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A Method of Calculation for d.c. Polarographic Catalytic Wave

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A new numerical method for theoretical analysis of polarographic catalytic current is proposed and applied to well-studied systems to prove that the method is dependable. In this method, a system of partial differential equations of diffusion is transformed to finite-difference form by using Crank–Nicolson difference scheme, and the latter is solved by using both Gauss–Seidel and successive over relaxation methods. Chemical kinetics terms in the diffusion equations is substituted by ones rewritten by three alternative procedures. The method has been applied to a system of copper(II) and hydrogen peroxide. Resulted rate constant of participating chemical reaction agrees with the rate constant obtained from bulk solution experiments. This and other results show that the method is a useful tool for theoretical analysis of catalytic waves.

Catalytic reaction in polarographic wave has been studied by several methods. The one, which was first used, was a method invented by Bridicka and Wiesner.[1] Although it is simple and appealing, the conception of reaction layer on which the method based is of an approximate nature. Hence numerical values of rate constants of chemical reactions, calculated by this method, are considered unreliable. Kolthoff and Parry found that the rate constant calculated from observed currents was of the order of 10^4 times greater than the one determined from the experiment of bulk solution kinetics in the Fe(III)–hydrogen peroxide system.[2]

Koutecky derived a rigorous solution for a pseudo-first-order reaction at the surface of the expanding sphere electrode.[3] He solved simultaneous differential equations of diffusion, with chemical kinetics terms, using the method of dimensionless parameters. Though it is ingenious, his method can not be applied to reactions of higher orders.

The same kind of simultaneous differential equations are arising in problems of ECE mechanisms. Galvez et al. derived explicit solutions of the simultaneous differential equations without the steady state approximation and obtained current-potential curves of ECE mechanisms.[4–6] However, application of their method is limited to (pseudo-) first-order reactions owing to the common defect of analytic method.

Today numerical method becomes increasingly a popular tool for electrochemists with increasingly easier accessibility to computers. Ruzic et al. solved problems of ECE mechanisms by the method of explicit finite-difference digital simulation, and reported d.c. and a.c. polarographic curves of several ECE mechanisms, calculated by their method.[7–11] However, the method is inherently inflexible with respect to setting boundary conditions, and it is very difficult to apply to more complex systems.

Ultimate aim of this study is to diagnose observed polarograms of catalytic nature by comparing with calculated curves based on several possible mechanisms, and to estimate rate constants. Candidate mechanisms may be of second order or higher. Number of chemical species participated is not necessarily confined to three or four. All methods mentioned above are insufficient to achieve this aim. Another mathematical method is needed in these circumstances.

Winograd used an implicit method of finite-difference to simulate spectro-electrochemical working curves for a diffusion controlled system, and state that the method was much more efficient than explicit method.[12] In this paper the implicit method of Crank–Nicolson is used for calculation of polarograms of a simple system of catalytic current. Before to do this, however, soundness of the method must be established.

Theory

The catalytic current in the Cu^{2+}–H_2O_2 system is well-known through the study of Kolthoff and Woods.[18] This reaction mechanism is given as follows.

$$Cu^{2+} + e^- \rightleftharpoons Cu^+ \tag{1}$$

$$Cu^+ + H_2O_2 \longrightarrow Cu^{2+} + OH^- + OH \tag{2}$$

$$Cu^+ + OH \longrightarrow Cu^{2+} + OH^- \tag{3}$$

To generalize treatment the above reaction scheme is rewritten as

$$O + e^- \rightleftharpoons R, \tag{4}$$

$$R + A \xrightarrow{k} O + B, \tag{5}$$

$$R + B \longrightarrow O, \tag{6}$$

where O represents copper(II) ion, R copper(I) ion, A hydrogen peroxide, and B hydroxyl radical in a scheme of Reactions (1)—(3), and the current is controlled by the rate of Reaction (5). Partial differential equations for concentrations of species in Reactions (4)—(6) are given as follows:

$$\frac{\partial C_O}{\partial t} = D_O\left(\frac{\partial^2 C_O}{\partial r^2}\right) + \left(\frac{2}{r}D_O - u\right)\frac{\partial C_O}{\partial r} + 2kC_AC_R, \tag{7}$$

$$\frac{\partial C_R}{\partial t} = D_R\left(\frac{\partial^2 C_R}{\partial r^2}\right) + \left(\frac{2}{r}D_R - u\right)\frac{\partial C_R}{\partial r} - 2kC_AC_R, \tag{8}$$

and

$$\frac{\partial C_A}{\partial t} = D_A\left(\frac{\partial^2 C_A}{\partial r^2}\right) + \left(\frac{2}{r}D_A - u\right)\frac{\partial C_A}{\partial r} - kC_R C_A, \tag{9}$$

where C_h is the concentration of a species h, C^*_h its value in bulk solution, D_h the diffusion coefficient of the species h, r the distance from the center of the electrode mercury drop, and

$$u = m/(4\pi\rho r^2). \tag{10}$$

Here m is the flow rate of mercury, and ρ the density of mercury. It is assumed that the center of mercury drop remains fixed.

