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Abstract

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DETERMINATION OF POLAROGRAPHIC DIFFUSION COEFFICIENTS BY MEANS OF A ROTATING DISK ELECTRODE

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In view of the fact that at present there are insufficiently reliable data on the so-called polarographic diffusion coefficients, i.e., diffusion coefficients in the presence of an excess of an indifferent electrolyte, the aim of the present investigation was to determine these diffusion coefficients by a reliable and comparatively simple method using a rotating electrode.

From the theory of convective diffusion at a rotating disk electrode, developed by V. G. Levich ([1]), the following expression for the diffusion coefficient follows:

$$D^{2/3} = \frac{1.62\, i\, \nu^{1/6}}{Fnc\sqrt{\omega}}, \tag{1}$$

where i is the current density, ω the angular velocity, c the concentration of the reduced ion in the bulk of the solution, ν the kinematic viscosity, and n the number of electrons participating in the reaction.

Using Levich' s equation, we calculated the diffusion coefficients of the ions Cd^{2+}, Tl^{+}, Pb^{2+}, and Zn^{2+}. The work was carried out with a copper amalgamated electrode in the form of a disk (diameter 4.997 ± 0.002 mm). Before the experiment the electrode was amalgamated for 24 hours, polished, washed with bidistillate, and again immersed in mercury for 2 hours. The electrode potential was measured relative to a normal calomel electrode by the usual potentiometric scheme. The experiments were conducted in a sealed cell in an atmosphere of hydrogen. The capacity of the cathode compartment of the cell was 80 ml; a platinum anode was placed in a side arm and separated from the cathode space by a stopcock. The determinations were carried out at $t = 25 \pm 0.1°$. The rotation speed of the electrode was usually 600-1000 rpm; in a number of experiments lower rotation speeds were used. All solutions were prepared from salts recrystallized twice or by dissolving pure metals. The supporting electrolyte salt was additionally purified for 4-5 hours on a platinum gauze in an atmosphere of hydrogen. As a rule, solutions with concentrations of 10^{-3}-10^{-4} mole/liter with respect to the reduced ion were used for the work.

Fig. 1

Figure 1: Fig. 1

The polarization curves for the ions Cd^{2+}, Tl^{+}, Pb^{+2}, and Zn^{2+}, constructed from the experimental data, have well-defined limiting-current plateaus, from which the magnitude of the limiting diffusion current was determined. As an example, Fig. 1 gives the polarization curve for Pb^{2+}. Over the entire range of measurements, proportionality was observed between the limiting current and the concentration of the reduced ion, and the experimental data showed good reproducibility. In the results of the measurements a correction was introduced for the background current, which did not exceed 1% of the total current.

Table 1 gives data on the diffusion coefficients of Cd^{2+}, Tl^{+}, Pb^{2+}, and Zn^{2+} in KCl supporting electrolyte, in comparison with data of other authors. The diffusion coefficients are expressed in $cm^2/sec \cdot 10^{-6}$.

It is evident from Table 1 that the diffusion coefficients determined with the aid of a rotating disk electrode are in good agreement with the diffusion coefficients determined by Stackelberg by the Cottrell method or calculated from the Ilković equation with the introduction of the corresponding semiempirical corrections (data marked with an asterisk); the discrepancy does not exceed 2%. The discrepancy with the data of the diffraction micromethod is somewhat greater.

Fig. 1. Polarization curve for the reduction of the lead ion in 1 N KCl supporting electrolyte,
$c = 3.27 \cdot 10^{-4}$ mol/l

For Zn^{2+} and Tl^{+} ions the diffusion coefficients were also determined over a wide range of supporting-electrolyte concentrations. For a more detailed comparison with the data obtained by Mischka ([5]) with the aid of the dropping electrode, the diffusion coefficients of zinc ions were determined in $KClO_3$ supporting electrolyte in the concentration range from 0.6 to 0.01 N.

Figure 2 presents the dependence of the diffusion coefficient of Zn^{2+} on the square root of the concentration of the supporting electrolyte ($KClO_3$). As is evident from Fig. 2, at higher $KClO_3$ concentrations the diffusion coefficient increases with increasing supporting-electrolyte concentration. A similar dependence of the diffusion coefficient on the supporting-electrolyte concentration was observed by Stackelberg, who explained the increase in the diffusion coefficient by complex formation.

