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Diffusion Coefficients of Thallium(I) and Cadmium(II) Ions in Aqueous Nitrate Solutions Determined Chronoamperometrically with a Thin-walled Hanging Mercury Drop Electrode

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Synopsis. The diffusion coefficients (D) of Tl^+ in 0.1 and 0.5 mol dm^{-3} KNO_3 and of Cd^{2+} in 1.0 mol dm^{-3} KNO_3 in the temperature range 5 °C—35 °C are given with additional data including activation energies. $kT/D\eta$, where η is the viscosity of the nitrate solution, depends primarily on the diffusing species.

A stationary mercury drop electrode hanging from a thin-walled capillary (HMDE) was found to be one of the most suitable means for reliable electrochemical determination of diffusion coefficients.[1,2] This report gives the diffusion coefficients measured by the HMDE method for thallium(I) and cadmium(II) ions in aqueous nitrate solutions at several temperatures.

When the diffusion current I_d at a spherical electrode is plotted against $t^{-1/2}$, where t is the time of electrolysis, a straight line should be obtained.[3] From the slope and intercept of the plot, with the known size of the electrode, the diffusion coefficient (D) and the product nc are determined independently from a single chronoamperogram, n being the charge number of the electrode reaction and c the bulk concentration of the electroactive species. A comparison of the observed value, $(nc)_{\mathrm{obsd}}$, with the known value, $(nc)_{\mathrm{calcd}}$, provides a useful means of assessing the extent to which the obtained D is reliable.

The linearity of the I_d *vs.* $t^{-1/2}$ plot is a qualitative criterion of experimental validity, but it is not sufficient. An example is given to demonstrate the importance of the "*nc* test" in a reliable diffusion coefficient measurement. All the plots for $[Fe(CN)_6]^{3-}$ in 1.0 mol dm^{-3} KCl were quite linear even when the $(nc)_{\mathrm{obsd}}$ values were incorrect. The D values calculated from such linear plots were unreasonably high, scattered, and varied with the cyanoferrate concentration. Thus, besides the reproducible surface of known area with high hydrogen overvoltage, an essential advantage of the use of an appropriately designed HMDE is its ability to approximate spherical diffusion satisfactorily.

Experimental

In earlier experiments a balanced-type HMDE[1] was used. Later a micrometer-type HMDE assembly MCI AS01 (Mitsubishi Chemical Industries, Ltd.) was adopted, its capillary end being drawn to give a tip of *ca.* 0.2 mm in outer diameter, from which a mercury drop of 0.8 mm—1.0 mm diam. was produced. The size of the drop was read by the rotation of the micrometer, which had been calibrated by weighing the mercury delivered. For such an HMDE the total error due to the shielding and the non-sphericity is estimated to be 1% or less.[2] Constancy and uniformity of the solution temperature were essential to maintain stagnancy. It was controlled within ±(0.002—0.05) °C, the fluctuation being larger at lower and higher temperatures.

The potentiostat with a current follower was essentially the same as that used previously[1] except that the high-speed pen recorder was replaced by a digital memory device (Biomation, Transient Recorder, Model 802), and the current signals stored therein were printed out. This arrangement eliminated the positive deviation at $t<1.5$ s caused by the delay in response of the pen recorder.[1] Another type of positive error in current magnitude was observed at much shorter times, $t<20$ ms, attributable to the saturation of the current follower during the initial period of electrolysis. The difficulty was readily circumvented by appropriate adjustment in the gain

Table 1. Diffusion coefficients of thallium(I) ions in aqueous potassium nitrate solutions

Supporting electrolyte[a]	T / K	Number of runs	$10^{10}\,D$ / $m^2\,s^{-1}$	$\Delta^{\neq}E_\mathrm{A}$ / kJ mol^{-1}	$\lambda\exp\left(\frac{\Delta^{\neq}S}{2R}\right)$ / nm	$kT/D\eta$ / nm
0.1 M KNO_3	288	6	15.3±0.2	15.8±1.7	0.26±0.09	2.3
	293	6	17.5±0.2			2.3
	298	29	19.4±0.1			2.4
	303	6	21.6±0.2			2.4
	308	4	23.5±0.5			2.5
0.5 M KNO_3	278.20	6	11.5±0.4	16.6±1.3	0.30±0.08	2.3
	283.22	6	12.8±0.1			2.4
	288.24	6	14.5±0.2			2.5
	293.48	6	16.9±0.2			2.5
	298.52	6	18.7±0.3			2.5
	302.89	3	20.3±0.4			2.6
1.0 M KNO_3	298.19	11	17.3±0.2	—	—	2.7

The uncertainty is 95% confidence limit. a) M=mol dm^{-3}.

