1950 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (8), 1950—1953 (1977) [Vol. 50, No. 8

Semiintegral Electroanalysis in the Absence of Supporting Electrolyte

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(Received January 24, 1977)

The limiting semiintegral of the current which flows when a stationary electrode is progressively polarized in the presence of electroactive species has been investigated under the condition of no supporting electrolyte present in the solution. The semiintegral, $m(t)$, of the current, $i(t)$, is defined by

$$m(t) = \frac{\mathrm{d}^{-1/2}}{\mathrm{d}t^{-1/2}}i(t) = \frac{1}{\pi^{1/2}}\int_0^t \frac{i(\lambda)}{(t-\lambda)^{1/2}}\mathrm{d}\lambda.$$

The electroreduction of a number of heavy metal ions has been studied at a mercury drop electrode and it was found that the limiting semiintegral is larger than that observed with excess supporting electrolyte present. The finding is in agreement with a simple theory which considers both diffusion and migration mass transfer processes. The factor by which the limiting semiintegral increases has been shown to depend on the diffusion coefficients and charge numbers of the cation and anion.

Basic theory of the new electroanalytical method "semiintegral electroanalysis" has been presented and experimentally verified in previous papers.[1,2] It has been also demonstrated[1,3] that semiintegral electroanalysis has the merit of being completely independent of the signal under typical electroanalytical conditions. The independence of the limiting semiintegral of current, $m(\tau)$, from the form of the applied potential signal permits a large resistance to be present in the solution without impairment of the analysis, so that semiintegral electroanalysis can tolerate very low or even zero supporting electrolyte concentrations. Existing theory,[1] however, is based on the assumption that the mass transport is by diffusion only, whereas migration must also be admitted if the supporting electrolyte concentration is not in excess. In this article we show both theoretically and experimentally that the proportionality between $m(\tau)$ and the electroactive concentration is maintained even in the total absence of supporting electrolyte. The constant of proportionality is, however, different from the excess supporting electrolyte case. The implication of these findings for semiintegral electroanalysis in such fresh waters as lakes and rivers is clear.

Theory

The exact treatment of any electroanalytical experiment under conditions in which both migration and diffusion are important is inordinately difficult. Nevertheless, there have been numerous attempts to overcome this difficulty,[4-10] especially in the context of chronopotentiometry. Some of these treatments have been very sophisticated and, in comparison, our present treatment is naive.

Consider a plane indicator electrode immersed in an unstirred solution containing only two ions: those of species O (cation) and P (anion), without any supporting electrolyte. Only the species O is reduced by the z_O electron reaction,

$$\mathrm{O(soln)} + z_\mathrm{O}e^- \longrightarrow \mathrm{R(solid\ or\ amalgam)} \tag{1}$$

to the initially-absent species R, which is uncharged. The solution is assumed to extend to infinity in the direction perpendicular to the electrode. According to the established theories,[11-13] the rate of change in concentration of O at a distance x from the electrode surface at a time t is presented by

$$\frac{\partial C_\mathrm{O}(x,t)}{\partial t} = -\frac{\partial J_\mathrm{O}(x,t)}{\partial x} = \frac{D_\mathrm{O}D_\mathrm{P}[z_\mathrm{O}-z_\mathrm{P}]}{[z_\mathrm{O}D_\mathrm{O}-z_\mathrm{P}D_\mathrm{P}]}\frac{\partial^2 C_\mathrm{O}(x,t)}{\partial x^2}, \tag{2}$$

where C is the concentration, J is the flux, D is the diffusion coefficient, z is the charge number, and the subscripts represent the species concerned. The flux of O is given by the following equation:

$$J_\mathrm{O}(x,t) = -\frac{1}{[z_\mathrm{O}D_\mathrm{O}-z_\mathrm{P}D_\mathrm{P}]} \times \left\{D_\mathrm{O}D_\mathrm{P}[z_\mathrm{O}-z_\mathrm{P}]\frac{\partial C_\mathrm{O}(x,t)}{\partial x} + \frac{D_\mathrm{O}i(t)}{AF}\right\}, \tag{3}$$

where $i(t)$ is the faradaic current at a time t, A is the electrode area, and F is the Faraday constant.

