THEORY OF SECOND- AND THIRD-ORDER RECIPROCAL DERIVATIVE CHRONOPOTENTIOMETRY FOR A REVERSIBLE REACTION

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Equations describing the second- and third-order reciprocal derivative chronopotentiometric curves, dt/dE *vs* E are deduced for a reversible reaction. Theoretical calculated values are verified experimentally.

Key words: Reciprocal derivative chronopotentiometry; Reversible reaction; Polarography; Hanging mercury drop electrode; Electrochemistry.

Reciprocal derivative chronopotentiometry (RDCP) is a novel and sensitive electroanalytical approach developed in recent years[1]. In this method, a constant reducing current is passed through the electrolytic cell and the dt/dE–E chronopotentiogram is recorded. A series of variations of this method has also been proposed, such as adsorption chronopotentiometry[2], constant current stripping chronopotentiometry[3], reciprocal derivative potentiometric stripping analysis[4] and reciprocal a.c. oscillochronopotentiometry[5]. They have been used in trace and ultratrace analysis. The distinct advantages of the reciprocal technique are: (i) the analytical signal can be greatly enhanced by reducing the charging current[6]; (ii) the resolution and analytical sensitivity are much better than in ordinary linear sweep voltammetry, with the limit of detection down to 10^{-7} mol l^{-1}.

Higher-order derivative is a very promising technique for enhancing the signal and improving analytical sensitivity[7,8]. Jin *et al.* have established the theory of second- and third-order differential adsorption chronopotentiometry[9]. Ruan *et al.* have studied the second-order RDCP, but they only gave a very rough verification of some main conclusions; detailed discussion and equation of the third-order RDCP are still lacking[10]. In this paper, we systematically studied the second- and third-order RDCP. Equations describing the d^2t/dE^2–E and d^3t/dE^3–E curves are presented and confirmed experimentally by using the $Cd^{2+}/Cd(Hg)$ reversible reaction at a hanging mercury drop electrode (HMDE) by the cubic spline interpolation method.

THEORETICAL

The assumptions used in this study are the same as those described before for the conventional chronopotentiometry: semi-infinite linear diffusion, unstirred solution and excess of inert electrolyte. We assume a reversible reduction of Ox, present in an initial concentration c_0^*, with a constant reduction current I_o, Ox + ne → Red. The change of electrode potential E *vs* time can be expressed as:

$$E = E' + (RT/nF)\ln\left[\left(\tau^{1/2} - t^{1/2}\right)/t^{1/2}\right], \qquad (1)$$

where $E' = E^0 - (RT/2nF)\ln(D_O/D_R)$, E^0 is the standard electrode potential, t is the time (s), D_O and D_R are the diffusion coefficients of Ox and Red, respectively. R, T, n and F have their usual electrochemical meanings. The transition time is defined as:

$$\tau^{1/2} = nF(\pi D_O)^{1/2}\, c_0^* / 2j\ , \qquad (2)$$

where j is the current density (A cm^{-2}). Let $G = nF/RT$ and $P = \exp[G(E - E')]$; then, the equation of reciprocal derivative chronopotentiometry can be written as:

$$dt/dE = -2G\tau P/(1 + P)^3\ . \qquad (3)$$

Equation of second-order RDCP is:

$$d^2t/dE^2 = -2G^2\tau P(1 - 2P)/(1 + P)^4\ . \qquad (4)$$

The peak height of d^2t/dE^2 *versus* E is:

$$(\mathrm{d}^2t/\mathrm{d}E^2)_{PP} = -0.2743G^2\tau \ . \qquad (5)$$

By differentiating Eq. (*4*), a mathematical expression for $\mathrm{d}^3t/\mathrm{d}E^3$–$E$ curve is obtained:

$$\mathrm{d}^3t/\mathrm{d}E^3 = -2G^3\tau P(4P^2 - 7P + 1)/(1+P)^5 \ . \qquad (6)$$

Let $\mathrm{d}^4t/\mathrm{d}E^4 = 0$, then we have $8P^3 - 33P^2 + 18P - 1 = 0$. Its approximate solutions are $P_1 = 0.06264$, $P_2 = 0.5716$ and $P_3 = 3.491$. By introducing P values into Eq. (*6*), three peaks are obtained

$$(\mathrm{d}^3t/\mathrm{d}E^3)_{PP1} = -0.05336G^3\tau \ , \qquad (7)$$

$$(\mathrm{d}^3t/\mathrm{d}E^3)_{PP2} = 0.20202G^3\tau \ , \qquad (8)$$

$$(\mathrm{d}^3t/\mathrm{d}E^3)_{PP3} = -0.09673G^3\tau \ . \qquad (9)$$

The peak heights of the $\mathrm{d}^3t/\mathrm{d}E^3$–$E$ curve are

$$(\mathrm{d}^3t/\mathrm{d}E^3)_{PP1,2} = 0.25538G^3\tau \ , \qquad (10)$$

$$(\mathrm{d}^3t/\mathrm{d}E^3)_{PP2,3} = 0.29875G^3 \ . \qquad (11)$$

The peak potentials (in mV) are (T = 298 K)

$$E_{PP1} = E' - 71.2/n \ , \qquad (12)$$

$$E_{PP2} = E' - 14.4/n \ , \qquad (13)$$

$$E_{PP3} = E' + 32.1/n \ . \qquad (14)$$

Table I lists the mathematical expressions describing the characteristic parameters of several forms of RDCP. Obviously, employing the derivative technique can greatly enhance the signals thus making the third-order RDCP the most sensitive.

