Study of Ion Transfer at a Liquid–Liquid Interface by Current Linear Sweep Voltammetry. 1. The 1,10-Phenanthroline–Phenanthrolinium System

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Study of Ion Transfer at a Liquid–Liquid Interface by Current Linear Sweep Voltammetry. 1. The 1,10-Phenanthroline–Phenanthrolinium System

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1,10-Phenanthroline (phen) and its protonated form (phen-H$^+$) extraction system were electrochemically studied at the water–1,2-dichloroethane (DCE) interface using current linear sweep voltammetry (CLSV). At scan rates, v, as high as 500 μA/s, the relationships of i_s vs $v^{1/3}$, $E(1/2)$ vs v, i_s vs $A^{2/3}$, and i_s vs $c_L^{2/3}$ were examined in this system to analyze its kinetics by means of diffusion control theory, where i_s is the saturation current, $E(1/2)$, the half-wave potential, A the interfacial area, and c_L the concentration of ligand in the bulk organic phase. A simple IR compensation method for the solution resistance was also developed. The linear relationship for i_s vs $v^{1/3}$ was maintained up to $v = 500$ μA/s from 0 μA/s, and $E(1/2)$ was constant in the range of $v = 0.25–500$ μA/s. The i_s changed linearly with $A^{2/3}$ ($A = 0.099–0.314$ cm^2) and with $c_L^{2/3}$ ($c_L = 0.05–0.5$ mM). These results demonstrate that within our experimental conditions the kinetics of this system is controlled entirely by the diffusion of phen from organic bulk phase to aqueous interface even at $v = 500$ μA/s.

INTRODUCTION

Ion-transfer kinetics at the liquid–liquid interface has been extensively investigated by electrochemical techniques[1-20] as well as by other methods.[21] In particular, dc polarography,[4-12] ac polarography,[17,19] cyclic voltammetry,[13-16] and chronopotentiometry[6,8,20] have been found to be very useful for the study of interfacial kinetics of ion transfer between two phases. The methods used in these studies include both potential and current sweep methods. The more recently developed current sweep method has been now widely applied to the analysis of the ion transfer kinetics.[4-12,20] Using current linear sweep voltammetry would permit extending study of kinetics to much faster reactions. Cyclic voltammetry (with potential sweep) has proven to be very useful,[13,15-19] especially for analyzing ion transfer processes which involve fast and/or complicated chemical reactions.

Current sweep chronopotentiometry has been employed to characterize redox electrode reactions.[22-25] Wang and Pang[20] developed this method for analyzing ion-transfer kinetics of metal extraction at liquid–liquid interface, which they called "Chronopotentiometry with cyclic linear current scanning". Their study was limited to low scan rates (<10 μA/s), however. In this work, we were able to extend this to high scan rates (<500 μA/s) which enabled us to analyze fast reaction kinetics in systems containing metal extractants. The technique is preferably named as current linear sweep voltammetry (CLSV) or current sweep cyclic voltammetry (CSCV), to clarify its relationship to voltammetry.

The kinetics of 1,10-phenanthroline (phen) and its protonated form (phen-H$^+$) extraction system at the water–1,2-dichloroethane (DCE) interface were investigated by using both current sweep polarography and CLSV. The relationships of i_s vs $v^{1/3}$, $E(1/2)$ vs v, i_s vs $A^{2/3}$, and i_s vs $c_L^{2/3}$, particularly at high scan rates ($v < 500$ μA/s), were examined to analyze its kinetics in terms of diffusion control theory (here i_s is the saturation current, $E(1/2)$ the half-wave potential, A the interfacial area, and c_L the concentration of ligand). Basing our analysis on principles of voltammetry, the saturation current rather than the transition time of chronopotentiometry and the half-wave potential have been employed.

EXPERIMENTAL SECTION

A previously reported computer-driven system for measuring CLSV or current scan polarograms and the relevant data analysis were used.[4,5,26] The current scan polarography cell for the ascending water electrode and/or the CLSV cell for the stationary water drop electrode both have 4-electrode configurations.[26] In the CLSV experiment the size of the stationary water drop

