Potential Step Voltammetry of Ion-Transfer at Liquid/Liquid Interface with Preceding Chemical Reaction.
Determination of the Rate and Equilibrium Constants from Voltammetric Curves

Hajime Katano* **and Mitsugi Senda**

Department of Bioscience, Fukui Prefectural University, Matsuoka-cho, Fukui 910-1195

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Theoretical equations of the potential step voltammograms for the ion-transfer with preceding chemical reaction have been derived. Results were applied to analyze the voltammetric behavior of 1,4,7,10,13,16-hexathiacyclooctadecane-assisted transfer of Pb^{2+} ion across the nitrobenzene/water interface from aqueous medium containing $citrate^{3-}$ ion. The dissociation and association rate constants and the equilibrium constant of Pb^{2+}–$citrate^{3-}$ complex in aqueous medium are determined to be $1.2\times10^{4}\ s^{-1}$ and $1.2\times10^{10}\ M^{-1}\ s^{-1}$ and $10^{6.0}\ M^{-1}$, respectively. The results are compared with those obtained by potential sweep voltammetry.

Ion-transfer voltammetry at the organic(O)/water(W) interface is useful for the study of equilibrium and dynamic properties of metal ion complexes in both O- and W-phases. In a previous paper,[1] theoretical equations of the current–potential curves in potential sweep voltammetry or cyclic voltammetry (CV) for the ion-transfer with preceding chemical reaction across the O/W interface have been derived. The results were applied to analyze the voltammetric behavior of the transfer of Pb^{2+} ion assisted by 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO) present in nitrobenzene (NB) from W-phase containing a ligand, $citrate^{3-}$ ion, to NB-phase, giving the association and dissociation rate constants and the equilibrium constant of Pb^{2+}–$citrate^{3-}$ complex in the aqueous medium.

In this study, theoretical equations of the current–time and current–potential relationships in potential step voltammetry or normal pulse voltammetry (NPV) for the reversible ionophore-assisted ion-transfer with preceding chemical reaction have been derived. These equations were applied to analyze the voltammetric behavior of the HTCO-assisted transfer of Pb^{2+} ion across the NB/W interface, which has been shown to be a reversible process,[2] coupled with the preceding dissociation reaction of Pb^{2+}–$citrate^{3-}$ complex in W-phase.[1] The rate and equilibrium constants of the complex formation have been determined from the voltammetric data. The results and discussion are given in this paper. It will be shown that potential step voltammetry or NPV can be applied advantageously in comparison with potential sweep voltammetry or CV to study the kinetics of the chemical reaction which precedes the charge transfer process.

Theory

We consider a reversible or nernstian transfer of a metal ion (M) initially present in W-phase across the O/W interface assisted by an ionophore (L) present in O-phase to form a 1 : 1 metal–ionophore complex (ML) in O-phase (see, assumptions (vi) and (vii) in Appendix). The ionophore-assisted ion-transfer may be expressed by

$$\mathrm{M(W)} + \mathrm{L(O)} \rightleftharpoons \mathrm{ML(O)}. \tag{1}$$

We also consider that, in W-phase, M ion associates with a ligand (Aw) to form a 1 : 1 metal-ligand complex (MAw):

$$\mathrm{M(W)} + \mathrm{Aw(W)} \rightleftharpoons \mathrm{MAw(W)}. \tag{2}$$

In the following, we assume (i) that L and ML species are soluble only in O-phase and (ii) that Aw and MAw species are soluble only in W-phase. We also assume (iii) that the concentration of L in O-phase is sufficiently large compared with the total concentration of M ionic species in O-phase and (iv) that the concentration of Aw in W-phase is sufficiently large compared with the total concentration of M ionic species in W-phase, so that the concentrations of L and Aw can be considered to remain constant throughout the O- and W-phases, respectively, while the ion-transfer process is taking place at the interface. Under the assumption (iv), the kinetics of the dissociation and association of MAw complex in W-phase may be expressed by

$$\mathrm{MAw(W)} \underset{k_\mathrm{f}^{\mathrm{W}\prime}}{\overset{k_\mathrm{b}^\mathrm{W}}{\rightleftharpoons}} \mathrm{M(W)}, \quad K^\mathrm{W} = k_\mathrm{f}^{\mathrm{W}\prime}/k_\mathrm{b}^\mathrm{W}, \tag{3}$$

where k_b^W is the dissociation rate constant and $k_\mathrm{f}^{\mathrm{W}\prime}$ the pseudo-monomolecular association rate constant of MAw complex in W-phase. The latter rate constant is related to the bimolecular association rate constant (k_f^W) of Eq. 2 by $k_\mathrm{f}^{\mathrm{W}\prime} = k_\mathrm{f}^\mathrm{W}\ {}^{*}c_\mathrm{Aw}^\mathrm{W}$, and the apparent formation constant (K^W) is related to the formal formation constant ($K^{\mathrm{W}}_{\mathrm{MAw}}$) of Eq. 2 by $K^{\mathrm{W}} = K^{\mathrm{W}}_{\mathrm{MAw}}\ {}^{*}c^{\mathrm{W}}_{\mathrm{Aw}}$, ${}^{*}c^{\mathrm{W}}_{\mathrm{Aw}}$ being the bulk concentration of Aw in W-phase. We further assume (v) that the ion-transfer reaction of Eq. 1 is preceded by the dissociation reaction of Eq. 3 at the interface. Then, the potential step voltammetric current ($i(t)$), as a function of time (t), of the ionophore-assisted transfer of M ion across a stationary plane O/W interface is given by (see Appendix).[3—5]