Initial conditions are

$$C_O = C^*_O,\quad C_A = C^*_A,\quad C_R = 0 \quad (t=0,\ r>0), \tag{11}$$

and boundary conditions are

$$C_O = 0,\ D_O\left(\frac{\partial C_O}{\partial r}\right) = -D_R\left(\frac{\partial C_R}{\partial r}\right),\ \left(\frac{\partial C_A}{\partial r}\right) = 0 \quad (t>0,\ r=a), \tag{12}$$

$$C_O = C^*_O,\ C_R = 0,\ C_A = C^*_A \quad (t>0,\ r=\infty). \tag{13}$$

The current, i, is given by

$$i = FD_O S(\partial C_O/\partial r)_{r=a}, \tag{14}$$

where a is the radius of the mercury drop, S the surface area of mercury drop, and F the Faraday constant. To facilitate calculation one introduces following transformations.

$$\begin{gathered} y_O = C_O/C^*_A,\ y_R = C_R/C^*_A,\ y_A = C_A/C^*_A, \\ x = (r-a)/L,\ d_O = D_O/D_A,\ d_R = D_R/D_A, \\ u' = m/(4\pi\rho a^2) \end{gathered} \tag{15}$$

In the above L is the representative length. With the aid of Eq. 15, Eq. 7 is transformed as follows.

$$\frac{L^2}{D_A}\frac{\partial y_R}{\partial t} = d_R\frac{\partial^2 y_R}{\partial x^2} + \left\{\frac{2d_R}{x+a/L} + \frac{Lx(x+2a/L)u'}{D_A(x+a/L)^2}\right\}\frac{\partial y_R}{\partial x} - \frac{2L^2 C^*_A}{D_A}ky_A y_R \tag{16}$$

Because the reaction proceeds in the neighborhood of the electrode surface, numerical results most desired are those in the proximity of the electrode surface. For this end, numerical integration of the differential equations is carried out more efficiently using a network, of which mesh is finer at near the electrode surface and becomes coarser with increasing the distance from the surface. Hence, one introduces a parameter given by

$$s = 1 - 1/(1+Hx), \tag{17}$$

where H is a constant.

Equation 16 is rewritten with the aid of Eq. 17.

$$\frac{\partial y_R}{\partial T} = d_R H^2(1-s)^4\frac{\partial^2 y_R}{\partial s^2} + \left\{\frac{2D_R}{x+a/L} + \frac{x(x+2a/L)}{(x+a/L)^2}U - 2d_R H(1-s)\right\}H(1-s)^2\frac{\partial C^*_A}{\partial s} - 2ky_R y_A, \tag{18}$$

where

$$\begin{aligned} T &= D_A t/L^2, \\ K &= L^2 C^*_A k/D_A, \\ U &= Lu/D_A. \end{aligned} \tag{19}$$

Equation 18 is solved by an implicit method of finite difference, Crank-Nicolson's method with some modifications.[14-16] If the domains of s and T are divided into equal intervals Δs and ΔT, respectively, the space and time coordinates are expressed as

$$s_i = i\Delta s,\ T_j = j\Delta T \tag{20}$$

$$x_i = i\Delta s/H(1+i\Delta s) \tag{21}$$

and the concentration $y_R(s,T)$ as

$$y_R(s,\ T) = y_R(i\Delta s, j\Delta T) = y_{R,i,j} \tag{22}$$

A finite-difference equation is derived from Eq. 18.

$$(E_{R,i} + \Delta TKy_{A,i,j+1})y_{R,i,j+1} = F_{R,i}y_{R,i+1,j+1} + G_{R,i}y_{R,i-1,j+1} + D_{R,i} - \Delta TKy_{A,i,j}y_{R,i,j} \tag{23}$$