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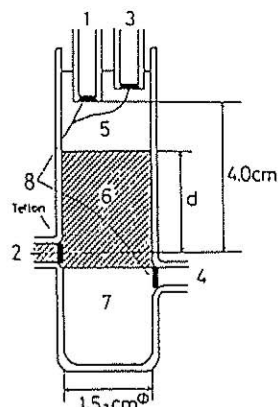
Figure 1. Electrolytic cell for flat interface electrode: (1) reference electrode for aqueous phase (RE1), (2) reference electrode for organic phase (RE2), (3) counter electrode for aqueous phase (CE1), (4) counter electrode for organic phase (CE2), (5) working aqueous solution, (6) working organic solution, (7) 2.8 M MgSO₄ aqueous solution, (8) sintered glass; interfacial area, 1.84 cm².

electrode was controlled as follows: the aqueous solution was fed at a slow constant flow rate (7.03×10^{-4} cm³ s⁻¹) by a syringe pump; measurement of drop time was initiated the moment a drop separated from the Teflon capillary. When 5–25 s elapsed (the capillary has a drop time of 53.5 s in a disconnected circuit under these conditions), the stopcock between the drop and the syringe pump was closed. The flat interface electrode cell was also employed for CLSV (Figure 1). The aqueous phase in Figure 1 (7) consists of 2.8 M magnesium sulfate used as an internal solution for the organic phase counter electrode (CE2). Its density ($d = 1.28$ g/cm³) is, logically, of higher density than DCE solution ($d = 1.25$ g/cm³). The cell to be studied can be described by

(RE1) Ag|AgCl|1M LiCl aq.|0.17M Na₂SO₄ aq.|working aq. soln.

|working DCE soln.|0.01M THA⁺TPB⁻ DCE|0.17M Na₂SO₄ aq.

|1M LiCl aq.|AgCl|Ag (RE2)

(CE1) Ag|AgCl|1M LiCl aq.|0.17M Na₂SO₄ aq.|working aq. soln.

|working DCE soln.|2.7₄M MgSO₄ aq.|0.17M Na₂SO₄ aq.

|1M LiCl aq.|AgCl|Ag (CE2)

Sodium sulfate (0.17 M) containing 0.01 M acetate buffer was used as the aqueous working solution. Tetraheptylammonium tetraphenylborate (THA⁺,TPB⁻) was used as a supporting electrolyte in the DCE phase. THA⁺,TPB⁻ was prepared by equilibrating an 0.5 M aqueous Na⁺,TPB⁻ solution with an equal volume of 0.5 M THA⁺,Br⁻ in DCE for about 30 min. The organic phase which contains essentially all of THA⁺,TPB⁻ was then washed with portions of water (equilibrated with DCE before use) of almost equal volume until both phases tested free of impurities. This usually required about three washings. The organic solution was slowly poured into a 3-fold volume of methanol. The white precipitate, THA⁺,TPB⁻, that formed was filtered and washed with methanol. Following recrystallization from methanol, this solid was dissolved in a minimum volume of DCE. All other chemicals were of analytical reagent grade and were employed without further purification.

In current scan voltammetry, though the applied current is accurately supplied at the test interface, the solution resistance (R_s) between RE1 and RE2 must be compensated for the interface potential. A compensation method was already established in current scan polarography[26] and also in CLSV.[20,27] In this work, we developed a simplified compensation method. Figure 2 shows the CLSVs for various distances (d) between RE2 and the test

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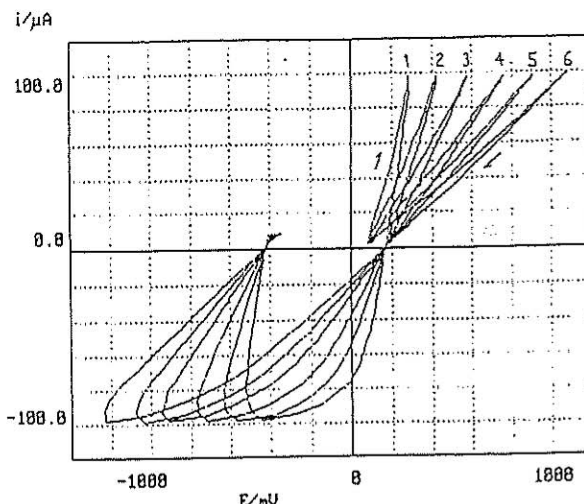

Figure 2. Current sweep cyclic voltammograms for various distances between RE2 and the test interface of base solutions. Aqueous phase, 0.17 M Na₂SO₄; organic phase, 0.01 M THA⁺TPB⁻-DCE solution; d/cm: (1) 1.0, (2) 1.5, (3) 2.0, (4) 2.5, (5) 3.0, (6) 3.5; $v = 98.0$ μA/s; compensation resistance (R_c), 2.5 kΩ. All CSCVs run after preelectrolysis, 1 μA, 2 s. Flat interface cell was used.