$$i(t) = {}_{\mathrm{r}}i(t)\frac{1}{\sigma^2 - 1}\left\{\exp[-lt] - 1 + \sigma^2\pi^{1/2}\sqrt{\frac{lt}{\sigma^2 - 1}} \times\exp\left[\frac{lt}{\sigma^2 - 1}\right]\left[\mathrm{erf}\left[\sigma\sqrt{\frac{lt}{\sigma^2 - 1}}\right] - \mathrm{erf}\left[\sqrt{\frac{lt}{\sigma^2 - 1}}\right]\right]\right\} \tag{4}$$

where

$${}_{\mathrm{r}}i(t) = \frac{i_{l,\mathrm{d}}(t)}{1 + \exp[-(zF/RT)(E - {}_{\mathrm{r}}E_{1/2})}, \tag{5}$$

$$\sigma = \frac{K^{\mathrm{W}}}{1 + \exp[-(zF/RT)(E - {}_{\mathrm{r}}E_{1/2})} > 1, \tag{6}$$

and

$$l = k_{\mathrm{f}}^{\mathrm{W}\prime} + k_{\mathrm{b}}^{\mathrm{W}}, \tag{7}$$

with the limiting diffusion current ($i_{l,\mathrm{d}}(t)$) defined by

$$i_{l,\mathrm{d}}(t) = \frac{zFA(D^{\mathrm{W}})^{1/2}}{(\pi t)^{1/2}}({}^{*}c^{\mathrm{W}}_{\mathrm{M}})_{\mathrm{t}} \tag{8}$$

and the reversible half-wave potential (${}_{\mathrm{r}}E_{1/2}$) defined by

$${}_{\mathrm{r}}E_{1/2} = E^{0\prime}_{\mathrm{M/ML}} - \frac{RT}{zF}\ln\left[\frac{1+K^{\mathrm{O}*}c^{\mathrm{O}}_{\mathrm{L}}}{K^{\mathrm{O}}}\right] + \frac{RT}{zF}\ln\sqrt{\frac{D^{\mathrm{W}}}{D^{\mathrm{O}}}} + \frac{RT}{zF}\ln[1+K^{\mathrm{W}}]. \tag{9}$$

In these equations, z is the charge number of M ion including sign; F, R, and T are used in the usual meanings; E is the applied potential; A is the surface area of the O/W interface; D^{α} is the common diffusion coefficient of M ion species in α-phase (α = O and W); $({}^{*}c^{\mathrm{W}}_{\mathrm{M}})_{\mathrm{t}}$ is the total concentration of M ion species in the bulk of W-phase; $E^{0\prime}_{\mathrm{M/ML}}$ is the formal potential of the ionophore-assisted ion-transfer reaction of Eq. 1 across the O/W interface; K^{O} is the formal formation constant of ML in O-phase, defined by Eq. A17 (see Appendix); and ${}^{*}c^{\mathrm{O}}_{\mathrm{L}}$ is the bulk concentration of L in O-phase. In Eq. 4, when $lt \rightarrow \infty$, $i(t)$ is reduced to the reversible or nernstian i–E curve (${}_{\mathrm{r}}i(t)$) defined by Eq. 5.

Equation 4 predicts that the $i(t)$–E curve has an S-shaped form and $i(t)$ approaches the limiting current at $(zF/RT)(E - {}_{\mathrm{r}}E_{1/2}) > 4.3$. Furthermore, when $K^{\mathrm{W}} \gg 1$ so that $\sigma^2 \gg 1$ and also when $lt \gg 1$ so that $\mathrm{erf}\,[lt] \cong 1$, Eq. 4 is reduced to

$$i(t) = {}_{\mathrm{r}}i(t)\{\pi^{1/2}(\Psi t)^{1/2}\exp[\Psi t]\mathrm{erfc}\,[(\Psi t)^{1/2}]\} \tag{10}$$

with

$$\Psi = l/\sigma^2, \tag{11}$$

and the limiting current ($i_{\mathrm{l}}(t)$) is given by

$$i_{\mathrm{l}}(t) = i_{l,\mathrm{d}}(t)\{\pi^{1/2}(\Psi' t)^{1/2}\exp[\Psi' t]\mathrm{erfc}\,[(\Psi' t)^{1/2}]\} \tag{12}$$

with

$$\Psi' = l/(K^{\mathrm{W}})^2. \tag{13}$$

It is noted that Eq. 10 is derived by assuming a steady state of the diffusion-chemical reaction in the immediate vicinity on W-side of the O/W interface.[6]