At lower $KClO_3$ concentrations the value of the diffusion coefficient decreases with increasing supporting-electrolyte concentration, which is apparently connected with the manifestation of interionic forces. The points lying in the region of low supporting-electrolyte concentrations (beginning with 0.1 N $KClO_3$ and below) fall on a straight line which, when extrapolated to infinite dilution, gives

Fig. 2

Figure 2: Fig. 2

the value of the diffusion coefficient $D = 7.10 \cdot 10^{-6}$ cm^2/sec, in good agreement with the value calculated from the Nernst equation for infinitely dilute solutions from the mobility $\lambda = 52.8$, namely: $D = 7.04 \times 10^{-6}$ cm^2/sec. Comparing the data on diffusion coefficients obtained for zinc at the rotating electrode with the polarographic diffusion coefficients determined by Mischka, we see a substantial difference both in the numerical values of the diffusion coefficients (which are higher than those obtained by us) and in the course of the dependence of the diffusion coefficient on the supporting-electrolyte concentration. According to Mischka' s data, over the entire concentration range the diffusion coefficients increase with increasing concen-

Table 1

Ion	Normality of KCl supporting electrolyte	Rotating-electrode method	Nonstationary diffusion in a capillary ([2])	Diffraction micromethod ([3], [4])
Cd^{2+}	1	7.72	7.89	7.16
Cd^{2+}	0.1	7.07	7.16	6.58
Tl^{+}	1	15.28	15.67*	
Tl^{+}	0.1	17.52	17.44*	
Pb^{2+}	1	8.95	9.17	8.06
Pb^{2+}	0.1	8.60	8.69	8.12
Zn^{2+}	1	7.30	7.23*	7.54
Zn^{2+}	0.1	6.62	6.73*	6.41

Fig. 2. Dependence of the diffusion coefficient of Zn^{2+} on the square root of the supporting-electrolyte concentration ($KClO_3$). c is expressed in mol/l.

of the background. The extrapolation he carried out to infinite dilution therefore somewhat corrects the experimental errors; however, even with such extrapolation an obviously overestimated value is obtained, $D = 7.6 \cdot 10^{-6}$ cm^2/sec.

To verify the correctness of the assumption stated above concerning the influence of complex formation on the magnitude of the diffusion coefficient, the experiments were repeated with the ion Tl^{+}, which is less prone to complex formation than the ion Zn^{2+}. The diffusion coefficients were determined against a sodium perchlorate background. The measurements were extended into the region of high dilutions of the background, down to

Fig. 3. Dependence of the diffusion coefficient of Tl^{+} on the square root of the background concentration ($NaClO_4$). c is expressed in mol/l

Fig. 3. Dependence of the diffusion coefficient of Tl+ on the square root of the background concentration (NaClO4). c is expressed in mol/l

Figure 3: Fig. 3. Dependence of the diffusion coefficient of Tl+ on the square root of the background concentration (NaClO4). c is expressed in mol/l

a concentration $c = 2 \cdot 10^{-4}N$ at a Tl^+ concentration of $10^{-4}N$. The determinations were made at low electrode rotation speeds (130-150 rpm) in order to avoid large ohmic potential drops that distort the shape of the polarization curve. In the calculations, a correction for migration was introduced; namely, the diffusion current i_d was calculated from the observed current i by the equation *

$$i = i_d \left[1 + \frac{1}{4}\frac{c_0}{c} - \frac{1}{8}\left(\frac{c_0}{c}\right)^2\right],$$

where c_0 is the concentration of the discharging cation and c is the background concentration. In addition, a correction was introduced for the change in concentration during electrolysis, not exceeding 1%.

Figure 3 presents the dependence of the diffusion coefficient of thallium on the square root of the background concentration. As can be seen, in this case the diffusion coefficient continuously decreases as the background concentration increases. The first ten points lie well on a straight line; extrapolating this line to infinite dilution gives $D_e = 19.90 \cdot 10^{-6}$ cm^2/sec. The diffusion coefficient for the Tl^+ ion, calculated by the Nernst equation for infinitely dilute solutions from the mobility $\lambda = 74.7$([6]) at 25°, is equal to $19.94 \cdot 10^{-6}$ cm^2/sec.

The good agreement of the extrapolated values of the diffusion coefficients with the diffusion coefficients calculated by the Nernst equation indicates the suitability of the rotating-electrode method for the accurate determination of polarographic diffusion coefficients.

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* This equation is obtained from the formulas given in (7) by expansion in a series in c_0/c, retaining the first three terms.

Note: Figure translations are in progress. See original paper for figures.