[5] has shown that in the absence of gelatin the values of $i_d/(cm^{2/3}t^{1/6})$ for several depolarizer ions remain constant and independent of the drop time.

Needless to say that before the theory of the polarographic diffusion current is more successfully worked out, we should be cautious in accepting tracer-diffusion coefficients evaluated from polarographic measurements.

Experimental

Preparation of Tracer.—Radioactive lead (Pb^{210}) prepared from the active deposit of aged radon tubes was used as tracer for Pb(II) ions. The radon tubes used were made of gold and were cut into small segments and leached with 1 ml. of 1 F nitric acid for 24 hr. To prepare the radioactive solution for diffusion measurements, a measured volume of this leach liquor was evaporated to dryness in a platinum crucible, the invisible residue was dissolved in aqueous potassium chloride solution of the desired concentration. All potassium chloride solutions used in the present work were made 0.002 F in Pb(II) to avoid adsorption errors and 0.0005 F in HCl (except those solutions containing gelatin) to prevent the hydrolysis of lead ion in dilute solutions. Zn^{65} was used as tracer for Zn(II) ions. This was obtained from the isotopes division of the U. S. Atomic Energy Commission at Oak Ridge, Tennessee.

Diffusion Measurement.—The improved capillary method[6] was used in the present work. The diffusion period of the present measurements varied from 3 to 4 days. For the measurements with Zn(II) ions, all the c_0- and c_{av}-samples were dried over anhydrous calcium chloride for at least 24 hours before being counted with a thin mica-window counter. For the measurements with Pb(II) ions, the c_{av}-samples obtained after each diffusion experiment were kept in a desiccator together with the c_0-samples for at least 40 days and then counted together. This waiting period is necessary for the lead samples for two reasons. Firstly, the β-radiation from Pb^{210} is too weak for direct counting and consequently we determine the amount of Pb^{210} by waiting until transient equilibrium is attained and then counting its daughter Bi^{210} (half-life = 5 days) which emits 1.2 Mev. β-radiation. The second and even more important reason is that the radioactive solution prepared according to the procedure described above actually contained both Pb^{210} and Bi^{210} (Po was not detected by the present

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[1] For the definition of tracer-diffusion coefficient, see J. H. Wang, THIS JOURNAL, **74**, 1182, 6317 (1952).

[2] See I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publ., Inc., New York, N. Y., 1952, Chap. IV.

[3] J. Koutecký, *Ceskoslovensky čas, fys.*, **2**, 117 (1952).

[4] M. von Stackelberg, *Z. Elektrochem.*, **57**, 338 (1953).

[5] L. Meites, THIS JOURNAL, **73**, 1581 (1951).

[6] J. H. Wang, C. V. Robinson and I. S. Edelman, *ibid.*, **75**, 466 (1953).

counting set-up and hence need not be considered here). In order to measure the tracer-diffusion of Pb^{210} alone, it was thus necessary to wait for at least 40 days (8 times the half-life of Bi^{210}) when practically all the Bi^{210} originally present in the samples had decayed into the harmless Po^{210} before counting. The assumption that the α-particles from Po^{210} were not detected by the present counting set-up was confirmed by the counting of these samples covered with aluminum absorbers. All the measurements were carried out at 25.00 +0.01°.

Adsorption Error and Its Elimination.—Although the concentration of the supporting electrolyte is above 0.02 F in all cases of the present work, there is the possibility that the Pb^{++} or Zn^{++} ions may be preferentially adsorbed from the electrolytic solution by the glass surface of the capillaries and consequently exhibit an "anomalous" tracer-diffusion coefficient. In fact it was found that when carrier-free Pb^{210} was used for the measurements, erroneous diffusion coefficients were obtained which cannot be reproduced with capillaries of different cross-sectional area and length. Even for the same capillary the measured diffusion coefficient varied with the length of diffusion time and previous treatment of the glass surface of the capillary. In the present work, this type of adsorption error was eliminated by adding enough inert lead salt in the solutions (both inside the capillaries and in the diffusion bath) to make the latter 0.002 F in Pb(II). Apparently when the concentration of Pb(II) in these solutions is 0.002 F or more, the fraction of Pb(II) adsorbed to the glass surface of each capillary is negligibly small as compared to that in the bulk of the solution. It was found that with these solutions containing inert Pb(II) the measured tracer-diffusion coefficients are reproducible and independent of the characteristics of the capillary, the diffusion time, and the concentration of Pb(II) provided that the latter is small as compared to that of the supporting electrolyte. For the same reason all solutions for the measurement of the diffusion of Zn(II) ions were made 0.005 F in Zn(II).