Experimental

The HTCO-assisted transfer of Pb^{2+} ion across the interface between NB and aqueous media was studied by means of potential step voltammetry. The electrochemical cell used for the electrochemical measurements can be represented by cell (I) (Chart 1): where TPnACl denotes n-tetrapentylammonium chloride, TPnATClPB means n-tetrapentylammonium tetrakis[4-chrolophenyl]borate, and $\mathrm{M = mol\,dm^{-3}}$. The polarized NB/W interface, that is, the test interface is indicated by an asterisk. The applied potential E is defined as the terminal potential of the reference electrode RE1 referred to that of RE2, and related to the Galvani potential difference across the O/W interface ($\Delta^{\mathrm{W}}_{\mathrm{O}}\phi$) by

$$E = \Delta^{\mathrm{W}}_{\mathrm{O}}\phi + \Delta E_{\mathrm{ref}}, \tag{14}$$

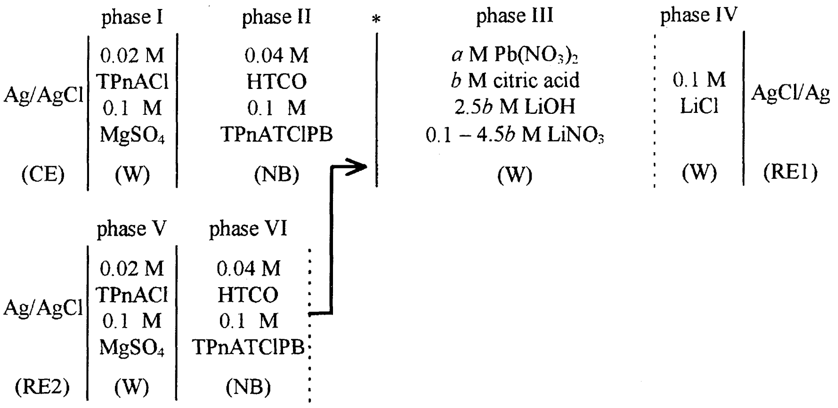
where ΔE_{ref} is determined by the reference electrode system consisting of cell (I). The reversible half-wave potential of tetramethylammonium (TMA^{+}) ion at the NB/W interface was determined to be 0.369 V by cyclic voltammetry with cell (I), in which phase III is replaced by 0.50 mM TMABr and 0.20 M $\mathrm{LiNO_3}$. The standard ion-transfer potential of TMA^{+} ion is reported to be $\Delta^{\mathrm{W}}_{\mathrm{O}}\phi^{0}_{\mathrm{TMA}} = 0.035$ V.[7] On an appropriate assumption,[8] ΔE_{ref} for cell (I) was determined to be 0.325 V.

In the potential step voltammetry, a potential step $\Delta E = E - E_{\mathrm{i}}$, E_{i} being the initial potential where the current due to the ion-transfer is negligibly small, is applied to the O/W interface at $t = 0$ and the resulting current was sampled as a function of t. The E_{i} was set at 0.35 V unless otherwise stated. The current was recorded after correction for the base current.

$\mathrm{Citrate}^{3-}$ ion was added to the test aqueous medium (phase III) as 1 : 2.5 citric acid–LiOH buffer. The ionic strength (I) of the medium was kept at $I = 0.1$ by addition of $\mathrm{LiNO_3}$. The pH of the test aqueous medium was determined to be pH = 5.8±0.2. The solution resistance between the terminal of the reference electrode RE1 and the tip of liquid junction (Phase VI(O)) of the reference electrode RE2 was usually about 3 kΩ or more. The cell potential was controlled by a laboratory-made potentiostat with a positive feedback iR compensation. All measurements were carried out at 25±0.5 °C. For further details of reagents, electrolysis cell, and instruments, see Ref. 2.

Results and Discussion

Figure 1 shows the plots of chronoamperometric currents sampled at a constant sampling time of $t_{\mathrm{s}} = 0.1$ s ($i(t_{\mathrm{s}})$) against E, that is, normal pulse voltammograms, of the HTCO-assisted transfer of Pb^{2+} ion across the NB/W interface at different ${}^{*}c^{\mathrm{W}}_{\mathrm{Aw}}$'s and at $({}^{*}c^{\mathrm{W}}_{\mathrm{M}})_{\mathrm{t}} = 0.10$ mM and ${}^{*}c^{\mathrm{O}}_{\mathrm{L}} = 40$ mM. The S-shaped i–E curves with well-defined limiting currents were observed. The half-wave potential shifted to more positive potentials with increased ${}^{*}c^{\mathrm{W}}_{\mathrm{Aw}}$, whereas the limiting current decreased with increased ${}^{*}c^{\mathrm{W}}_{\mathrm{Aw}}$. Such results confirm again[1] that the voltammetric behavior of the HTCO-assisted transfer of Pb^{2+} ion from W-phase containing $\mathrm{citrate}^{3-}$ ion to NB-phase should be interpreted by CE mechanism, that



cell (I)

Chart 1.

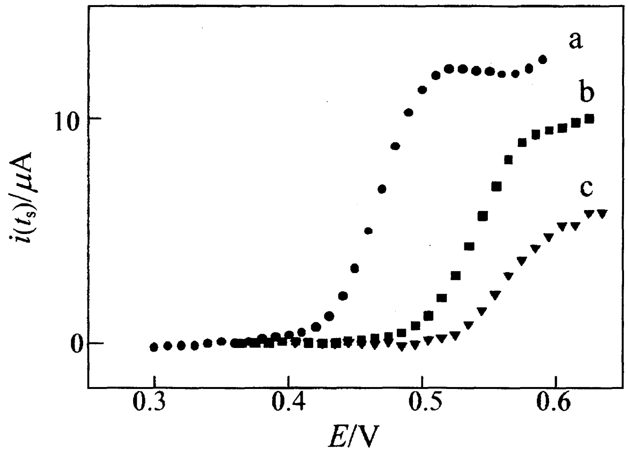


Fig. 1. Plots of chronoamperometric currents sampled at a constant sampling time of $t_{\rm s}$ = 0.1 s, $i(t_{\rm s})$, against applied potential, E, that is, normal pulse voltammograms, of HTCO-assisted transfer of $\mathrm{Pb^{2+}}$ ion across the NB/W interface at ${}^*c^{\rm W}_{\rm Aw}$ = a; 0 (●), b; 1.0 (■), and c; 5.0 (▼) mM and at $({}^*c^{\rm W}_{\rm M})_{\rm t}$ = 0.10 mM and ${}^*c^{\rm O}_{\rm L}$ = 40 mM.