Where

$$E_{R,i} = 1 + \frac{\Delta T}{\Delta s^2}d_R H^2(1-s_i)^4 \tag{24}$$

$$F_{R,i} = \frac{\Delta T}{2\Delta s}H(1-s_i)^2\left\{\frac{d_R H(1-s_i)^2}{\Delta s} + \frac{d_R}{x_i + a_{j+1}/L} + \frac{x_i(x_i+2a_{j+1}/L)}{2(x_i+a_{j+1}/L)^2}U_{j+1} - d_R H(1-s_i)\right\} \tag{25}$$

$$G_{R,i} = \frac{\Delta T}{2\Delta s}H(1-s_i)^2\left\{\frac{d_R(1-s_i)^2}{\Delta s} - \frac{d_R}{x_i + a_{j+1}/L} - \frac{x_i(x_i+2a_{j+1}/L)}{2(x_i+a_{j+1}/L)^2}U_{j+1} + d_R H(1-s_i)\right\} \tag{26}$$

$$D_{R,i} = F_{R,i}y_{R,i+1,j} + G_{A,i}y_{R,i-1,j} + \left\{1 - \frac{\Delta T}{\Delta s^2}d_R H^2(1-s_i)^4\right\}y_{R,i,j} \tag{27}$$

In much the same way the equations concerning with species A and O are transformed as follows.

$$E_{O,i}y_{O,i,j+1} = F_{O,i}y_{O,i+1,j+1} + G_{O,i}y_{A,i-1,j+1} + D_{O,i} + \Delta TK(y_{A,i,j+1}y_{R,i,j+1} + y_{A,i,j}y_{R,i,j}) \tag{28}$$

$$(E_{A,i} + \Delta TKy_{R,i,j+1}/2)y_{A,i,j+1} = F_{A,i}y_{A,i+1,j+1} + G_{A,i}y_{A,i-1,j+1} + D_{A,i} - \Delta TKy_{A,i,j}y_{R,i,j}/2 \tag{29}$$

Boundary conditions in finite-difference form are expressed in two alternative ways as shown in the following.

(i) The boundary condition $(D_O(\partial C_O/\partial r)_a = -D_R(\partial C_R/\partial r)_a)$ at the current time $(j+1)$ is expressed with concentrations at the nodes $(0,j+1)$, $(1,j+1)$, and $(2,j+1)$, and Eq. 30 is derived after some modifications.

$$\begin{aligned} y_{R,0,j+1} = {} & -(4y_{R,1,j+1}-y_{R,2,j+1})/3-d_O(4y_{O,1,j+1} \\ & -y_{O,2,j+1}-3y_{O,0,j+1})/3d_R \end{aligned} \tag{30}$$

The first derivative $(y'_{R,1,j+1})$ of $y_{R,1,j+1}$ is given as

$$\begin{aligned} y'_{R,1,j+1} = {} & (y_{R,2,j+1}+4y_{R,1,j+1}-5y_{R,0,j+1} \\ & -2\Delta s y'_{R,0,j+1})/8\Delta s + (y_{R,2,j}+4y_{R,1,j} \\ & +5y_{R,0,j}-2\Delta s y'_{R,0,j})/8\Delta S, \end{aligned} \tag{31}$$

where $y'_{R,0,j+1}$ is calculated by

$$\begin{aligned} y'_{R,0,j+1} &= \frac{4y_{R,1,j+1}-y_{R,2,j+1}-3y_{R,0,j+1}}{2\Delta s} \\ &= -\frac{d_O}{2\Delta s d_R}(4y_{O,1,j+1}-y_{O,2,j+1}-3y_{O,0,j+1}), \end{aligned} \tag{32}$$

the second derivative $(y''_{R,1,j+1})$ is written as

$$\begin{aligned} y''_{R,1,j+1} = {} & (y_{R,2,j+1}-2y_{R,1,j+1}+y_{R,0,j+1})/2(\Delta s)^2 \\ & + (y_{R,2,j}-2y_{R,1,j}+y_{R,0,j})/2(\Delta S)^2. \end{aligned} \tag{33}$$

Introduction of Eqs. 31—33 to Eq. 18 gives

$$\begin{aligned} & (1+E-F+\Delta TKy_{A,1,j+1})y_{R,1,j+1} = \\ & \quad (E/2-F/4)(y_{R,2,j+1}+y_{R,2,j}) \\ & \quad + (E/2-5F/4)(y_{R,0,j+1}+y_{R,0,j}) \\ & \quad + (1-E+F-\Delta TKy_{A,1,j})y_{R,1,j} \\ & \quad - \Delta s F(y'_{R,0,j+1}+y'_{R,0,j})/2, \end{aligned} \tag{34}$$

where

$$E = \Delta T d_R H^2(1-s_i)^4/(\Delta s)^2 \tag{35}$$

$$\begin{aligned} F = {} & \frac{\Delta T}{\Delta s}H(1-s_i)^2\left\{\frac{d_R}{x_i+a_{j+1}/L}\right. \\ & \left. +\frac{x_i(x_i+2a_{j+1}/L)}{2(x_i+a_{j+1}/L)^2}U_{j+1}-d_R H(1-s_i)\right\}. \end{aligned} \tag{36}$$

The value of $y_{R,1,j+1}$ is calculated with Eq. 34.