Table I. Distance between RE2 and the Test Interface (d), Inverse of Slope ($R_1 = E/i$), and Solution Resistance (R)

d/cm	R_1/kΩ	R/kΩ[a]	d/cm	R_1/kΩ	R/kΩ[a]
1.0	1.2	3.7	2.5	5.9	8.4
1.5	2.6	5.1	3.0	7.5	9.9
2.0	4.1	6.6	3.6	9.1	11.6

[a] $R = R_1 + R_c$ ($R_c = 2.5$ kΩ: compensation resistance). See the figure caption of Figure 2 for other conditions.

Table II. Analytical Results of Saturation Currents (i_s) and Half-Wave Potential ($E(1/2)$) for Various Scan Rates (v) from the Voltammograms of Figure 5[a]

v/(μA/s)	log (v/(μA/s))	i_s/μA	log (i_s/μA)	$E(1/2)$/V vs $E_{1/2(TEA)}$
488	2.689	185	2.266	0.108
245	2.389	149	2.172	0.102
98.0	1.991	110	2.040	0.101
50.2	1.701	84.3	1.926	0.102
25.2	1.401	68.0	1.832	0.093
10.1	1.003	49.8	1.697	0.101
5.04	0.702	40.5	1.608	0.100
2.52	0.401	31.7	1.501	0.105
1.01	0.003	25.4	1.406	0.100

av $E(1/2) = 0.101 \pm 0.004$

[a] See the caption of Figure 5 for other conditions.

interface in basic solutions. Adding the inverse of the slope ($R_1 = E/i$) for the backward scan (which is the anodic current portion of the supporting electrolyte) to the compensation resistance (R_c), the sum ($R = R_1 + R_c$) is plotted versus d (cm), resulting in a straight line. Analysis of the data from Figure 2 for d, R_1, and R are given in Table I. The equation of this line is R (kΩ) = $0.35 \pm 0.15 + (3.20 \pm 0.0_6)d$, with a correlation coefficient, r = 0.999. This result shows that when R_1 is zero (which means that a backward ion transfer resistance of supporting electrolyte becomes zero at this condition), the compensation is perfect ($R_s = R_c$). On the other hand, the value of R at $d = 0$ cm represents the resistance of aqueous solution at 4.0-cm distance in the cell. The electrode area is 1.84 cm²; therefore, the specific resistances of 0.17 M sodium sulfate aqueous solution and of 0.01 M THA⁻TPB⁻-DCE solution are calculated to be 0.16 ± 0.07 kΩ cm and $5.73 + 0.11$ kΩ cm, respectively. Figure 3 shows CLSVs for various R_c at $d = 1.0$ cm. In this case, the R_c value which should be compensated is determined to be 3.5 ± 0.15 kΩ from the above relation between R and d. It is proven that when $R_1 = 0$ Ω (in
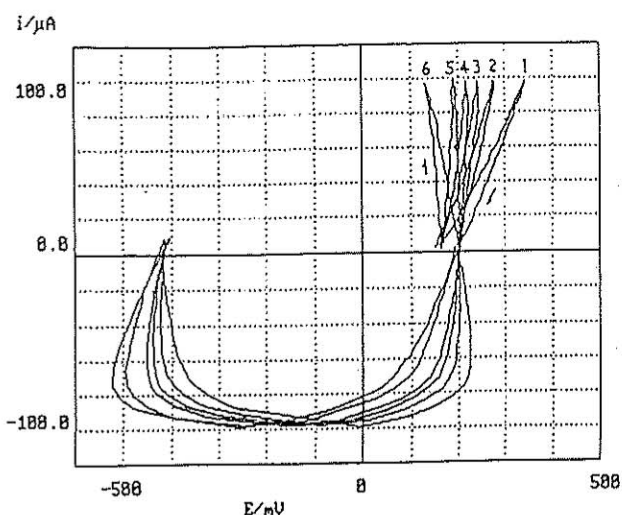
Figure 3. Current sweep cyclic voltammograms for various compensation resistances (R_c). $R_c/k\Omega$: (1) 2.5, (2) 3.0, (3) 3.5, (4) 3.7, (5) 4.0, (6) 4.5; d = 1.0 cm. Other conditions were the same as those of Figure 2.
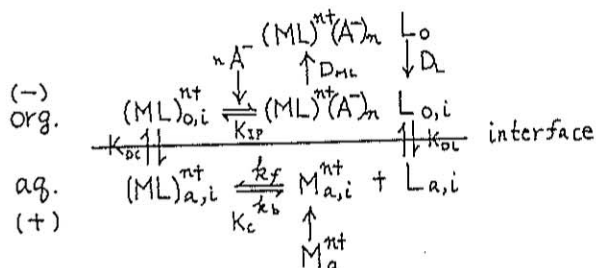