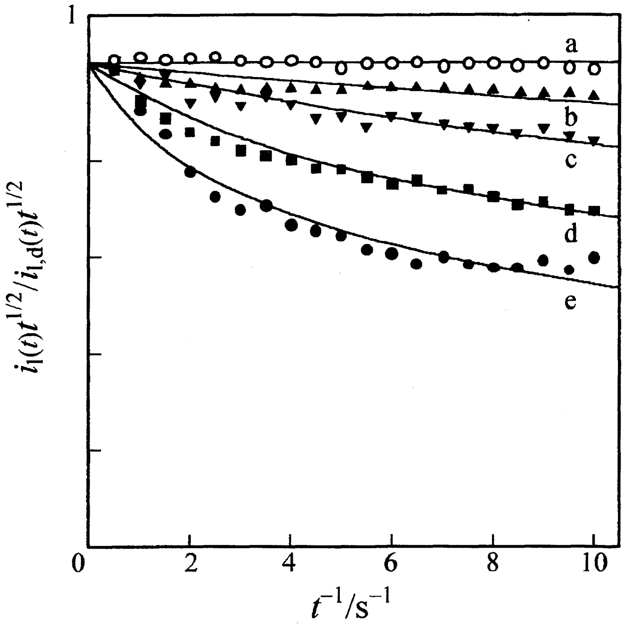


Fig. 2. Plots of $i_{\rm l}(t)t^{1/2}$ against t^{-1} at ${}^*c^{\rm W}_{\rm Aw}$ = a; 0 (○), b; 0.50 (▲), c; 1.0 (▼), d; 2.0 (■), and e; 5.0 (●) mM and $({}^*c^{\rm W}_{\rm M})_{\rm t}$ = 0.10 mM, $i_{\rm l}(t)$ being measured at E = 0.54 V for plot a and at E = 0.64 V for plots b, c, d, and e. The ordinate is normalized by $i_{l,\rm d}(t)$ (see, text).

is, ion-transfer with preceding chemical reaction.

Plot a in Fig. 2 shows the plot of $i_{\rm l}(t)t^{1/2}$ observed at ${}^*c^{\rm W}_{\rm Aw}$ = 0 and $({}^*c^{\rm W}_{\rm M})_{\rm t}$ = 0.10 mM against t^{-1}, $i_{\rm l}(t)$ being measured at E = 0.54 V. In the figure, the ordinate is normalized by $i_{\rm l,d}(t)$ obtained for each ${}^*c^{\rm W}_{\rm Aw}$'s (see below). The observed $i_{\rm l}(t)t^{1/2}$ was nearly independent of t from 0.1 to 2 s, indicating that the limiting current is a diffusion-controlled current, defined by Eq. 8, in the range of t tested. The 95% confidence limit of the mean value of $i_{\rm l}(t)t^{1/2}$ ($= i_{\rm d}(t)t^{1/2}$) at $({}^*c^{\rm W}_{\rm M})_{\rm t}$ = 0.10 mM was determined to be 3.74±0.04 $\mu\mathrm{A\,s^{1/2}}$, giving $D^{\rm W}$ = $(7.6_1 \pm 0.1_6) \times 10^{-6}$ $\mathrm{cm^2\,s^{-1}}$ by Eq. 8, which is in harmony with $D^{\rm W}$ = 8.28×10^{-6} $\mathrm{cm^2\,s^{-1}}$ obtained by polarography with a dropping mercury electrode.[9] Furthermore, $i(t_{\rm s})$ at $t_{\rm s}$ = 0.1 s was analyzed as a function of E (see, plot a in Fig. 1). The regression line of the E vs. $\log\,[i(t_{\rm s})/(i_{l,\rm d}(t_{\rm s}) - i(t_{\rm s}))]$ plot was expressed by

$$E/\mathrm{V} = (0.463 \pm 0.002) + (0.032 \pm 0.002)\log\,[i(t_{\rm s})/(i_{\rm l,d}(t_{\rm s}) - i(t_{\rm s}))], \tag{15}$$

with $MS_{\rm E}$ of 6×10^{-6} $\mathrm{V^2}$, $MS_{\rm E}$ being the mean square error.[10] The slope of 0.032±0.002 V/decade is in agreement with the theoretical value of 0.0296 V/decade for a reversible transfer of a divalent ion. The ${}_{\rm r}E_{1/2}$ was determined to be 0.463±0.002 V, which coincides with ${}_{\rm r}E_{1/2}$ = 0.463 V obtained by cyclic voltammetry.[11] These results indicate again that the HTCO-assisted transfer of $\mathrm{Pb^{2+}}$ ion in the absence of $\mathrm{citrate^{3-}}$ ion is a diffusion-controlled reversible process.