Results and Discussion

Diffusion of Small Amount of Pb(II) Ion in Aqueous KCl Solutions.—The results of these measurements are summarized in Table I. Each value listed in Table I is the average result of 6 measurements. All solutions listed in Table I are 0.002 F in Pb(II) and 0.0005 F in HCl and contain no gelatin. The temperature was kept at 25.00 ± 0.01° for all the measurements. These values of D in Table I are plotted *vs.* $\sqrt{c}$ of KCl in Fig. 1. The value of D at infinite dilution in Table I was calculated from conductive data with $\Lambda^\circ_{\mathrm{PbCl}_2} = 147.0$ given by Norman and Garrett,[7] and the accepted value of $\lambda^\circ_{\mathrm{Cl}^-} = 76.36$ by means of Nernst's formula.

TABLE I

TRACER DIFFUSION COEFFICIENTS OF Pb(II) ION IN KCl (AQ.) AT 25°

Concn. (formular wt./l.)	$D_{\mathrm{pb(II)}} \times 10^5$ (cm.²/sec.)	Concn. (formular wt./l.)	$D_{\mathrm{pb(II)}} \times 10^5$ (cm.²/sec.)
0.00	(0.940)	1.00	1.001 ± 0.005
.02	.941 ± 0.009	2.00	0.937 ± .012
.10	.970 ± .012	3.00	.859 ± .016
.25	.988 ± .010	4.00	.794 ± .018
.70	1.025 ± .012		

Figure 1 shows clearly that as the concentration of the supporting electrolyte decreases indefinitely, our measured value of the tracer-diffusion coefficient for Pb(II) ion approaches a value which is in agreement with Nernst's limiting value from conductance data. This agreement is an independent check on the reliability of the present results.

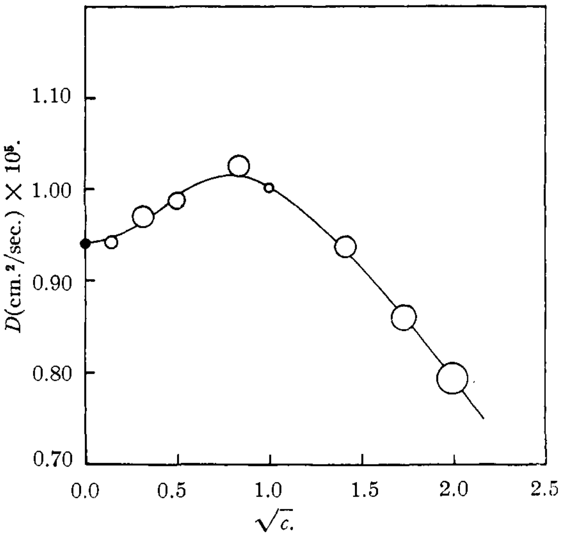

Fig. 1.—Tracer-diffusion coefficient of Pb(II) ion in aqueous potassium chloride solutions at 25°. The shaded point represents $D^\circ_{\mathrm{Pb}^{++}}$ at infinite dilution calculated from conductance data.

The change of D *vs.* $\sqrt{c}$ of the supporting electrolyte as depicted in Fig. 1 is considerably different from those found for Na^+, Cl^- and Ca^{++}.[1,8,9]

Fromherz,[10] in his study of the absorption spectra of lead halide solutions, has shown the existence of relatively high concentrations of PbCl^+ ions. There are also evidences[11] that in concentrated chloride solutions complex ions such as PbCl_3^- exist. In view of the existence of these complex ions, we may take Fig. 1 as suggesting that ions such as PbCl^+ have higher tracer-diffusion coefficient than the simple hydrated Pb^{++} ion in solutions of moderate concentrations. Similar observations have been made by von Stackelberg[4] in his studies with a linear stationary electrode on the diffusion of Pb(II) ion in KCl solutions containing 0.01% by weight of gelatin. However, von Stackelberg's diffusion coefficients may not be directly comparable to the present values because of the possible complications due to the presence of gelatin described in the following section.