EXPERIMENTAL

Instrumentation

A model DPSA-3 differential stripping analyser (Shangdong Seventh Electronic Factory, China) and a laboratory-built device were used for obtaining dt/dE–E chronopotentiograms, which were recorded with an X–Y recorder (Model 3086-11, Hokushiu Electric Co., Yokogama, Japan) or an oscilloscope (Jiangsu Yangzhong Electronic Equipment Factory, China). Three electrodes were employed. A hanging mercury drop electrode (HMDE), having the area 0.0302 cm^2, was the working electrode, saturated calomel and platinum foil were the reference and counter electrodes, respectively. The cell was thermostatted at 25 °C.

Chemicals

All chemicals were of analytical grade. All solutions were made in twice distilled water. A series of experiments was carried out with a Cd^{2+} solution in 0.2 M $NaNO_3$ or 0.1 M KCl supporting electrolyte. Prior to each test, the solution was deaerated by passing pure nitrogen for 15 min.

Procedure

The experimental procedure for obtaining the dt/dE–E curve was similar in principle to that described previously[11]. Instead of using an electronic simulator proposed by Ruan and Chang[10], we determined the d^2t/dE^2 and d^3t/dE^3 *vs* E by numerical differentiation of dt/dE–E curve. The values of dt/dE measured at different potentials were input to a microcomputer and the second- and third-order derivatives were directly calculated by the cubic spline interpolation[12]. A smoothing procedure employing a five-point cubic polynomial fit was used both before and after the differentiation[13]. All programs were written using GW-BASIC language.

TABLE I
Equations describing characteristic parameters of several forms of RDCP (T = 298 K)

Methods	Sensitivity, peak height/τ	Peak-to-peak separation, mV
$dt/dE–E$	$(dt/dE)_P/\tau = 11.5n$	$77.4/n$
$d^2t/dE^2–E$	$(d^2t/dE^2)_{PP}/\tau = 416n^2$	$59.5/n$
$d^3t/dE^3–E$	$(d^3t/dE^3)_{PP1,2}/\tau = 15\ 091n^3$	$56.8/n$
	$(d^3t/dE^3)_{PP2,3}/\tau = 17\ 653n^3$	$46.5/n$

RESULTS AND DISCUSSION

Verification of Second- and Third-Order RDCP Chronopotentiograms

Figure 1 gives theoretical and experimental results of second- and third-order RDCP chronopotentiograms. The theoretical and experimental curves are in agreement.

Dependence of Peak Height on Concentration of Reactant c_0^* and Current Density j

Equation (*5*) indicates that the peak height of the $(\mathrm{d}^2t/\mathrm{d}E^2)_{PP}$ is proportional to the transition time τ; therefore there will be a linear relationship between the square root of the $(\mathrm{d}^2t/\mathrm{d}E^2)_{PP}$ and c_0^* or $1/j$. The same dependence is also predicted by Eqs (*10*) and (*11*) for $(\mathrm{d}^3t/\mathrm{d}E^3)_{PP}$. Experimental results confirmed these conclusions: the linearity was satisfactory (Figs 2 and 3).

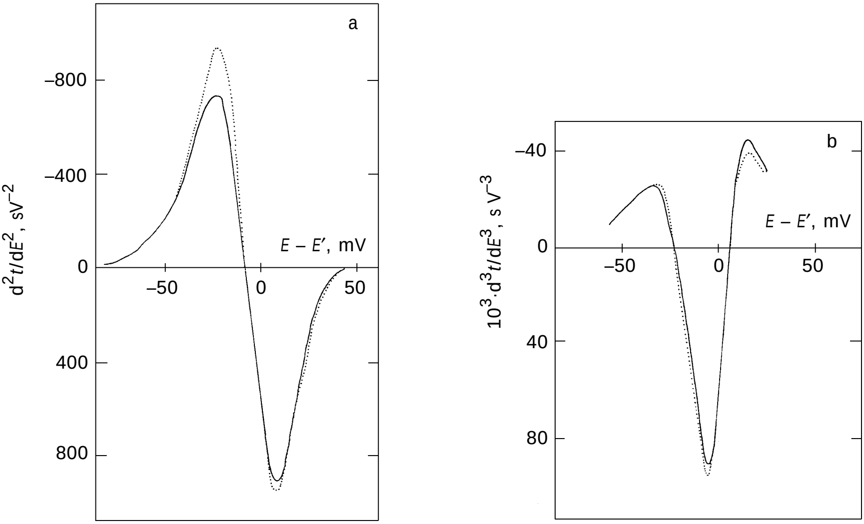

FIG. 1

Comparison of theoretical (full line) and experimental (dotted line) curves for two kinds of RDCP chronopotentiograms: a $\mathrm{d}^2t/\mathrm{d}E^2$–$E$, b $\mathrm{d}^3t/\mathrm{d}E^3$–$E$. Solution composition was $2 \cdot 10^{-4}$ M Cd^{2+} and 0.2 M $NaNO_3$; $j = 1.4 \cdot 10^{-4}$ A cm^{-2}, $T = 298$ K

Properties of Second- and Third-Order RDCP Chronopotentiograms

We have carefully investigated properties of second- and third-order RDCP chronopotentiograms: peak-to-peak height and peak-to-peak separation. Experimental and theoretical values are virtually coincident (Table II).