(ii) The boundary conditions $(D_O(\partial C_O/\partial r)_a = -D_R(\partial C_R/\partial r)_a)$ is expressed with concentrations at nodes $(0,j+1)$, $(1,j+1)$, $(2,j+1)$, and $(3,j+1)$, and Eq. 37 is obtained with some modifications.

$$\begin{aligned} y_{R,0,j+1} = {} & -(2y_{R,3,j+1}-9y_{R,2,j+1}+18y_{R,1,j+1})/11 \\ & -d_O(2y_{O,3,j+1}-9y_{O,2,j+1}+18y_{O,1,j+1} \\ & -11y_{O,0,j+1})/11d_R \end{aligned} \tag{37}$$

The derivatives at $i=1$ are expressed as following equations.

$$\begin{aligned} y'_{R,1,j+1} = {} & -(y_{R,3,j+1}-9y_{R,2,j+1}-9y_{R,1,j+1}+17y_{R,0,j+1} \\ & +6\Delta s y'_{R,0,j+1})/36\Delta s-(y_{R,3,j}-9y_{R,2,j} \\ & -9y_{R,1,j}+17y_{R,0,j}+6\Delta s y'_{R,0,j})/36\Delta S, \end{aligned} \tag{38}$$

$$\begin{aligned} y''_{R,1,j+1} = {} & (-2y_{R,3,j+1}+27y_{R,2,j+1}-54y_{R,1,j+1} \\ & +29y_{R,0,j+1}+6\Delta s y'_{R,0,j+1})/36(\Delta s)^2 \\ & +(-2y_{R,3,j}+27y_{R,2,j}-54y_{R,1,j} \\ & +29y_{R,0,j}+6\Delta s y'_{R,0,j})/36(\Delta S)^2, \end{aligned} \tag{39}$$

$y'_{R,0,j+1}$ in the above is calculated by

$$\begin{aligned} y'_{R,0,j+1} &= (2y_{R,3,j+1}-9y_{R,2,j+1}+18y_{R,1,j+1} \\ &\quad -11y_{R,0,j+1})/6\Delta s \\ &= -(d_O/6\Delta s d_R)(2y_{O,3,j+1}-9y_{O,2,j+1} \\ &\quad +18y_{O,1,j+1}-11y_{O,0,j+1}). \end{aligned} \tag{40}$$

Introduction of Eqs. 38—40 to Eq. 18 results

$$\begin{aligned} & (1+3E/2-F/2+\Delta TKy_{A,1,j+1})y_{R,1,j+1} = \\ & \quad (-E-F)(y_{R,3,j+1}+y_{R,3,j})/18 \\ & \quad + (-3E/4+F/2)(y_{R,2,j+1}+y_{R,2,j}) \\ & \quad + (1-3E/2+F/2-\Delta TKy_{A,1,j})y_{R,1,j} \\ & \quad + (29E/36-17F/18)(y_{R,0,j+1}+y_{R,0,j}) \\ & \quad + (E/6-F/3)\Delta s(y'_{R,0,j+1}+y'_{R,0,j}). \end{aligned} \tag{41}$$

The value of $y_{R,1,j+1}$ is calculated with Eq. 41.

It is, however, not possible to apply the method described above to the case where chemical kinetics terms are written with concentrations of second order or higher.

Morihara and Chen reported a procedure which makes possible to transform a higher order function to a linear function. Application of their procedure to the parenthesis in the right-hand side of Eq. 23 yields Eq. 42.13)

$$\begin{aligned} & y_{A,i,j+1}y_{R,i,j+1} + y_{A,i,j}y_{R,i,j} \\ & \quad = y_{A,i,j+1}y_{R,i,j} + y_{A,i,j}y_{R,i,j+1} \end{aligned} \tag{42}$$

Introduction of Eq. 42 to 28 gives

$$\begin{aligned} & (E_{R,i}+\Delta TK_{A,i,j})y_{R,i,j+1} = F_{R,i}y_{R,i+1,j+1} \\ & \quad + G_{R,i}y_{R,i-1,j+1} + D_{R,i} - \Delta TKy_{A,i,j+1}y_{R,i,j}. \end{aligned} \tag{43}$$