Discussion on the Effect of Gelatin.—Since the majority of accurate data in the literature of polarography are for solutions containing 0.01% by weight of gelatin, it is necessary for us to examine the effect of gelatin on the measured tracer-diffusion coefficient. Determinations of the tracer-diffusion coefficient of Pb(II) ion in 1.0 F KCl solutions containing gelatin have been made in the present work. The results indicate that there is an appreciable decrease in the tracer-diffusion coefficient of Pb(II) ion in 1.0 F KCl solution as the gelatin content or the pH of the solution or both are raised. But since only a small portion of published polarographic diffusion current data have been reported for solutions of specific pH and since the nature of the gelatin-electrode surface interaction is not yet fully understood, there is at the moment little hope of making

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[7] J. W. Norman and A. B. Garrett, THIS JOURNAL, **69**, 110 (1947).

[8] J. H. Wang and S. Miller, *ibid.*, **74**, 1611 (1952).

[9] J. H. Wang, *ibid.*, **74**, 1612 (1952); *ibid.*, **75**, 1769 (1953).

[10] H. Fromherz, *Z. physik. Chem.*, **153**, 321 (1931); *ibid.*, 382 (1931).

[11] L. M. Koreman, *J. Gen. Chem. U.S.S.R.*, **16**, 157 (1946).

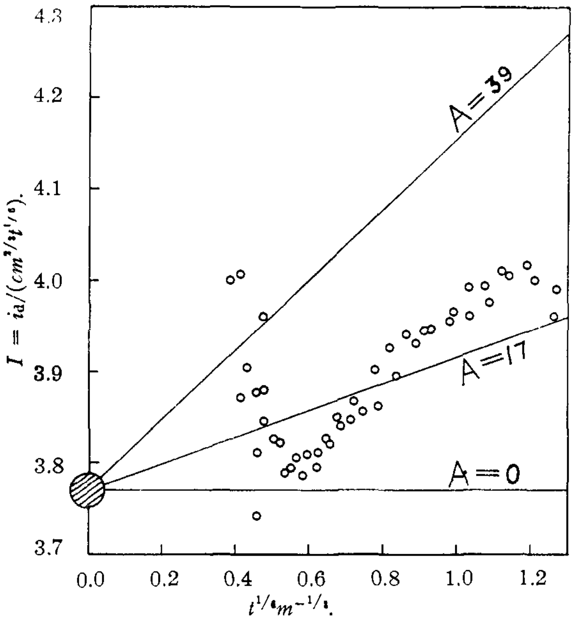

Fig. 2.—Comparison of equation (2) with polarographic diffusion current data for Pb(II) ion in 0.1 *F* HCl + 0.1 *F* KCl solution containing 0.009% by wt. of gelatin.[16]

quantitative application of this kind of data to polarography. However, these data do indicate that in salt solutions of unspecified *p*H the effect of gelatin on the tracer-diffusion coefficient of Pb(II) ion may not always be negligible.

Diffusion of Pb(II) Ion in 0.1 *F* KCl + 0.1 *F* HCl Solution.—For the purpose of comparison with the polarographic diffusion current data of Pb(II) in 0.1 *F* KCl + 0.1 *F* HCl solution reported by Meites,[12] the tracer-diffusion coefficient of Pb(II) in 0.1 *F* KCl + 0.1 *F* HCl solution without gelatin has been determined. The average result of nine such measurements is