Table 2. Diffusion coefficients of cadmium(II) ions in aqueous nitrate solutions

Supporting electrolyte[a)]	T / K	Number of runs	$10^{10}\,D$ / $\mathrm{m^2\,s^{-1}}$	$\Delta^{\neq}E_A$ / kJ mol^{-1}	$\lambda\exp\left(\frac{\Delta^{\neq}S}{2R}\right)$ / nm	$kT/D\eta$ / nm
0.1 M KNO_3	298.35	4	7.40±0.03	—	—	6.3
1.0 M KNO_3	278.12	8	4.18±0.03	18.5±0.9	0.27±0.05	6.4
	283.17	12	4.89±0.03			6.6
	288.25	13	5.67±0.06			6.5
	295.17	10	6.76±0.08			6.3
	298.15	3	7.31±0.10			6.4
	303.01	6	8.26±0.08			6.3
	308.34	7	9.07±0.05			6.5
1.0 M $NaNO_3$	298.01	12	6.71±0.05	—	—	6.4

The uncertainty is 95% confidence limit. a) M=mol dm^{-3}.

of the follower. The whole system is capable of recording diffusion currents from a few milliseconds. The time range 100 ms—10 s was used in the present set of experiments.

Preparation of the reagents and solutions and the procedure of chronoamperometry have been described in detail.1) The chronoamperograms were first examined for linearity against $t^{-1/2}$. The deviating points that reflected the convective disturbance of diffusion layer at longer times1) were omitted, and the values of $(nc)_{\mathrm{obsd}}$ were calculated for each set of measurements. If the mean value of $(nc)_{\mathrm{obsd}}$ agreed with $(nc)_{\mathrm{calcd}}$ within the limits of experimental error for 95% confidence, the value of D that best reproduced the observed chronoamperogram was obtained by the least-squares method by using the value of $(nc)_{\mathrm{calcd}}$.

Results and Discussion

The diffusion coefficients for thallium(I) and cadmium (II) ions in nitrate solutions (Tables 1 and 2, respectively) were critically selected from the data obtained in the authors' laboratory since 1970. The values for 0.1 mol dm^{-3} KNO_3 at 25 °C supersede the corresponding ones presented earlier.1)

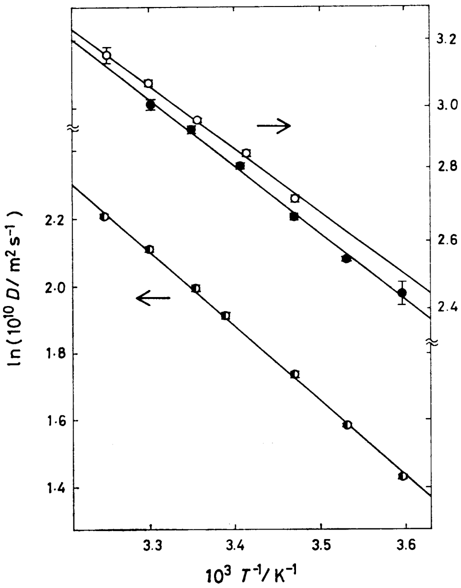

Fig. 1. Arrhenius plots of D.
○: Tl^+ in 0.1 mol dm^{-3} KNO_3, ●: Tl^+ in 0.5 mol dm^{-3} KNO_3, ◐: Cd^{2+} in 1.0 mol dm^{-3} KNO_3. The error bars correspond to the uncertainty at 95% confidence.

The Arrhenius plots of the three systems gave curves slightly convex upward (Fig. 1). The average experimental activation energies of diffusion, $\Delta^{\neq}E_A$, are calculated by linearly approximating the curved plots. It is noted that these figures are comparable to 16.7 kJ mol^{-1} of the diffusion of water molecules in 0.1 mol dm^{-3} KNO_3.4)

According to Eyring's absolute rate theory, the intercept of the Arrhenius plot is related to $\lambda\exp(\Delta^{\neq}S/2R)$, where $\Delta^{\neq}S$ is the entropy of activation of diffusion, λ is the distance between two successive equilibrium positions of the diffusing particle in the solution, and R the gas constant.5) The values for this quantity falling around 0.3 nm suggest that $\Delta^{\neq}S$ cannot differ appreciably from zero. A similar value, 0.34 nm, is calculated from the data4) for the diffusion of water in 0.1 mol dm^{-3} KNO_3.

The viscosity, η, of the supporting electrolyte solutions was estimated by inter- and extrapolation of the tabulated data,6) and $kT/D\eta$ are calculated. The result seems to depend primarily on the diffusing species, being fairly insensitive to the temperature and concentration of the supporting electrolyte, as might be expected from the Einstein-Stokes relation or Eyring's theory.5)

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