In much the same way as Eq. 43 is derived from Eq. 23, Eq. 44 is resulted from Eq. 29.

$$\begin{aligned} & (E_{A,i}+\Delta TK_{R,i,j}/2)y_{A,i,j+1} = F_{A,i}y_{A,i+1,j+1} \\ & \quad + G_{A,i}y_{A,i-1,j+1} + D_{A,i}-\Delta TKy_{A,i,j+1}y_{R,i,j}/2 \end{aligned} \tag{44}$$

Although Morihara–Chen's procedure is useful as shown above, it becomes powerless when it is applied to fractional order of reaction. Following two procedures are proposed to replace it in the case of fractional order of reaction.

The first of them is as follows. In this procedure, the value of concentrations in chemical kinetics terms in the $(n+1)$-th iteration are replaced with the values of concentrations resulted by n-th iteration. The concentrations at each successive repetitions are expressed as

$$(y_{A,i,j+1})_{n+1} = (y_{A,i,j+1})_n + \delta_1 \tag{45}$$

$$(y_{\mathrm{R},i,j+1})_{n+1} = (y_{\mathrm{R},i,j+1})_n + \delta_2, \tag{46}$$

where n is the number of iteration, and δ_1 and δ_2 are differences in successive iterations. If the values of δ_1 and δ_2 approach to zero with increasing n, the product of the left-hand sides of Eqs. 45 and 46 becomes

$$(y_{\mathrm{A},i,j+1})_{n+1}(y_{\mathrm{R},i,j+1})_{n+1} = (y_{\mathrm{A},i,j+1})_n(y_{\mathrm{R},i,j+1})_n. \tag{47}$$

Equation 47 shows that the value of left-hand side of Eq. 47 is known at the beginning of the $(n+1)$-th iteration. Introduction of Eq. 47 to Eqs. 23 and 29, and modification give following relations.

$$\begin{aligned} E_{\mathrm{R},i}(y_{\mathrm{R},i,j+1})_{n+1} &= F_{\mathrm{R},i}(y_{\mathrm{R},i+1,j+1})_{n+1} \\ &\quad + G_{\mathrm{R},i}(y_{\mathrm{R},i-1,j+1})_{n+1} + D_{\mathrm{R},i} - \Delta TKy_{\mathrm{A},i,j}y_{\mathrm{R},i,j} \\ &\quad - \Delta TK(y_{\mathrm{A},i,j+1})_n(y_{\mathrm{R},i,j+1})_n \end{aligned} \tag{48}$$

$$\begin{aligned} E_{\mathrm{A},i}(y_{\mathrm{A},i,j+1})_{n+1} &= F_{\mathrm{A},i}(y_{\mathrm{A},i+1,j+1})_{n+1} \\ &\quad + G_{\mathrm{A},i}(y_{\mathrm{A},i-1,j+1})_{n+1} + D_{\mathrm{A},i} - \Delta TKy_{\mathrm{A},i,j}y_{\mathrm{R},i,j}/2 \\ &\quad - \Delta TK(y_{\mathrm{A},i,j+1})_n(y_{\mathrm{R},i,j+1})_n/2 \end{aligned} \tag{49}$$

The second procedure is as follows. The values at $T+\Delta T$ may be replaced by the values at T if the rate constant of chemical reaction is not so large. Hence Eq. 42 is written as

$$y_{\mathrm{A},i,j+1}y_{\mathrm{R},i,j+1} + y_{\mathrm{A},i,j}y_{\mathrm{R},i,j} = 2y_{\mathrm{A},i,j}y_{\mathrm{R},i,j}. \tag{50}$$

Using the above relation Eqs. 23 and 29 are rewritten as

$$\begin{aligned} E_{\mathrm{R},i}y_{\mathrm{R},i,j+1} &= F_{\mathrm{R},i}y_{\mathrm{R},i+1,j+1} + G_{\mathrm{R},i}y_{\mathrm{R},i-1,j+1} \\ &\quad + D_{\mathrm{R},i} - 2\Delta TKy_{\mathrm{A},i,j}y_{\mathrm{R},i,j} \end{aligned} \tag{51}$$

$$\begin{aligned} E_{\mathrm{A},i}y_{\mathrm{A},i,j+1} &= F_{\mathrm{A},i}y_{\mathrm{A},i+1,j+1} + G_{\mathrm{A},i}y_{\mathrm{A},i-1,j+1} \\ &\quad + D_{\mathrm{A},i} - \Delta TKy_{\mathrm{A},i,j}y_{\mathrm{R},i,j} \end{aligned} \tag{52}$$

Three sets of equations (i.e. Eqs. 43 and 44, and Eqs. 48 and 49, and Eqs. 51 and 52) are derived in place of Eqs. 23 and 29. The latter two sets of equations are derived by new procedures of which dependability must be tested.