$$D \times 10^5 = 0.963 \pm 0.011$$

Comparison of the Tracer-diffusion Coefficients of Pb(II) Ion with Polarographic Diffusion Current Data.—The variation of the "diffusion current constant," $i_d/(cm^{2/3}t^{1/6})$, with $t^{1/6}m^{-1/3}$ for Pb(II) in 1 *F* KCl + 0.01% gelatin solution has been studied by Lingane and Loveridge.[2] Strehlow, Mädrich and von Stackelberg[5] have made similar studies for Pb(II) in 0.1 *F* + 0.01% gelatin solution. Unfortunately neither group of workers used solutions of controlled *p*H. Thus because of the possible enrichment of gelatin due to adsorption near the electrode surface and because of the uncertainty in the *p*H of their solutions, it seems difficult for us to decide what values of *D* should be used for theoretical computation. On the other hand, the diffusion current data of Pb(II) ion in 0.1 *F* KCl + 0.1 *F* HCl + 0.009% gelatin solution obtained by Meites[16] should be useful for comparison with theoretical calculations based on the present measured value of *D* in the absence of gelatin, because in such highly acid solution we may assume that the fraction of Pb(II) bound to gelatin is negligible. Indeed, Tanford[13] found that the fraction of Pb(II) bound to bovine serum albumin decreases rapidly when the *p*H of the solution is lowered from 7 to 4, and that below *p*H 3 the "diffusion current constant" is independent of *p*H and is equal to that in the absence of albumin. Likewise if we assume that the fraction of Pb(II) bound to gelatin in 0.1 *F* KCl + 0.1 *F* HCl + 0.009% gelatin solution is negligible, we may use the above-measured tracer-diffusion coefficient of Pb(II) ion ($D \times 10^5 = 0.936 \pm 0.011$ cm.²/sec.) in this solution to calculate $i_d/(cm^{2/3}t^{1/6})$ by means of equation 1. The results are illustrated in Fig. 2 where the three straight lines represent equation 1 with the constant *A* equal to 0, 17 and 39, respectively.

In contrast to earlier statements,[2] Fig. 2 shows clearly that the deviations of the values of $I = i_d/(cm^{2/3}t^{1/6})$ calculated by means of equation 2 with $A = 39$ are much larger than those with $A = 17$. However the agreement between the latter values and experimental data cannot be considered as satisfactory. Further work in this direction is necessary before definite conclusions can be drawn.

Moreover, according to Meites[16] the "diffusion current constant" of Pb(II) ion in 0.1 *F* KCl + 0.1 *F* HCl solution in the absence of gelatin is independent of drop time and remains at the constant value of 3.992 ± 0.013 from $t = 2$ to $t = 10$ sec. But if we compute the "diffusion current constant" from the measured value of *D* by means of equation 1 with $A = 0$ we get $I = 3.77 \pm 0.02$ which is 5.5% lower than his experimental value. This discrepancy also seems to deserve further investigation.

Results on the Diffusion of Small Amount of Zn(II) Ion in Aqueous Solutions.—The tracer-diffusion coefficients of Zn(II) ion in aqueous potassium chloride solutions determined in the present work are listed in Table II. All solutions listed in Table II were made 0.005 *F* in Zn(II) and 0.0005 *F* in HCl. Each value of *D* listed in Table III is the average result of 6 measurements. The value of *D* at infinite dilution in Table I was calculated from conductance data by means of Nernst's formula with $\lambda^{\circ}_{Zn^{++}} = 53.1$.[14]

TABLE II

TRACER-DIFFUSION COEFFICIENTS OF Zn(II) ION IN KCl (AQ.) AT 25°

Concn. (formular wt./l.)	$D_{Zn(II)} \times 10^5$ (cm.²/sec.)	Concn. (formular wt./l.)	$D_{Zn(II)} \times 10^5$ (cm.²/sec.)
0.00	(0.71)	1.00	0.818 ± 0.008
.05	.714 ± 0.010	1.40	.878 ± .010
.10	.729 ± .010	2.00	.940 ± .010
.28	.736 ± .010	3.00	.971 ± .010
.60	.751 ± .013	4.00	.951 ± .015
.70	.788 ± .013		

The tracer-diffusion coefficients of Zn(II) ion in aqueous potassium nitrate solutions are listed in Table IV. All solutions listed in Table IV were made 0.005 *F* in Zn(II) and 0.0005 *F* in hydrogen ion concentration. Since these tracer-diffusion coefficients of Zn(II) ion in potassium nitrate solutions were determined merely for comparison with those in the chloride solutions instead of for

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[12] L. Meites, THIS JOURNAL, **73**, 3724 (1951).