Similarly, the observed $i_{\rm l}(t)t^{1/2}$ at different ${}^*c^{\rm W}_{\rm Aw}$'s were plotted against t^{-1} (see plots b, c, d, and e in Fig. 2), $i_{\rm l}(t)$ being measured at E = 0.64 V, and Eq. 12 was fitted to the plots. The 95% confidence limits on the mean value of $i_{l,\rm d}(t)t^{1/2}$, that is, extrapolated values of $i_{\rm l}(t)t^{1/2}$ to $t^{-1} = 0$ were determined to be 3.62±0.04, 3.67±0.06, 3.55±0.07,

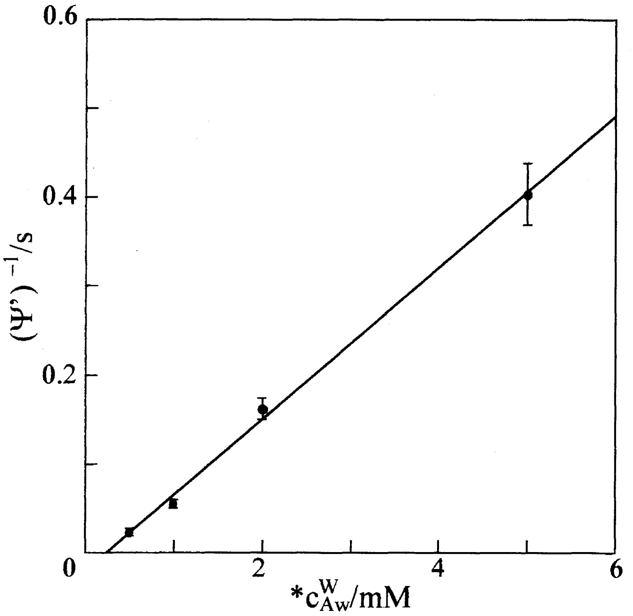


Fig. 3. Plot of $(\Psi')^{-1}$ against $^{*}c^{W}_{Aw}$. Vertical bars indicate the 95% confidence intervals.

and 3.95±0.25 μA $s^{1/2}$ at $^{*}c^{W}_{Aw} = 0.5$, 1.0, 2.0, and 5.0 mM, respectively. These values coincide with each other and with $i_{l,d}(t)t^{1/2} = 3.74$ μA $s^{1/2}$ obtained above at $^{*}c^{W}_{Aw} = 0$, within experimental errors. Also, using these $i_{l,d}(t)t^{1/2}$-values, the 95% confidence limits on the mean value of $(\Psi')^{-1}$ $(= (K^{w})^2/l)$ are determined to be $(\Psi')^{-1} = (2.3\pm0.4)\times10^{-2}$, $(5.5\pm0.5)\times10^{-2}$, $(1.6\pm0.1)\times10^{-1}$, and $(4.0\pm0.4)\times10^{-1}$ s at $^{*}c^{W}_{Aw} = 0.5$, 1.0, 2.0, and 5.0 mM, respectively. The solid lines on plots b, c, d, and e in Fig. 2 indicate the values calculated by Eq. 12 on the $(\Psi')^{-1}$ -values.

When $K^{W} \gg 1$ (see below), the measured values of $(\Psi')^{-1}$ can be approximated by

$$(\Psi')^{-1} = ((K^{W}_{MAw})^2/k^{W}_{f})^{*}c^{W}_{Aw}. \qquad (16)$$

In Fig. 3 the measured values of $(\Psi')^{-1}$, described above, are plotted against $^{*}c^{W}_{Aw}$. The regression line fitted to the plot is expressed by

$$(\Psi')^{-1}/s = (85\pm14)(^{*}c^{W}_{Aw}/M) + (-0.02\pm0.04), \qquad (17)$$

with MS_E of 1.2×10^{-4} s^2, which is shown by the solid line in Fig. 3, giving $K^{W}_{MAw}/(k^{W}_{f})^{1/2} = 9.2\pm0.8$ $M^{-1/2}$ $s^{1/2}$. The result is in harmony with $K^{W}_{MAw}/(k^{W}_{f})^{1/2} = 6.3\pm1.1$ $M^{-1/2}$ $s^{1/2}$ obtained by potential sweep voltammetry.[1]

Figure 4 shows the plots of $i(t)t^{1/2}$, measured at various E's and normalized by $i_{l,d}(t) = 3.74(t/s)^{-1/2}$ μA, against t^{-1} at $^{*}c^{W}_{Aw} = 2.0$ mM and $(^{*}c^{W}_{M})_t = 0.10$ mM. Equation 10 was fitted to the plots to determine Ψ^{-1} and $_{r}i(t)/i_{l,d}(t)$ each for given E values. The determined values of Ψ^{-1} increased with increasing E, in accordance with the prediction from Eq. 11 with Eq. 6, and approached a limiting value of $(\Psi')^{-1} = (1.6\pm0.1)\times10^{-1}$ s with increased E, which is in good agreement with the calculated value of $(\Psi')^{-1} = (1.7\pm0.3)\times10^{-1}$ s by Eq. 17 at $^{*}c^{W}_{Aw} = 2.0$ mM. Also, in Fig. 5, the determined values of $_{r}i(t)/i_{l,d}(t)$ are plotted against E. The regression line of the E vs. $\log[_{r}i(t)/(i_{l,d}(t) - {}_{r}i(t))]$ plot, according to Eq. 5, was expressed by

$$E/\mathrm{V} = (0.560\pm0.002) + (0.036\pm0.003) \times\log[_{r}i(t)/(i_{l,d}(t) - {}_{r}i(t))], \qquad (18)$$

with MS_E of 5×10^{-6} V^2. The solid line in Fig. 5 indicates the calculated value by Eq. 18. The slope of 0.036±0.003 V/decade appears slightly large compared with the theoretical value of a reversible transfer of a divalent ion, which may be ascribed to uncompensated iR potential drop. The