In order to establish the soundness of present numerical method, the method was applied first to reconfirm well-known relationships between the diffusion current and the concentration of depolarizer, and between the diffusion current and the height of mercury column. In this case the value of reaction rate constant is zero, and the boundary conditions are given as follows.

$$C_0 = C_0^* \quad (t=0,\ r>0) \tag{53}$$

$$C_0 = 0 \quad (t>0,\ r=a) \tag{54}$$

$$C_0 = C_0^* \quad (t>0,\ r=\infty) \tag{55}$$

Then the method was applied to a system of copper(II)-hydrogen peroxide system.

Experimental

All chemicals used were of reagent grade. The concentration of hydrogen peroxide in stock solution was determined by iodometry.[19] Stock solutions of cadmium(II) sulfate and copper(II) sulfate were made by dissolving weighed amounts of anhydrous salts. The solution of copper(I) ion was prepared by dissolving copper(I) chloride dissolved in 1.0 M† hydrochloric acid from which dissolved oxygen was expelled with bubbles of pure nitrogen. The concentration of copper(I) ion was determined from the diffusion current of copper(II) ion after the oxidation of copper(I) ion by pure oxygen.

Measurements of catalytic wave were carried out in the solution of 1.0 M HCl and 0.005% gelatin. An electrolysis cell with a hole of 0.5 mm in diameter at bottom of the cell was used to prevent contamination of mercury ions through oxidation of mercury collected on the bottom of the cell. A Hokuto Denko Model HA-104 Potentio-Galvanostat was used for application of potential with three-electrode arrangement. Catalytic currents were measured at the end of life of mercury drop. Measurements were carried out within 70 min after preparation of test solutions, in order to avoid the influence of their composition variation. The oxygen was expelled from test solutions with bubbling pure nitrogen through the solutions for 50 min. The diffusion coefficient of both reactants and products were determined from respective diffusion current. Measurements of diffusion currents were carried out in the same conditions as measurements of the catalytic wave, except the absence of the hydrogen peroxide.

The numerical computation in the present method was programmed with Gauss-Seidel method and succesive over relaxation method by using FORTRAN, and performed on a FACOM M382 computer in DATA PROCESSING CENTER KYOTO UNIVERSITY.

Results and Discussion

In order to confirm that the present method reproduces the relationship between the diffusion current and the concentration of depolarizer, the method was applied to the diffusion current of copper(II) ion in a solution of 1.0 M HCl and 0.005% gelatin. It was confirmed by computation that the diffusion current was proportional to the concentration of copper(II) ion, and that observed values of diffusion currents agreed with calculated ones. The value of diffusion coefficient used in the computation is taken from the Ref. 2.

Table 1 shows relation between the height of mercury column and the diffusion currents of copper(II) ion. Observed data agree with ones calculated.

The instantaneous current was also calculated with this method. The current-time curve of diffusion current is proportional to $t^{1/6}$ according to Ilkovic

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† 1 M=1 mol dm^{-3}.

equation, to $t^{1/5.2}$ according to the equation introduced by Koutecky,[3] and to $t^{1/5.3}$ according to the present numerical method.

The soundness and the accuracy of this method was confirmed by above results that the observed relationships between the diffusion currents and the concentration of depolarizer and between the diffusion currents and the height of mercury column were both reproduced by the present method, and that a current-time curve of instantaneous current calculated with this method agrees with one calculated from Koutecky's equation.[3] Therefore it may be concluded that this method can be used for the aim of present study, theoretical analysis of the catalytic currents.