[13] C. Tanford, *ibid.*, **74**, 211 (1952).

[14] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, Appendix A.

direct use in polarography, only three measurements were made for each solution listed in III. Consequently these tracer-diffusion coefficients are in general less accurate than those listed in Table **II**.

TABLE III

TRACER-DIFFUSION COEFFICIENTS OF Zn(II) ION IN KNO_3 (AQ.) AT 25°

Concn. (formular wt./l.)	$D_{Zn(II)} \times 10^6$ (cm.²/sec.)	Concn. (formular wt./l.)	$D_{Zn(II)} \times 10^5$ (cm.²/sec.)
0.00	(0.71)	1.00	0.730 ± 0.005
.05	.69 ± 0.014	1.50	.75 ± .01
.20	.69 ± .009	2.00	.74 ± .015
.50	.70 ± .015	2.50	.69 ± .015

Results of the measurements on the tracer-diffusion of Zn(II) ion in aqueous 1.0 F NH_4OH + 1.0 F NH_4Cl solutions with and without gelatin are listed in Table IV.

TABLE IV

TRACER-DIFFUSION COEFFICIENTS OF Zn(II) ION IN 1.0 F NH_4OH + 1.0 F NH_4Cl SOLUTIONS AT 25°

Concn. of gelatin (% by wt.)	No. of measurements	$D_{Zn(II)} \times 10^5$ (cm.²/sec.)
0.00	9	1.03 ± 0.015
.01	6	1.02 ± .015
.10	6	1.02 ± .015

Discussion of the Diffusion Data on Zn(II) Ion.—According to Onsager,[15] the tracer-diffusion coefficient, D_j, of ionic species j in a dilute solution containing other kinds of ions i may in appropriate units be written as

$$D_j = \frac{RT\lambda^0_j}{|Z_j|F^2} - \frac{\lambda^0_j|Z_j|F}{3N\mathfrak{D}} \times 2.694 \times 10^{16} \sqrt{\frac{4\pi}{\mathfrak{D}RT}}\,[1 - \sqrt{d(\omega_j)}]\,\sqrt{\sum_i c_i Z^2_i} \qquad (3)$$

where Z_i is the charge in electronic units and c_i the concentration in moles per liter of ion i, λ^0_j the limiting equivalent conductance of ion j, $\mathfrak{D}$ the dielectric constant of the solvent, k the Boltzmann constant, F the Faraday constant, T the absolute temperature and $d(\omega_j)$ and a function given by

$$d(\omega_j) = \frac{1}{\sum_i c_i Z^2_i} \sum \frac{c_i|Z_i|\lambda^0_i}{(\lambda^0_i/|Z_i|) + (\lambda^0_j/|Z_j|)} \qquad (4)$$

For the diffusion of tracer amount of ions of species 1 in salt solution containing ions of species 2 and 3, we have

$$c_1 \cong 0, \text{ and } c_2|Z_2| = c_3|Z_3| \qquad (5)$$

and hence (4) can be written as

$$d(\omega_1) = \frac{|Z_1|}{|Z_2| + |Z_3|}\left[\frac{|Z_2|\lambda^0_2}{|Z_2|\lambda^0_1 + |Z_1|\lambda^0_2} + \frac{|Z_3|\lambda^0_3}{|Z_3|\lambda^0_1 + |Z_1|\lambda^0_3}\right] \qquad (6)$$

For the tracer-diffusion of Zn(II) ion in aqueous KNO_3 solutions, if we take $\lambda^0_{Zn^{++}} = 53.1$, $\lambda^0_{K^+} = 73.52$, $\lambda_{NO_3^-} = 71.44$[14] we obtain from equations 3 and 6

$$D_{Zn^{++}} \times 10^5 = 0.71 - 0.32\sqrt{c} \qquad (7)$$

Values of D listed in Tables II and III are plotted *vs.* $\sqrt{c}$ in Fig. 3. The straight line in the dilute concentration region represents equation 7. It may be noticed from Fig. 3 that although the tracer-diffusion coefficient of Zn(II) ion in KNO_3 solutions (lower curve) seems to approach the Nernst limiting value from the above Onsager equation, there is considerable resemblance between this curve and those found for Na^+ and Ca^{++}.[1,8,9]