Figure 4. Schematic illustration of the simple solvent extraction system of the metal ion (M^{n+})–ligand (L) complex.

this case, in R_c = 3.7 kΩ), the compensation is perfect. It should be noted that this method can be also employed in using a stationary drop interface electrode.

RESULTS AND DISCUSSION

A simple ion-transfer process for metal solvent extraction, which includes an organic solution of a neutral ligand, L, and an aqueous solution of a metal ion, M^{a+}, is shown as Figure 4 (see Appendix for other symbols). The recent publication by Matsuda et al.[12] detailing theoretical considerations applicable to ion-transfer polarography has helped us with derivations developed in this paper.

The simplest case to consider in such a system is that in which the process kinetics are controlled only by the diffusion of ligand from the organic phase to the interface ($c_L \ll c_M$), because all the other processes, i.e., the distribution of L, the metal complexation, the ion transfer at the interface, and ion-pair formation are much faster than the organic phase ligand diffusion of L. This also includes the diffusion rates of all species in this system. When an anodic current (c_{MLA} = 0 initially) is observed, the ion-transfer process giving rise to it can be described the following scheme:
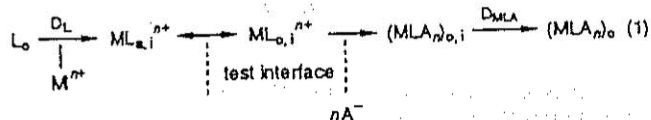
This scheme represents the same condition as the simplest ion-transfer process:

$$(\text{ion})_a^{n+} \leftrightarrow (\text{ion})_o^{n+}$$
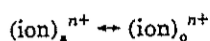
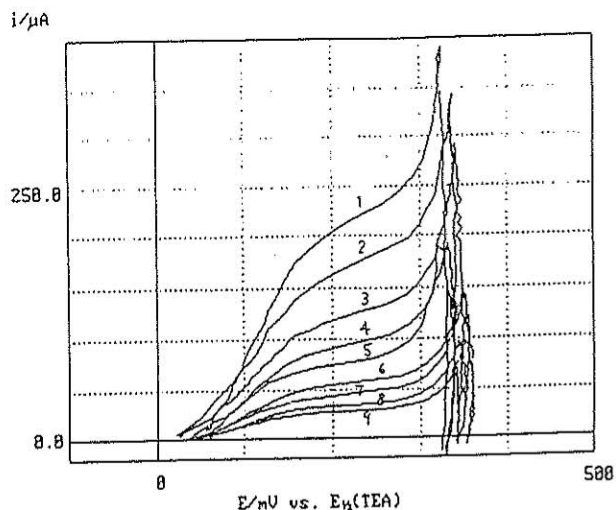In this condition, the relation between the saturated current,

Figure 5. Current linear sweep voltammograms of phen-H$^+$ system for various scan rates (v). Aqueous phase, 0.17 M Na$_2$SO$_4$, pH 4.6 buffered by 0.01 M sodium acetate and acetic acid; organic phase, 0.2 mM phen + 0.01 M THA$^+$TPB$^-$DCE solution; v/μA s^{-1}: (1) 488, (2) 245, (3) 98.07, (4) 50.2, (5) 25.2, (6) 10.1, (7) 5.04, (8) 2.52, (9) 1.01.

i_s, and various parameters was found to be[20]

$$i_s = (3\pi^{1/2}/4)^{2/3}(nFAc_L)^{2/3}D_L^{1/3}v^{1/3} \qquad (2)$$

and the half-wave potential, $E(1/2)$

$$E(1/2) = E_{1/2}^r - (0.0155/n) \text{ at 298 K} \qquad (3)$$

As may be seen from eq 2, i_s changes linearly with n and A, with c_L to the $^2/_3$ power, and with D_L and v to the $^1/_3$ power. Thus, the dependence of i_s upon these parameters is distinctly different from that of the peak current for potential linear sweep voltammetry (PLSV) or potential sweep cyclic voltammetry (PSCV).[28-30] The independence of $E(1/2)$ of all parameters except for n and T, shown in eq 3, is also the case of the peak potential for PLSV and cyclic voltammetry.[28-30]

The ion-transfer kinetics of phen-H$^+$ system was studied by CLSV at scan rates up to 500 μA/s. This work demonstrated that this system, known from polarographic studies[4] to be diffusion-controlled, retains this characteristic even at high scan rates. Anodic waves of CLSV for this system for various scan rates are given in Figure 5. The shape of CLSV traces, which have no peaks as do those in PSCV, are unchanged with increasing scan rates; the current, however, increases with scan rate.