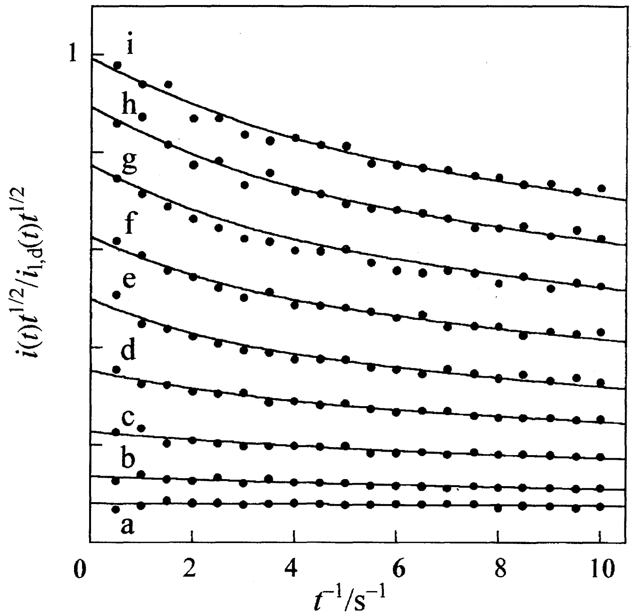


Fig. 4. Plots of $i(t)t^{1/2}$ measured at E = a; 0.52, b; 0.53, c; 0.54, d; 0.55, e; 0.56, f; 0.57, g; 0.58, h; 0.59, and i; 0.60 V against t^{-1} at $^{*}c^{W}_{Aw} = 2.0$ mM and $(^{*}c^{W}_{M})_t = 0.10$ mM. The ordinate is normalized by using $i_{l,d}(t) = 3.74(t/s)^{-1/2}$ μA.

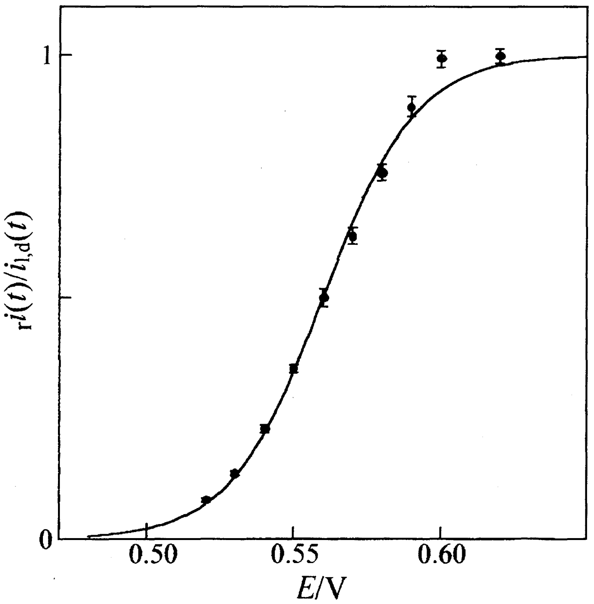


Fig. 5. Plot of $_{r}i(t)/i_{l,d}(t)$ against E at $^{*}c^{W}_{Aw} = 2.0$ mM. Vertical bars indicate the 95% confidence intervals.

${}_{\mathrm{r}}E_{1/2}$, was determined to be 0.560±0.002 V from the intercept, which is in good agreement with ${}_{\mathrm{r}}E_{1/2} = 0.559 \pm 0.002$ V obtained by potential sweep voltammetry.[1] Thus, using Eq. 9, $\log K^{\mathrm{W}}_{\mathrm{MAw}}$ was determined to be 6.0±0.1, where ${}_{\mathrm{r}}E_{1/2} = 0.463 \pm 0.002$ V at ${}^{*}c^{\mathrm{W}}_{\mathrm{Aw}} = 0$, as stated above, was used for the value of $E^{0\prime}_{\mathrm{M/ML}} - (RT/zF) \ln [(1+K^{\mathrm{O}*}c^{\mathrm{O}}_{\mathrm{L}})/K^{\mathrm{O}} + (RT/zF]) \ln [(D^{\mathrm{W}}/D^{\mathrm{O}})^{1/2}]$. The $\log K^{\mathrm{W}}_{\mathrm{MAw}}$ value is in harmony with $\log K^{\mathrm{W}}_{\mathrm{MAw}} = 6.2_5 \pm 0.2$ obtained by potential sweep voltammetry[1] as well as the thermodynamic formation constant of $\log K^{\mathrm{W}}_{\mathrm{MAw}} = 6.50$ obtained by potentiometry with a Pb electrode.[12]