Equation 2 is identical with Fick's second law except that the diffusion coefficient is replaced by the composite constant $D_\mathrm{O}D_\mathrm{P}(z_\mathrm{O}-z_\mathrm{P})/(z_\mathrm{O}D_\mathrm{O}-z_\mathrm{P}D_\mathrm{P})$. Accordingly, when combined with the initial condition,

$$C_\mathrm{O}(x,0) = C_\mathrm{O} = \mathrm{constant}, \tag{4}$$

corresponding to a uniform O concentration before electrolysis, and the boundary condition,

$$C_\mathrm{O}(\infty,t) = C_\mathrm{O}, \tag{5}$$

appropriate to semiinfinite conditions, the equation

$$\frac{\partial^{1/2}}{\partial t^{1/2}}[C_\mathrm{O}(x,t)-C_\mathrm{O}] = -\sqrt{\frac{D_\mathrm{O}D_\mathrm{P}(z_\mathrm{O}-z_\mathrm{P})}{z_\mathrm{O}D_\mathrm{O}-z_\mathrm{P}D_\mathrm{P}}}\frac{\partial C_\mathrm{O}(x,t)}{\partial x} \tag{6}$$

may be derived in a strictly analogous way to that used[14] in establishing the theory of semiintegral electroanalysis with excess supporting electrolyte. $\partial^{1/2}/\partial t^{1/2}$ is the partial semidifferentiation operator with respect to t and the semidifferentiation operator, $\mathrm{d}^{1/2}/\mathrm{d}t^{1/2}$, is defined by

$$\frac{\mathrm{d}^{1/2}}{\mathrm{d}t^{1/2}}f(t) = \frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{1}{\pi^{1/2}}\int_0^t \frac{f(\lambda)}{(t-\lambda)^{1/2}}\mathrm{d}\lambda\right].$$

Since only the species O reacts at the electrode, the

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fluxes of each species at the electrode surface are given by

$$J_O(0,t) = \frac{-i(t)}{z_O AF}, \tag{7}$$

and

$$J_P(0,t) = 0. \tag{8}$$

The combination of Eqs. 3, 6, and 7 produces

$$\frac{\partial^{1/2}}{\partial t^{1/2}}[C_O(0,t)-C_O] = \frac{z_P\sqrt{D_P}i(t)}{z_O AF\sqrt{D_O}\sqrt{z_O - z_P}\sqrt{z_O D_O - z_P D_P}}. \tag{9}$$

Semiintegrating Eq. 9 and rearranging terms, we obtain

$$m(t) = z_O AF\sqrt{D_O}[C_O(0,t)-C_O]\frac{\sqrt{z_O - z_P}\sqrt{z_O D_O - z_P D_P}}{z_P\sqrt{D_P}}. \tag{10}$$

The limiting semiintegral of current at the time τ, when the concentration of O at the electrode surface is equal to zero, is

$$m(\tau) = z_O AF\sqrt{D_O}C_O\left[\frac{\sqrt{z_O - z_P}\sqrt{z_O D_O - z_P D_P}}{-z_P\sqrt{D_P}}\right] \tag{11}$$

$$= m(\tau)_{\text{xse}}\sqrt{\frac{D_O}{D_{OC}}}\sqrt{1-\frac{z_O}{z_P}}\sqrt{1-\frac{z_O D_O}{z_P D_P}}, \tag{12}$$

where $m(\tau)_{\text{xse}}$ and D_{OC} are the semiintegral of current at the time τ and the diffusion coefficient of O respectively in the solution containing excess supporting electrolyte. Equation 11 is the basic relationship between the limiting semiintegral and concentration for this method in the absence of supporting electrolyte. Equation 11 will be verified by testing experimentally Eq. 12 in the remainder of this paper.

Experimental

The salts $Cd(NO_3)_2$, $CdCl_2$, $CdSO_4$, $Ni(NO_3)_2$, $NiCl_2$ $NiSO_4$, $Cu(NO_3)_2$, $CuSO_4$, $Cu(CH_3COO)_2$, $Zn(NO_3)_2$, $ZnSO_4$, $Pb(NO_3)_2$, $TlNO_3$, and $InCl_3$ were used as solutes. The concentration of solutions for the present study was 1.00 mmol/l or 5.00 mmol/l. In order to measure limiting semiintegral in excess supporting electrolyte, 100 mmol/l or 200 mmol/l KNO_3 was used as a supporting electrolyte. The electrolytic solutions were deoxygenated by bubbling argon gas. The reagents were generally of laboratory grade or in some cases analytical grade. The distilled water for solutions and cleaning of glassware was further deionized by ion exchange resin, the conductivity corresponding to less than 0.02 ppm NaCl.