A linear relationship is obtained between log i_s (μA) and log v (μA/s):

$$\log i_s = (1.38 \pm 0.01) + (0.33 \pm 0.01) \log v \qquad r = 0.998$$

The observed slope, 0.32$_8$, agrees with that shown in eq 2, 0.33$_2$, within experimental error ($\sim$5%). The half-wave potential, $E(1/2)$, was independent of the scan rate throughout the range studied. These results also show that phen-H$^+$ system is controlled only by the diffusion of phen even at scan rates up to 500 μA/s. Relating log i_s and log v will be very useful for analyzing similar data whether or not a system is diffusion controlled.

The dependence of i_s upon the electrode area, A, and the concentration of phen, c_{phen}, were examined experimentally. The stationary drop interface electrode was employed so that the dependence of i_s upon c_{phen} and the half-wave potential could be compared with those of the polarogram at the same

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Table III. Dependence of Saturation Current (i_s) upon Interfacial Area (A)

t_1/s^a	$A'/cm^{2\ b}$	$A/cm^{2\ c}$	log (A/cm^2)	$i_s/\mu A$	log $(i_s/\mu A)$
25.00	0.327	0.314	−0.504	27.9	1.445
20.0	0.282	0.233	−0.571	25.0	1.398
15.0	0.233	0.219	−0.659	21.2	1.326
10.0	0.178	0.164	−0.785	17.4	1.242
5.0	0.112	0.099	−1.006	12.5	1.097

[a] Elapsed time during water solution flowing. [b] $A' = 4.84((7.03 \times 10^{-4})t_1)^{2/3}$. [c] $A = A' - 0.013$. $c_{phen} = 0.200$ mM, pH 4.6, and $v = 19.6$ $\mu A/s$.

Table IV. Dependence of Limiting Current (i_l) for Polarogram and Saturation Current (i_s) for CLSV upon Concentration of phen (c_{phen}) and these Half-Wave Potentials ($E_{1/2}$, $E(1/2)$)

	polarography[e]		CLSV[b]	
log (c_{phen}/mM)	log $(i_l/\mu A)$	$E_{1/2}/V^c$	log $(i_s/\mu A)$	$E(1/2)/V^c$
−0.320	1.411	0.110	1.682	0.100
−0.621	1.106	0.115	1.477	0.107
−0.922	0.808	0.113	1.270	0.102
−1.320	0.375	0.118	1.044	0.097
−1.621	0.057	0.121		

[a] $m = 6.33 \times 10^{-3}$ cm³/s, $t = 6.92$ s, $v = 0.10$ $\mu A/s$. [b] $A = 0.314$ cm², $v = 19.6$ $\mu A/s$. [c] Half-wave potential of TEA ($E_{1/2}$(TEA)) was used as the standard potential.

experimental conditions. The drop surface area, assumed to be spherical, was calculated from the flow rate of syringe (7.03×10^{-4} cm³ s⁻¹) and the time of flow (5–25 s), which was corrected for the shielded area (0.013 cm²) was subtracted.[5] The scan rate was 19.6 $\mu A/s$. The results are given in Table III. The plot of five points of log i_s vs log (A) gives a straight line:

$$\log i_s = (1.79 \pm 0.01_2) + (0.69 \pm 0.02) \log A$$

$r = 0.998$. The observed slope 0.69 agrees within 3.9% with that from eq 2 (0.67).