The chemical kinetic terms in finite-difference equations are expressed in four different forms. The first is expressed in Eqs. 23 and 29 which were derived by straight forward way, the second is shown in Eqs. 43—44 which were derived by using the procedure proposed by Morihara and Chen, and the third and fourth are respectively, expressed in Eqs. 48—49 and Eqs. 51—52 which were derived by the procedures proposed in the present paper. It is found that the numerical computation by using the fourth is more efficient than using others (see Appendex). The differences of four corresponding values obtained with using the four procedures were smaller than one per cent. Differences of converged values obtained with using various values of ΔT and ΔS were within the limits considered generally permissible. These facts show that the procedures proposed in the present study are dependable. Besides, it must be noted that proposed two procedures are applicable to chemical kinetics term with fractional orders. The boundary condition $(D_O(\partial C_O/\partial r)_a=-D_R(\partial C_R/\partial r)_a)$ is written in two forms. These are shown in Eqs. 30—34 and Eqs. 35—41. The former expresses the condition with using the values of functions at three nodes near the electrode surface, whereas the latter with using values at four nodes. It is found that the time consumed for numerical computation using the former is about twice as large as one consumed using the latter. Difference of two corresponding values computed by the two procedures are small and below the level of error considered generally permissible. Therefore it is concluded that the proposed numerical method for catalytic currents is dependable.

Table 1. Diffusion Current of 2.03 mM Cu(II) Ion in 1 M HCl and 0.01% Gelatin

Height of mercury column H / cm	Flow rate of mercury m / 10^{-3} g s^{-1}	Diffusion current i_d / μA	
		observed	calculated[a)]
50	0.675	10.26	10.08
60	0.831	11.28	11.05
70	0.998	12.08	12.02
80	1.147	12.86	12.79
88	1.268	13.46	13.42

a) Values of parameters used for computation are as follows. $\Delta T=3.69\times10^{-4}$, $\Delta S=0.01$, and $L=0.01$ cm.

The values of diffusion coefficients used for numerical computations were chosen as ones which gave smallest differences between calculated currents and with observed ones. This procedure produced a value of 0.750×10^{-5} cm^2 s^{-1} for the diffusion coefficient of cadmium ion. This value agrees well with the value in the Ref. 2. Therefore the procedure is usable.

The method was applied to the catalytic current in the Cu^{2+}–H_2O_2 system. The diffusion currents of species participated in the catalytic current were measured in a solution of 1.0 M HCl and 0.005% gelatin. Table 2 shows values of diffusion coefficients, which were used for computation and gave best agreements of calculated diffusion currents with observed ones.

Table 2. Diffusion Current and Diffusion Coefficient

	i_d/C / μA mM^{-1}	T[a)] / s	D / 10^{-5} cm^2 s^{-1}	D[c)] / 10^{-5} cm^2 s^{-1}
Cu^{2+}	6.40	5.62	0.720	0.72
Cu^+	4.68	5.14	1.502	—
H_2O_2	8.95[b)]	4.68	1.420	—

a) Dropping time at a potential corresponding to the diffusion current plateau. b) The diffusion current was measured in a solution of 1.0 M $NaNO_3$ and 0.005% gelatin, because it was partly obscured by hydrogen discharge wave in a solution of 1.0 M HCl and 0.005 % gelatin. c) These value are quoted from the Ref. 2.

Table 3. Reaction Rate calculated from Koutecky's Method and Numerical Method in 2.03 mM Cu^{2+}, 1.0 M HCl, and 0.01% Gelatin

$[H_2O_2]$ / mM	i_l/i_d	k / l mol^{-1} s^{-1}	
		Koutecky's method	Present method[a)]
2.18	1.396	131.8	55.0
5.45	1.986	106.8	55.0
10.9	2.398	77.3	55.0
21.8	3.121	65.9	55.0
43.6	4.236	60.7	55.0
76.3	5.478	58.0	55.0
109.0	6.274	53.3	55.0
141.7	7.197	53.9	55.0

a) Values of parameters used for computation are as follows. $\Delta T=3.69\times10^{-4}$, $\Delta S=0.01$, and $L=0.01$ cm.

Table 3 shows that the catalytic currents and the reaction rate constants, calculated by Kouteckey's method and the present method. The value of reaction rate constant of Reaction (2) was given as $55.0\pm0.5\ \mathrm{l\ mol^{-1}\ s}$ by which gave best agreements between calculated catalytic currents and observed ones. The value calculated with Koutecky's method[17] decreases with increasing concentration of hydrogen peroxide.

Table 4 shows that variation of the catalytic current with increase of the height of mercury column. The present method gives the same value of reaction rate constant as ones in Table 3. But the value calculated with Koutecky's method increases with increase of the height of mercury column.

From the numerical computation for the catalytic wave, it was found that the value of the reaction rate constant is $55.0\ \mathrm{l\ mol^{-1}\ s}$ as shown in Tables 3 and 4. This value differs from one reported by Kolthoff and Woods.[18] But in their paper, the rate constant of oxidation of copper(I) by hydrogen peroxide in chloride medium, was determined by observing increase of the cathodic wave of copper(II) ion with time. They gave a value of $58\ \mathrm{l\ mol^{-1}\ s}$ which agrees with the result of the present study.