Three electrodes, cell and instrumentation were substantially the same as previously reported.[1,2] Simple or capped ramp signals were applied to a hanging mercury drop electrode *vs.* a saturated calomel electrode by using a mercury pool as a counter electrode. All the experimental work was carried out at room temperature (≈22°C).

In polarography, difficulties frequently arise from the presence of polarographic maxima. Similar difficulties have been experienced in the present study. The maxima were suppressed, whenever possible, by prepolarizing the hanging mercury drop electrode at the initial (equilibrium) potential for a few minutes. In more severe cases the addition of small quantities of methyl red or a freshly prepared solution of gelatin (0.2%) was required. In general it was found that the maxima were more pronounced in solutions without supporting electrolyte, possibly because the current density is less uniform.

Results and Discussion

As typical examples of investigated species, Figs. 1 and 2 show the neopolarograms of 1.00 mmol/l $Cd(NO_3)_2$ and $TlNO_3$, respectively, in the absence of supporting electrolyte together with those in excess supporting electrolyte. The "neopolarograms" are the graphs *vs.* potential, E, of the semiintegral of current, m. The value m is measurable in the unit[1] of A $s^{1/2}$ or C $s^{-1/2}$. The shape of neopolarograms in the absence of supporting electrolyte is apparently deformed by the potential drop resulting from a large resistance present in solution, however the semiintegral levels off at a plateau. The upward slope of the plateau is more pronounced than in the presence of supporting electrolyte.[15] The limiting semiintegral values were determined by the empirical procedure illustrated by the dashed lines in curve I of Fig. 1.

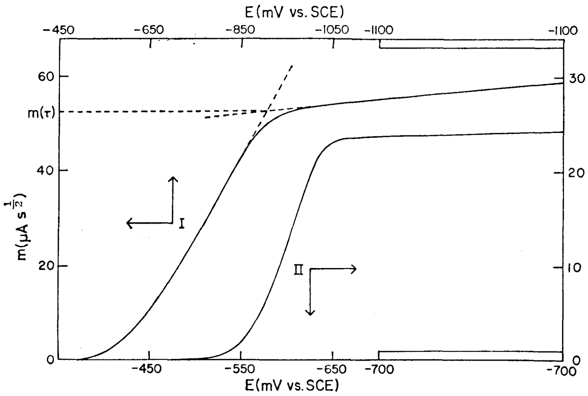

Fig. 1. Neopolarograms of 1.00 mmol/l $Cd(NO_3)_2$ in the absence and presence of supporting electrolyte. Electrode area: 4.69×10^{-2} cm², Scan rate: 100 mV/s, supporting electrolyte: I none, II 100 mmol/l KNO_3.

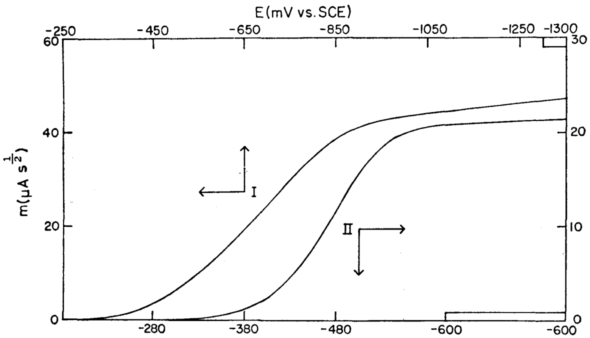

Fig. 2. Neopolarograms of 1.00 mmol/l $TlNO_3$ in the absence and presence of supporting electrolyte. Conditions as in Fig. 1.

In order to verify Eq. 12 the limiting semiintegrals in both the absence of supporting electrolyte and the presence of excess supporting electrolyte were measured for various salts of uni-, bi-, and ter-valent cations, and their ratios are listed in Table 1. The limiting semi-

Table 1. $m(\tau)/m(\tau)_{xse}$ ratios for various salts
Salt concentration: 1.00 mmol/l, electrode area: 4.69×10^{-2} cm².