CLSV and polarographic runs were conducted on solutions in which c_{phen} varied from 2.39×10^{-5} to 4.78×10^{-4} M, and the i_s and $E(1/2)$ of CLSV, as well as the polarographic limiting current (i_l) and $E_{1/2}$ were obtained (Table IV). In the polarographic experiment, the flow rate was 6.3×10^{-3} cm³ s⁻¹, with a drop time of 6.9 s in the vicinity of the wave. The scan rate was 19.6 $\mu A/s$ and A was 0.313 cm² in measuring CLSV. The dependence of i_l and i_s upon c_{phen} (mM) can be described by

$$\log i_l = (1.75 \pm 0.01) + (1.04 \pm 0.01) \log c_{phen} \qquad r = 0.999_7$$

$$\log i_s = (1.88 \pm 0.02) + (0.64 \pm 0.02) \log c_{phen} \qquad r = 0.998$$

The polarographic results are in reasonable agreement with the Ilkovic equation, since the observed slope, 1.04, differs by 4.2% from theory. The CLSV results also conform well, since the observed slope, 0.64, is within 3.9% of that predicted in eq 2. The polarographic and CLSV half-wave potentials, $E_{1/2}' = (0.102 \pm 0.004)$ V and $E(1/2) = (0.115 \pm 0.004)$ V, respectively, differed by only 0.013 ± 0.006 V, as expected from eq 3, when n is 1. This result also means that $E(1/2)$ is independent of c_{phen}. Hence, this relation applies whether or not a sysem is perfectly controlled by diffusion.

CONCLUSIONS

It was proved in phen-H⁺ system that i_s changed linearly with $v^{1/3}$ even at $v = 500$ $\mu A/s$, $A^{2/3}$ and $c_L^{2/3}$, and that $E(1/2)$

did not change with these parameters. These results show that phen-H⁺ extraction process is controlled only by diffusion of phen from organic phase to interface of water phase even at the high scan rates of CLSV. The demonstrated utility of CLSV for the analysis of processes involving ion transfer has provided the basis for further studies of metal extraction systems now under way in our laboratory.

ACKNOWLEDGMENT

APPENDIX

Derivation of Equations. For eq 1, in which the rate-determining step is the diffusion of ligand from the organic bulk phase to the interface of water phase, the partial-differential equations for time (t) and distance (x) from the interface for diffusion to a stationary planar interface are[31,32]

$$\frac{dc(L_{o,i})}{dt} = D_L \frac{d^2c(L_{o,i})}{dx^2} \qquad (A1)$$

and

$$\frac{dc(MLA_{o,i})}{dt} = D_{MLA} \frac{d^2c(MLA_{o,i})}{dx^2} \qquad (A2)$$

The boundary conditions for $t = 0$ and any x are

$$c(L_{o,i}) = c_L \qquad (A3)$$

$$c(MLA_{o,i}) = c_{MLA} \qquad (A4)$$

and, for $t > 0$ and $x \rightarrow \infty$

$$c(L_{o,i}) \rightarrow c_L \qquad (A5)$$

$$c(MLA_{o,i}) \rightarrow c_{MLA} \qquad (A6)$$

For $t > 0$ and $x = 0$

$$D_L \frac{dc(L_{o,i})}{dx} = -D_{MLA} \frac{dc(MLA_{o,i})}{dx} = \frac{i(t)}{nFA} \qquad (A7)$$

where $i(t)$ is the instantaneous current at time, t.

The assumptions that Fick's law is applicable to each species independently and that coupled chemical reactions exert no influence are incorporated in eqs A1 and A2. Equation A7 assumes that there is no accumulation or adsorption of ion-transfer active material at the interface.

Here, assuming that the concentration terms are reasonable approximations of the activities, the potential at a time, t, is[4]

$$E(t) = E^\circ + \frac{RT}{nF} \ln \frac{c(MLA_{o,i})}{c(L_{o,i})} + \frac{RT}{nF} \ln \frac{K_{DL}K_c}{K_{IP}} - \frac{RT}{nF} \ln (c_M c_A{}^n) \quad (A8)$$

At the reversible half-wave potential, $E_{1/2}^r$

$$D_{MLA}^{1/2} c(MLA_{o,i}) = D_L^{1/2} c(L_{o,i})$$

therefore, from eq A8

$$E_{1/2}^r = E^\circ + \frac{RT}{nF} \ln \left(\frac{D_L}{D_{MLA}}\right)^{1/2} + \frac{RT}{nF} \ln \frac{K_{DL}K_c}{K_{IP}} - \frac{RT}{nF} \ln (c_M c_A{}^n) \quad (A9)$$

(31) Delahay, P. *New Instrumental Methods in Electrochemistry*; Wiley (Interscience): New York, 1954.
(32) Smith, D. E. *Electroanalytical Chemistry*; Marcel Dekker: New York, 1966; Vol. 1, p 1.