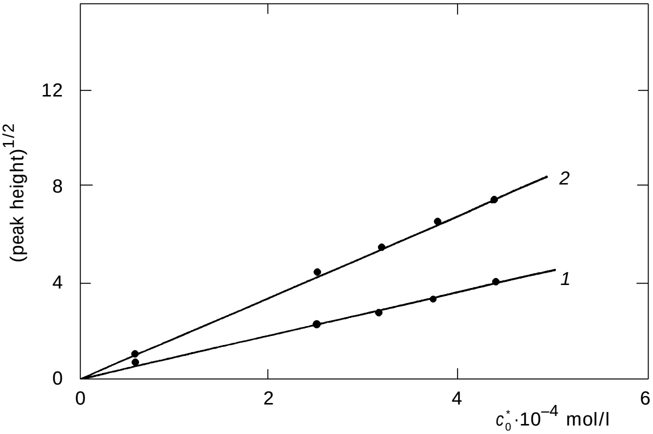

FIG. 2

Dependence of square root of peak height on c_0^* in 0.1 M KCl and Cd^{2+} at $j = 1.7 \cdot 10^{-4}$ A cm^{-2}: *1* $(d^2t/dE^2)_{PP}$, *2* $(d^3t/dE^3)_{PP}$

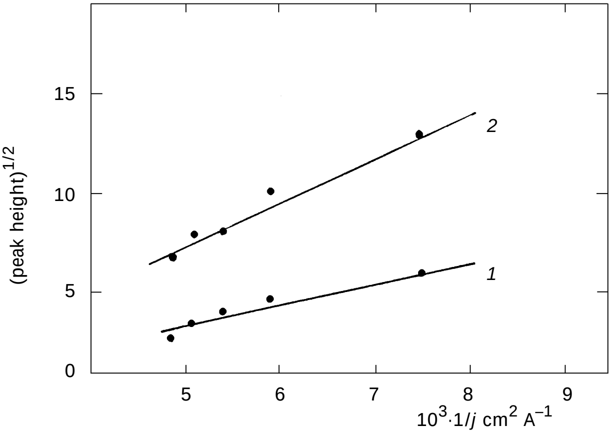

FIG. 3

Dependence of square root of peak height on 1/*j* in 0.1 M KCl and $4 \cdot 10^{-4}$ M Cd^{2+}: *1* $(d^2t/dE^2)_{PP}$, *2* $(d^3t/dE^3)_{PP}$

TABLE II
Experimental verification of the theory (0.2 M $NaNO_3$–$2 \cdot 10^{-4}$ M Cd^{2+}, $j = 1.4 \cdot 10^{-4}$ A cm^{-2}, $T = 298$ K)

Parameters	Theoretical	Experimental
Second-order RDCP d^2t/dE^2–E curve		
Peak-to-peak height, s/V^2		
$(d^2t/dE^2)_{PP}$	1 628	1 854
Peak-to-peak separation, mV		
$W_{1,2}$	29.8	28.4
Third-order RDCP d^3t/dE^3–E curve		
Peak-to-peak height, s/$V^3 \cdot 10^3$		
$(d^3t/dE^3)_{PP1,2}$	118	133
$(d^3t/dE^3)_{PP2,3}$	138	147
Peak-to-peak separation, mV		
$W_{1,2}$	28.4	28.4
$W_{2,3}$	23.3	20.4

CONCLUSION

The derivative technique has been applied to reciprocal derivative chronopotentiometry for a typical reversible reaction at the hanging mercury drop electrode. Theoretical and analytical characteristics were investigated for second- and third-order RDCP. The higher-order RDCP has several advantages over the conventional chronopotentiometry: (i) the basic instrumentation necessary for this method can be very inexpensive, compared with other conventional voltammetric instrumentation; (ii) the signal can be remarkably enhanced by differentiation. The higher the order of the derivative, the higher is the signal; (iii) interference of the charging current can be efficiently eliminated by derivatives. At potentials where we can assume that the electrode double-layer capacity is constant the charging contribution is: $E_c = j(R_s + t/C_d)$ (ref.[14]), where R_s and C_d are the solution resistance and differential capacity of electrode double-layer, respectively. Therefore,

$dt/dE_c = C_d/j$. Obviously, the corresponding capacitive portion of the derivative signal is reduced to zero since dC_d/dE is zero.

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