Using $K^{\mathrm{W}}_{\mathrm{MAw}}/(k^{\mathrm{W}}_{\mathrm{f}})^{1/2} = 9.2 \pm 0.8\ \mathrm{M}^{-1/2}\,\mathrm{s}^{1/2}$ and $\log K^{\mathrm{W}}_{\mathrm{MAw}} = 6.0 \pm 0.1$, the 90% confidence limits on the mean values of $k^{\mathrm{W}}_{\mathrm{f}}$ and $k^{\mathrm{W}}_{\mathrm{b}}$ for 1 : 1 Pb^{2+}–citrate^{3-} complex can be calculated to be $(1.2 \pm 0.6) \times 10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $(1.2 \pm 0.3) \times 10^{4}\ \mathrm{s}^{-1}$, respectively, whereas potential sweep voltammetry gave $k^{\mathrm{W}}_{\mathrm{f}} = (8.0 \pm 7.3) \times 10^{10}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $k^{\mathrm{W}}_{\mathrm{b}} = (4.50 \pm 2.5) \times 10^{4}\ \mathrm{s}^{-1}$.[1] The $k^{\mathrm{W}}_{\mathrm{f}}$ is on the order of the rate constants for a diffusion-controlled bimolecular reaction.[13] Also, it is noted that $K^{\mathrm{W}} \gg 1$ and $lt \gg 1$ at $t > 0.1$ s, as assumed in the discussion above.

The potential step voltammetry has also been applied to analyze the transfer of protonated procaine across NB/W interface, and to determine the rate constants of the proton transfer between procaine and acid components of Good's buffers.[14,15]

In potential step voltammetry or NPV, the kinetics of the preceding chemical reaction is analyzed on the basis of the limiting current, which is free from the potential control error. In contrast, in potential sweep voltammetry or CV, the kinetics is analyzed on the basis of the peak current which is affected by the potential control error. The potential control error such as that due to uncompensated *iR* drop may not completely be eliminated even with a three- or four-electrode potentiostat. This will be one reason why the relative standard deviations of the $K^{\mathrm{W}}_{\mathrm{MAw}}/(k^{\mathrm{W}}_{\mathrm{f}})^{1/2}$-value determined by NPV was 9%, which is much smaller than that of 17% by CV (see above). In conclusion, potential step voltammetry or NPV can be applied advantageously in comparison with potential sweep voltammetry or CV to study the kinetics of the chemical reaction which precedes the charge transfer process.

Appendix

Let the O/W interface be placed as the origin of coordinates ($x = 0$) and the O- and W-phases in the regions $-\infty < x \leq 0$ and $0 \leq x < +\infty$, respectively. The diffusion process of the M and MAw in W-phase can be formulated for their concentrations $c^{\mathrm{W}}_{\mathrm{M}}$ and $c^{\mathrm{W}}_{\mathrm{Aw}}$, respectively, by

$$\frac{\partial c^{\mathrm{W}}_{\mathrm{M}}}{\partial t} = D^{\mathrm{W}} \frac{\partial^2 c^{\mathrm{W}}_{\mathrm{M}}}{\partial x^2} - k^{\mathrm{W}\prime}_{\mathrm{f}} \left(c^{\mathrm{W}}_{\mathrm{M}} - \frac{1}{K^{\mathrm{W}}} c^{\mathrm{W}}_{\mathrm{MAw}} \right) \tag{A1}$$

and

$$\frac{\partial c^{\mathrm{W}}_{\mathrm{MAw}}}{\partial t} = D^{\mathrm{W}} \frac{\partial^2 c^{\mathrm{W}}_{\mathrm{MAw}}}{\partial x^2} + k^{\mathrm{W}\prime}_{\mathrm{f}} \left(c^{\mathrm{W}}_{\mathrm{M}} - \frac{1}{K^{\mathrm{W}}} c^{\mathrm{W}}_{\mathrm{MAw}} \right). \tag{A2}$$

On introducing new variables ψ^{W} and ϕ^{W} defined by

$$\Psi^{\mathrm{W}} = c^{\mathrm{W}}_{\mathrm{M}} + c^{\mathrm{W}}_{\mathrm{Aw}} \tag{A3}$$

and

$$\phi^{\mathrm{W}} = c^{\mathrm{W}}_{\mathrm{M}} - \frac{1}{K^{\mathrm{W}}} c^{\mathrm{W}}_{\mathrm{MAw}}, \tag{A4}$$

Equations A1 and A2 can be transferred into

$$\frac{\partial \Psi^{\mathrm{W}}}{\partial t} = D^{\mathrm{W}} \frac{\partial^2 \Psi^{\mathrm{W}}}{\partial x^2} \tag{A5}$$

and

$$\frac{\partial \phi^{\mathrm{W}}}{\partial t} = D^{\mathrm{W}} \frac{\partial^2 \phi^{\mathrm{W}}}{\partial x^2} - l \Psi^{\mathrm{W}}. \tag{A6}$$

The initial and boundary conditions are given by

$$t = 0, \qquad 0 \leq x < +\infty :$$

$$\psi^{\mathrm{W}} = {}^{*}c^{\mathrm{W}}_{\mathrm{M}} + {}^{*}c^{\mathrm{W}}_{\mathrm{Aw}} = ({}^{*}c^{\mathrm{W}}_{\mathrm{M}})_{\mathrm{t}} \tag{A7a}$$

and

$$\phi^{\mathrm{W}} = 0, \tag{A7b}$$

$$t > 0, \qquad x = 0 :$$

$$D^{\mathrm{W}} \left[\frac{\partial \psi^{\mathrm{W}}}{\partial x} \right]_{x=0} = f(t) \tag{A8a}$$

and

$$D^{\mathrm{W}} \left[\frac{\partial \psi^{\mathrm{W}}}{\partial x} \right]_{x=0} = f(t), \tag{A8b}$$