From eqs A8 and A9

$$E(t) = E_{1/2}{}^r - \frac{RT}{nF} \ln \frac{D_L{}^{1/2}}{D_{MLA}{}^{1/2}} + \frac{RT}{nF} \ln \left[\frac{c(MLA_{o,i})}{c(L_{o,i})} \right]$$

or

$$c(L_{o,i}) = c(MLA_{o,i}) \frac{D_{MLA}{}^{1/2}}{D_L{}^{1/2}} e^{-(nF/RT)[E(t) - E_{1/2}{}^r]} \quad (A10)$$

Equation A10 states the Nernst equation.

Employing the Laplace transformation in eqs A1–A7 and A10 yields[25,28,29,33,34] for interfacial concentrations

$$c(L_{o,i}) = c_L - \int_0^t \frac{i(t-u)\, du}{nFA(\pi D_L{}^u)^{1/2}} \quad (A11)$$

$$c(MLA_{o,i}) = c_{MLA} \int_0^t \frac{i(t-u)\, du}{nFA(\pi D_{MLA}{}^u)^{1/2}} \quad (A12)$$

For simplicitiy, we shall assume at this stage that MLA_o is initially absent from the organic solution; i.e., $c_{MLA} = 0$. Substituting eqs A11 and A12 into eq A10 and rearranging yields the integral expression:

$$e^{-j(t)} = \frac{1 - \int_0^t \frac{\psi(t-u)\, du}{(\pi u)^{1/2}}}{\int_0^t \frac{\psi(t-u)\, du}{(\pi u)^{1/2}}} \quad (A13)$$

where

$$\psi(t) = i(t)/nFAc_L D_L{}^{1/2}) \quad (A14)$$

and

$$j(t) = (nF/RT)[E(t) - E_{1/2}{}^r] \quad (A15)$$

Defining B and P as

$$B = \int_0^t \frac{\psi(t-u)\, du}{(\pi u)^{1/2}} \quad (A16)$$

and

$$P = e^{-j(t)} \quad (A17)$$

Eq A13 becomes

$$P = (1-B)/B \quad (A18)$$

Here, for the condition of the CLSV

$$i(t) = i_0 + vt \quad (A19)$$

where i_0 is the initial current and v the scan rate. From eqs A14 and A19

$$\Psi(t) = Hi(t) = Hi_0 + Hvt \quad (A20)$$

$$\text{where } H = 1/(nFAc_L D_L{}^{1/2}). \quad (A21)$$

Substituting eq A20 into eq A16 and integrating, one obtains

$$B = (2H/\pi^{1/2})i_0 t^{1/2} + (4H/3\pi^{1/2})vt^{3/2} \quad (A22)$$

(33) Senda, M.; Tachi, I. Bull. Chem. Soc. Jpn. 1955, 28, 632.
(34) Caslaw, H.S.; Jaeger, J. C. Conduction of Heat in Solids; Oxford: New York, 1947; p 57.

Therefore, from eqs A13–A15, A21, and A22, we have

$$E(t) =$$

$$E_{1/2}{}^r + \frac{RT}{nF} \ln \frac{\left[2i_0 t^{1/2} + \frac{4vt^{3/2}}{3} \right]}{\pi^{1/2} nFAc_L D_L{}^{1/2} - 2i_0 t^{1/2} - \frac{4vt^{3/2}}{3}} \quad (A23)$$

For the Saturated Current, i_s. Equation A23 shows finally the instantaneous potential for the current linear sweep voltammetry. This equation shows also that the shape of CLSV is different from that of PLSV but similar to that of polarogram. Therefore, the voltammogram should have a saturated current, i_s, at a time, $t \rightarrow t_s$. Then eq A18 is

$$P = (1-B)/B \rightarrow 0$$

that is to say, $E(t)$ is undefined at $t \rightarrow t_s$, then $B = 1$. Therefore, when $i_0 = 0$

$$t_s = (3\pi^{1/2}/4Hv)^{2/3}$$

From eq A19

$$i_s = i(t_s) = (3\pi^{1/2}/4H)^{2/3} v^{1/3}$$

Finally

$$i_s = (3\pi^{1/2}/4)^{2/3} (nFAc_L)^{2/3} D_L{}^{1/3} v^{1/3} \quad (A24)$$

Equation A24 signifies that i_s changes linearly with n, A, and c_L to the $2/3$ power, and D_L and v to the $1/3$ power. The dependence of i_s upon these parameters is much different from that of the peak current for PLSV or cyclic voltammograms[28-30] upon the above parameters. If i_s and i in the place of t_s and t are used in eq A23, respectively, and it is rearranged, we obtain the equation

$$E(t) = E_{1/2}{}^r + \frac{RT}{nF} \ln [i_s{}^{3/2} - i^{3/2}] \quad (A25)$$

Consequently, eqs A24 and A25 are similar to equations in the literature for chronopotentiometry.[20,22-25] Equations A24 and A25, however, are voltammetric expressions of these equations.