Figure 1 shows that the relation between the ratio of the catalytic current to the diffusion current of copper(II) ion (i_l/i_d) and the concentration of hydrogen peroxide. It shows that the observed point are on the calculated curve.

The relation between the ratio (i_l/i_d) and the height of mercury column is shown in Fig. 2, where observed points are on the calculated curve.

The value of the rate constant calculated by Koutecky's method decreases with increasing concentration of hydrogen peroxide. This is explained as follows. In the Koutecky's method, it is assumed that the concentration of hydrogen peroxide in the reaction layer is same as to that in the bulk solution. However, that is not the case.

On the contrary the present method gives the only one value for reaction rate constant which is consistent with all experimental data.

Conclusion

A new numerical method is proposed for numerical solution of diffusion equations with chemical kinetics

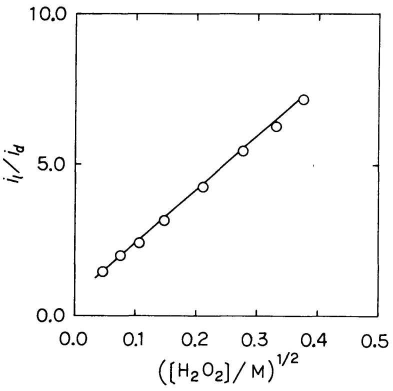

Fig. 1. Plots of i_l/i_d for mixtures of H_2O_2 with 2.03 mM Cu^{2+} in 1 M HCl and 0.01% gelatin. ○: Observed data, a solid curve; calculated data.

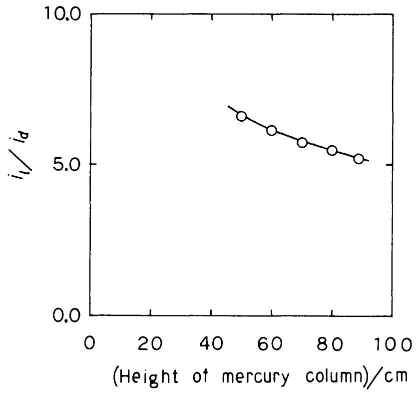

Fig. 2. Effect of the height of mercury column on the catalytic wave. 2.03 mM Cu^{2+}, 76.3 mM, 1 M HCl, and 0.01% gelatin. ○: Observed data, a solid curve; calculated data.

Table 4. Reaction Rate Constant Calculated from Koutecky's Method and Numerical Method in 2.03 mM Cu^{2+}, 76.3 mM H_2O_2, 1.0 M HCl, and 0.01% Gelatin

Height of mercury head H / cm	Flow rate of mercury m / 10^{-3} g s^{-1}	i_l/i_d	Dropping time t / s	k / l mol^{-1} s^{-1} Koutecky's method	k / l mol^{-1} s^{-1} Present[a)] method
50	0.675	6.55	9.08	47.0	55.0
60	0.831	6.12	7.52	49.5	55.0
70	0.998	5.75	6.44	51.0	55.0
80	1.147	5.46	5.62	52.7	55.0
88	1.268	5.26	5.04	54.6	55.0

a) Values of parameters used for computation are as follows. $\Delta T=3.69\times10^{-4}$, $\Delta S=0.01$, and $L=0.01$ cm.

terms, and is established as a useful tool for theoretical analysis of the catalytic current. Diffusion equations with chemical kinetic terms are transformed to finite-difference equations using the implicit method of Crank–Nicolson. New two procedures are proposed for the purpose of rewriting chemical kinetics terms. These are applicable even to chemical kinetics terms with fractional order. The boundary condition $(D_O(\partial C_O/\partial r)_a = -D_R(\partial C_R/\partial r)_a)$ is written in two forms. The one expresses the boundary condition with the values of functions at three nodes near the electrode surface, whereas the other with the values of four nodes. It is found that the time consumed for numerical computation using former is about twice as large as one consumed using latter. The dependability of these procedures is proved through comparison of values of functions obtained with one obtained using other procedures.

Appendix

Differences between calculated values of the catalytic current were within ±0.3%, irrespective of computational procedures used for chemical kinetics terms, when values of ΔT, ΔS, and L were, respectively, 0.369×10^{-14}, 0.01, and 0.01 cm. Times consumed for computations were 5.01, 5.86, 5.12, and 3.56 s with first, second, third, and fourth procedures, respectively. These values show that the fourth procedure is most efficient.

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