$$t > 0, \qquad x \to +\infty :$$

$$\psi^{\mathrm{W}} = {}^{*}c^{\mathrm{W}}_{\mathrm{M}} + {}^{*}c^{\mathrm{W}}_{\mathrm{Aw}} = ({}^{*}c^{\mathrm{W}}_{\mathrm{M}})_{\mathrm{t}} \tag{A9a}$$

and

$$\phi^{\mathrm{W}} = 0, \tag{A9b}$$

where $f(t)$ is the total flux of M ion at the interface. Then, by using the standard method,[3—5] the surface concentration of M in W-phase, ${}^{\mathrm{s}}c^{\mathrm{W}}_{\mathrm{M}}$, can be expressed by

$${}^{\mathrm{s}}c^{\mathrm{W}}_{\mathrm{M}} = \frac{1}{1 + K^{\mathrm{W}}} \left[({}^{*}c^{\mathrm{W}}_{\mathrm{M}})_{\mathrm{t}} - \frac{1}{(D^{\mathrm{W}})^{1/2}} \int_0^t \frac{f(u)(1 + k^{\mathrm{W}} \exp[-l(t-u)])}{\pi^{1/2}(t-u)^{1/2}} \mathrm{d}u \right]. \tag{A10}$$

Similarly, the diffusion process of the sum of M and ML in O-phase can be expressed for the concentration of the sum of M and ML in O-phase ($\psi^{\mathrm{O}} = c^{\mathrm{O}}_{\mathrm{M}} + c^{\mathrm{O}}_{\mathrm{ML}}$) by

$$\frac{\partial \Psi^{\mathrm{O}}}{\partial t} = D^{\mathrm{O}} \frac{\partial^2 \Psi^{\mathrm{O}}}{\partial x^2}. \tag{A11}$$

The initial and boundary conditions are given by

$$t = 0, \qquad -\infty < x \leq 0 :$$

$$\psi^{\mathrm{O}} = 0,$$

$$t > 0, \qquad x = 0 : \tag{A12}$$

$$D^{\mathrm{W}} \left[\frac{\partial \psi^{\mathrm{W}}}{\partial x} \right]_{x=0} = f(t) = \frac{i(t)}{zFA}, \tag{A13}$$

$$t > 0, \qquad x \to -\infty :$$

$$\psi^{\mathrm{O}} = 0. \tag{A14}$$

Then, the surface concentration of the sum of M and ML $({}^{\mathrm{s}}c^{\mathrm{O}}_{\mathrm{M}})_{\mathrm{t}}$ in O-phase is expressed by

$$({}^{\mathrm{s}}c_{\mathrm{M}}^{\mathrm{O}})_{\mathrm{t}} = \frac{1}{(D^{\mathrm{O}})^{1/2}} \int_0^t \frac{f(u)}{\pi^{1/2}(t-u)^{1/2}} \mathrm{d}u. \tag{A15}$$

In this study, we assume (vi) that the rates of the formation and dissociation of ML in O-phase, that is,

$$\mathrm{M(O)} + \mathrm{L(O)} = \mathrm{ML(O)}, \tag{A16}$$

are sufficiently fast so that the following relationships for the concentrations of M, L, and ML in O-phase is valid at

$$t > 0, \qquad -\infty < x \leq 0:$$
$$K^{\mathrm{O}} = \frac{c_{\mathrm{ML}}^{\mathrm{O}}}{c_{\mathrm{M}}^{\mathrm{O}} c_{\mathrm{L}}^{\mathrm{O}}}. \tag{A17}$$

We also assume (vii) that the rate of ion-transfer at O/W interface (see Eq. 1) is sufficiently fast so that Nernst equation for the surface concentration of M in W-phase and L and M in O-phase is valid at

$$t > 0, \qquad x = 0:$$
$$\frac{{}^{\mathrm{s}}c_{\mathrm{ML}}^{\mathrm{O}}}{{}^{\mathrm{s}}c_{\mathrm{M}}^{\mathrm{W}}\, {}^{\mathrm{s}}c_{\mathrm{L}}^{\mathrm{O}}} = \lambda_{\mathrm{E}} = \exp\left[\frac{zF}{RT}(E - E_{\mathrm{M/ML}}^{0\prime})\right]. \tag{A18}$$

Combination of Eqs. A10 and A15 with Eq. A18 gives

$$(D^{\mathrm{W}})^{1/2}({}^{*}c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}} = (1 + \frac{1}{\lambda_E'}) \int_0^t \frac{f(u)}{\pi^{1/2}(t-u)^{1/2}} \mathrm{d}u$$
$$+K^{\mathrm{W}} \int_0^t \frac{f(u) \exp\left[-l(t-u)\right]}{\pi^{1/2}(t-u)^{1/2}} \mathrm{d}u \tag{A19}$$

with

$$\lambda_{\mathrm{E}}' = \exp\left[\frac{zF}{RT}(E - {}_{\mathrm{r}}E_{1/2})\right], \tag{A20}$$

where ${}_{\mathrm{r}}E_{1/2}$ is defined by Eq. 9.

When λ_{E}' is constant and independent from t, Eq. A19 is easily solved to give Eq. 4. Note that for sufficiently positive potential of E, that is, when $1/\lambda_{\mathrm{E}} \rightarrow 0$, Eq. 4 is reduced to the equation of the limiting current with preceding chemical reaction (see Eq. 26 in Ref. 3).

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