For the Half-Wave Potential, $E_{1/2}$. The condition of $E(1/2)$ is expressed by

$$i[t(1/2)] = i_s/2$$

Hence

$$t(1/2) = t_s/2 = (1/2)(3\pi^{1/2}/4H)^{2/3} v^{-2/3} \quad (A26)$$

When $i_0 = 0$, from eqs A19, A22, and A26, we have

$$i[t(1/2)] = (1/2)(3\pi^{1/2}/4H)^{2/3} v^{1/3} \quad (A27)$$

and

$$B = 1/(2 \times 2^{1/2}) \quad (A28)$$

We obtain the final equation for $E(1/2)$ from eqs A21, A23, A27, and A28

$$E(1/2) = E_{1/2}{}^2 + (RT/nF) \ln [1/(2 \times 2^{1/2} - 1)] \quad (A29)$$

and at 298 K

$$E(1/2) = E_{1/2}{}^r - (0.016/n) \quad (A30)$$

Equation A29 or A30 demonstrates that $E(1/2)$ does not change with any parameters except for n and T. This dependence is similar to the case of the peak potential for PLSV or cyclic voltammetry.[28-30] For the cathodic current at initial conditions, $c_M = 0$ and $c_{MLA} > 0$, when the system is controlled entirely by diffusion of MLA_o, instead of by eqs

A23–A25, A29, and A30, the following equations obtain:

$$E(t) = E_{1/2}^{r} -$$

$$\frac{RT}{nF} \ln \frac{\left[2i_0 t^{1/2} + \frac{4\upsilon t^{3/2}}{3} \right]}{\left[\pi^{1/2} nFAc_{MLA} D_{MLA}^{1/2} - 2i_0 t^{1/2} - \frac{4\upsilon t^{3/2}}{3} \right]} \quad (A31)$$

Using i_s and i when $i_0 = 0$

$$E(t) = E_{1/2}^{r} - \frac{RT}{nF} \ln \left[\frac{i^{-3/2}}{i_s^{3/2} - i^{3/2}} \right] \quad (A32)$$

$$i_s = -(3\pi^{1/2}/4)^{2/3} (nFAc_{MLA})^{2/3} D_{MLA}^{1/3} \upsilon^{1/3} \quad (A33)$$

$$E(1/2) = E_{1/2}^{r} - \frac{RT}{nF} \ln \left[\frac{1}{2 \times 2^{1/2} - 1} \right] \quad (A34)$$

at 298 K

$$E(1/2) = E_{1/2}^{r} + (0.016/n) \quad (A35)$$

Equations A23–A25 and A29–A35 can be used for the analysis of both CLSV and current sweep cyclic voltammetry.

GLOSSARY

subscripts

a	aqueous phase species
b	backward reaction
f	forward reaction
i	species at interface
o	organic phase species

symbols

A	electrode area
A or A$^-$	anion
$c(S)$	instantaneous concentration of species, S
c_s	concentration of bulk phase species, S
D	diffusion constant
$E_{1/2}$	half-wave potential of CLSV
E^o	standard ion-transfer potential
$E_{1/2}^{r}$	reversible half-wave potential of polarogram
$E(t)$	instantaneous potential at t
F	Faraday constant
i_0	initial current
i_s	saturated current of CLSV
$i(t)$	instantaneous current at time t
k	rate constant of complex formation
$K_c = [(ML)_{a,i}^{n+}]/[M_{a,i}^{n+}][L_{a,i}]$	first complex formation constant
$K_{DC} = [(ML)_{o,i}^{n+}]/[(ML)_{a,i}^{n+}]$	distribution constant of complex
$K_{DL} = [L_{o,i}]/[L_{a,i}]$	distribution constant of L
$K_{IP} = [(MLA_n)_{o,i}]/[(ML)_{o,i}^{n+}][A_{o,i}^-]^n$	ion pair formation
L	ligand
M or M^{n+}	metal ion
n	number of transferred charges at interface
R	gas constant
t	time
T	absolute temperature
υ	scan rate