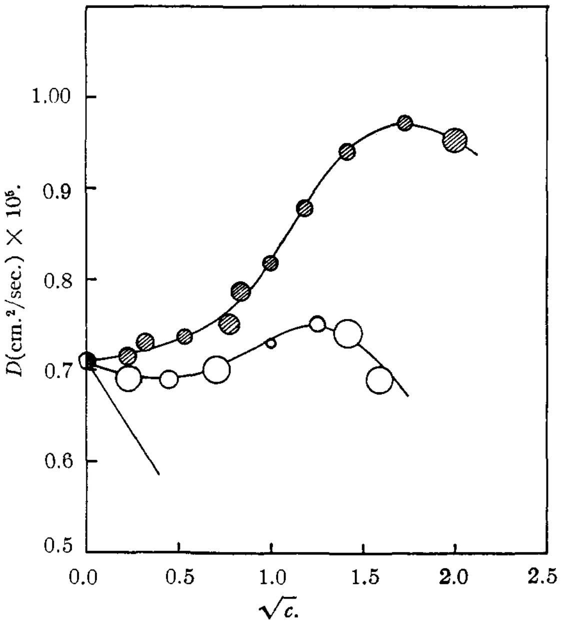

Fig. 3.—Tracer-diffusion coefficient of Zn(II) ion in aqueous potassium chloride (upper curve) and potassium nitrate (lower curve) solutions at 25°; ◑, $D^0_{Zn^{++}}$ at infinite dilution calculated from conductance data.

In contrast to this, Fig. 3 shows that the tracer-diffusion coefficient of Zn(II) ion in KCl solutions (upper curve) increases very rapidly with salt concentration and reaches a maximum value of 0.97 × 10^{-5} cm.²/sec. at about 3 F. Since the NO_3^- ion and the Cl^- ion have limiting equivalent conductances of equal order of magnitude (and hence approximately equal effective radii in solution), it does not seem possible to give even a qualitative explanation of the difference between the two curves in Fig. 1 on the basis of ionic interaction or the distortion of water structure alone. A possible explanation of this observed difference is that a considerable amount of complex ions such as $ZnCl^+$, etc., exist in the KCl solution and that these complex ions diffuse much faster than the simple hydrated Zn^{++} ion, causing the measured over-all tracer-diffusion coefficient of Zn(II) to increase with KCl concentration. If this is true we may interpret the lower curve in Fig. 1 as suggesting that relatively very little such complex ions exist in KNO_3 solutions at equivalent concentrations. Indeed there is a considerable amount of evidence in the literature to support this kind of view. For example, by comparing the measured activity coefficients of magnesium and zinc salts, Stokes and Levien[16] have shown that while there is a considerable amount of complex ion formation in zinc chloride solutions no detectable amount exist in

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[15] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

[16] R. H. Stokes and B. J. Levien, THIS JOURNAL, **68**, 333 (1946).

zinc nitrate solutions. The fact that the two curves in Fig. 1 converge to the same point at infinite dilution, which is in agreement with Nernst's limiting value, may be considered as an independent check on the reliability of the present measurements.

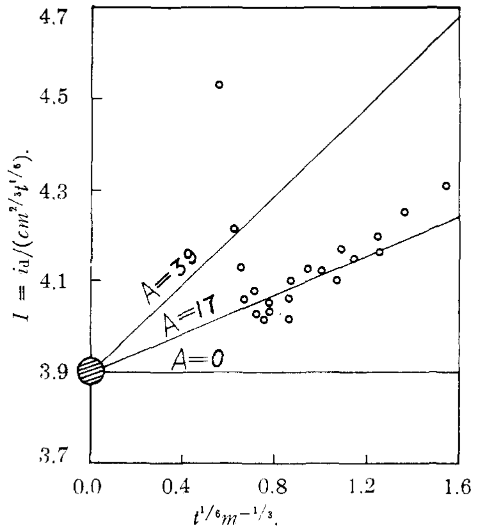

Fig. 4.—Comparison of equation 5 with polarographic diffusion current data for Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution containing 0.01% by wt. of gelatin.[9]

It may also be of interest to point out that the tracer-diffusion coefficient of Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution is 45% higher than that of Zn(II) ion at infinite dilution. This shows that the tetrammino-zinc ion, $Zn(NH_3)_4^{++}$, diffuses much faster than the simple hydrated Zn^{++} ion in solutions of equivalent concentrations.