Salt	Concn of KNO_3 (mmol/l)	$m(\tau)$ (μA s$^{1/2}$)	$m(\tau)/m(\tau)_{xse}$ Exptl	Theor.
$Cd(NO_3)_2$	0	57.2	2.49	2.34
	100	23.0		
$CdCl_2$	0	46.3	2.20	2.31
	100	21.0		
$CdSO_4$	0	39.2	1.74	1.87
	100	22.5		
$Ni(NO_3)_2$	0	57.0	2.33	2.28
	100	24.5		
$NiCl_2$	0	54.5	2.36	2.25
	100	23.1		
$NiSO_4$	0	42.8	1.83	1.82
	100	23.4		
$Cu(NO_3)_2$	0	49.1	2.00	2.33
	100	24.6		
$CuSO_4$	0	35.0	1.50	1.86
	200	23.4		
$Cu(CH_3COO)_2$	0	58.3	2.48	2.69
	200	23.5		
$Zn(NO_3)_2$	0	51.5	2.17	2.43
	200	23.7		
$ZnSO_4$	0	38.7	1.65	1.94
	200	23.5		
$TlNO_3$	0	42.0	2.06	2.12
	100	20.4		
$Pb(NO_3)_2$	0	66.7	2.56	2.68
	100	26.1		
$InCl_3$	0	61.1	1.97	2.80
	100	31.0		

integral in the absence of supporting electrolyte was, in general, about twice larger than that observed in the excess supporting electrolyte, the ratio $m(\tau)/m(\tau)_{xse}$ being the largest for $Pb(NO_3)_2$ and the smallest for $CuSO_4$.

Table 2. Diffusion coefficients at infinite dilution at 25 °C[16)]

Cation	$D\times10^6$ (cm²/s)	Anion	$D\times10^6$ (cm²/s)
K^+	19.8	Cl^-	20.3
Tl^+	20.0	NO_3^-	19.2
Pb^{2+}	9.8	CH_3COO^-	10.9
Cd^{2+}	7.2	SO_4^{2-}	10.8
Zn^{2+}	7.2		
Cu^{2+}	7.2		
Ni^{2+}	6.9		
In^{3+}	5.6		

Table 2 shows literature values[16)] of diffusion coefficients (except the case of In^{3+}) for various ions under the condition of infinite dilution at 25 °C. For the case of In^{3+}, the known limiting equivalent conductances of ions λ°,[17)] of ter-valent lanthanide cations were plotted against the crystal ionic radii, r.[18)] There is a linear relationship between the two quantities as shown in Fig. 3. The limiting equivalent conductance of 1/3 In^{3+} was estimated to be 63.5 cm² Ω^{-1} equiv^{-1} from the line of Fig. 3 and the ionic radius 0.81 Å,[18)] whence the diffusion coefficient at infinite dilution of In^{3+} was calculated from the Nernst-Einstein equation. Table 3 shows the diffusion coefficients of metal ions in excess supporting electrolyte from the literature[19)] together with the values of Cu^{2+}, Ni^{2+}, and In^{3+} evaluated by semiintegral electroanalysis. The theoretical $m(\tau)/m(\tau)_{xse}$ ratios were calculated from Eq. 12 by using the diffusion coefficients in Tables 2 and 3, and are listed in Table 1. Apart from $InCl_3$, the theoretical ratios generally compare well with the values obtained by experiment, though the theoretical ratios are usually slightly larger than the experimental values. This tendency possibly suggests some existence of hydrolysis reaction such as

$$Cu^{2+} + H_2O \rightleftarrows CuOH^+ + H^+,$$

$$CuOH^+ + 2e^- \rightleftarrows Cu(amalgam) + OH^-.$$

In the case of $InCl_3$, the experimental ratio is much smaller than the theoretical value. We believe this result to be due to a hydrolysis reaction of In^{3+}, because 10 mmol/l aqueous solutions of $InCl_3$ began to produce white suspensions in the originally clear solutions a few hours after preparing at a room temperature. The formation rate was accelerated on heating, but the suspension disappeared on adding acid. Another possible cause is the presence of complex ions such as $[InCl]^{2+}$ and $[InCl_2]^+$ formed with chloride ion, but this explanation is unlikely because a similar $m(\tau)/m(\tau)_{xse}$

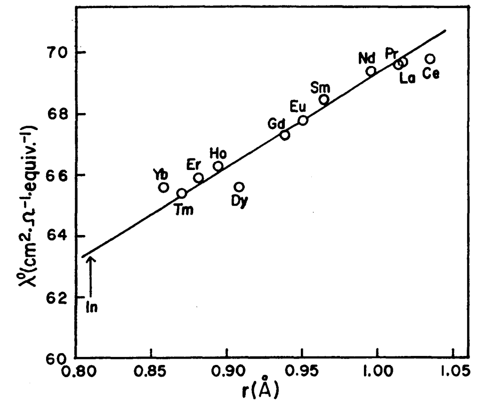

Fig. 3. Relationship between limiting equivalent ionic conductances and crystal ionic radii for ter-valent cations at 25 °C.