Data in Table IV also show clearly that gelatin has no appreciable effect on the tracer-diffusion coefficient of Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution containing less than 0.1% of gelatin. This result is not unexpected for it is well-known that proteins in general combine with ions of the transition metals in a manner similar to the combination of these metal ions with ammonia and amino acids to form complex ions and metal–chelate compounds. Since in the solutions listed in Table V the concentrations of gelatin are negligibly small as compared to the great excess of competing ammonia molecules, the fraction of Zn(II) bound to gelatin in such solutions must be negligibly small. Consequently, the tracer-diffusion coefficient of Zn(II) ions in these solutions should be practically unaffected by the presence of gelatin.

Comparison of the Tracer-diffusion Coefficient of Zn(II) Ion with Polarographic Diffusion Current Data.—By using the tracer-diffusion coefficient of the Zn(II) ion in 1.0 *F* NH_4OH + 1.0 *F* NH_4Cl solution determined in the present work, the "diffusion current constant," $I = i_d/(cm^{2/3}t^{1/6})$, is calculated as linear functions of $t^{1/6}m^{-1/3}$. The calculated results are plotted in Fig. 4 as three straight lines corresponding to A = 0, 17 and 39, respectively. The experimental points in Fig. 4 are taken from the careful measurements of Lingane and Loveridge.[2] Examination of Fig. 4 shows clearly that the deviation of equation 1 with A = 39 or A = 0 from the experimental values is much larger than that with A = 17. But the agreement between the experimental points and equation 1 with A = 17 does not seem satisfactory enough for us to conclude definitely that the latter is valid. More work in this direction is desirable.

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New Haven, Connecticut

[Contribution from the Oak Ridge National Laboratory]

The Electrical Conductivity of Uranyl Sulfate in Aqueous Solution[1]

By Robert D. Brown, W. B. Bunger, William L. Marshall and C. H. Secoy

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The conductance of uranyl sulfate in aqueous solution has been determined at 0°, 25°, 50°, 90°, 125° and 200° in concentrations ranging from 10^{-4} to 7.28 *N*. A value of Λ^0_{25} = 131 ohms^{-1} cm.^{2} equiv.$^{-1}$ has been obtained when correction is made for the conductivity of H^+, $U_2O_5^{++}$ and HSO_4^- present from hydrolysis. This corresponds to a value for $\lambda^0_{UO_2^{++}}$ of 51 ohms^{-1} cm.^{2} equiv.$^{-1}$. The degree of dissociation of uranyl sulfate into simple ions at 25° has been determined from conductivity data and tentative values for the mean activity coefficients have been calculated. These values have been used to determine the dissociation constant. Conductometric titrations with sulfuric acid of uranyl sulfate solutions containing dissolved UO_3 show that UO_3 behaves as a weak base in aqueous solution and exhibits a strong buffering action.

The conductivity of uranyl sulfate in aqueous solution has been investigated at several temperatures and in various concentrations. The only previous work of this nature is that of Dittrich[2] and of Jones.[3] Each of these investigators measured the conductivity of uranyl sulfate at 25° in concentrations ranging from one equivalent per liter of solution to 1/4096 equivalent per liter. There is wide disagreement between the two sets of experimental data. The present results are in good agreement with the work of Dittrich.

Experimental

Materials.—A stock solution of uranyl sulfate, prepared by dissolving pure UO_2 in C.P. sulfuric acid and adjusting the uranium/sulfate ratio on the basis of analytical deter-

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(1) Presented before the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 15-19, 1953.

(2) C. Dittrich, *Z. physik. Chem.*, **29**, 449 (1899).

(3) H. C. Jones, Carnegie Inst. Wash. Publ. No. 170 (1912).