Table 3. Diffusion coefficients in excess supporting electrolyte at 25 °C[19)]

Ion	Supporting electrolyte		$D\times10^6$ (cm²/s)
Tl^+	0.1 mol/l	KNO_3	18.2
Pb^{2+}	0.1 mol/l	KNO_3	8.28
Cd^{2+}	0.1 mol/l	KNO_3	6.90
Zn^{2+}	0.1 mol/l	KNO_3	6.38
Cu^{2+}	0.1—0.2 mol/l	KNO_3	6.94[a)]
Ni^{2+}	0.1 mol/l	KNO_3	6.86[a)]
In^{3+}	0.1 mol/l	KNO_3	5.23[a)]

a) Value evaluated by semiintegral electroanalysis.

ratio was observed in the case of $In(NO_3)_3$ solute.

Table 1 shows that Eq. 12 applies whether the reduction product is solid or amalgam, because most metals among investigated species are soluble in a mercury electrode but the metallic nickel does not form an amalgam.

In the classical polarography using a dropping mercury electrode, Lingane and Kolthoff[20] obtain the following relation between the initial limiting current, i_l, without supporting electrolyte present and the diffusion current, i_d, in an excess of indifferent electrolyte

$$\frac{i_l}{i_d} = \sqrt{\frac{D_O D_P[z_O - z_P]}{D_{OC}[z_O D_O - z_P D_P]}}\left[\frac{1}{1 - T_O}\right] \tag{13}$$

for cation reductions, where T_O is the transference number of O. It should be realized by the comparison between Eqs. 12 and 13 that $m(\tau)/m(\tau)_{xse}$ ratio observed in this semiintegral electroanalysis at higher scan rate of potential is identical with i_l/i_d ratio in classical polarography.

TABLE 4. $m(\tau)/m(\tau)_{xse}$ RATIOS AT DIFFERENT SCAN RATES OF POTENTIAL

Conditions: Electroactive species: 1.00 mmol/l $CdCl_2$, electrode area: 4.69×10^{-2} cm².

		$m(\tau)$ (μA s$^{1/2}$) Scan rate (mV/s) 50	100	200	500	
Concn of KNO_3 (mmol/l)	100	20.8	21.1	21.0	21.1	
	0	46.6	45.8	46.5	46.2	
$\frac{m(\tau)}{m(\tau)_{xse}}$ Exptl		2.23	2.17	2.22	2.19	2.21(av.)
Theor.		2.31	2.31	2.31	2.31	

TABLE 5. $m(\tau)/m(\tau)_{xse}$ RATIOS AT DIFFERENT CONCENTRATIONS OF ELECTROACTIVE SPECIES

Condition: Electrode area: 4.69×10^{-2} cm².

		$m(\tau)$ (μA s$^{1/2}$)			
Species		$Cd(NO_3)_2$		$TlNO_3$	
Concn of species (mmol/l)		1.00	5.00	1.00	5.00
Concn of KNO_3 (mmol/l)	100	23.0	120	20.4	95.7
	0	57.2	273	42.0	210
$\frac{m(\tau)}{m(\tau)_{xse}}$ Exptl		2.49	2.28	2.06	2.19
Theor.		2.34	2.34	2.12	2.12

The dependencies of $m(\tau)/m(\tau)_{xse}$ ratio on the scan rate for $CdCl_2$ and on concentration for $Cd(NO_3)_2$ and $TlNO_3$ are tested in Tables 4 and 5, respectively. The ratio is independent of scan rate and concentration as the theory predicts.

Thus the applicability of semiintegral electroanalysis in the absence of supporting electrolyte has been demonstrated. It is found that the sensitivity of detection is about twice as great as that with excess supporting electrolyte, but is dependent on the nature of the counter ion.

The financial support of the National Research Council of Canada is gratefully acknowledged.

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