MECHANISMS AND CHARACTERISTICS OF ELECTRODE REACTIONS OF ANALYTICAL INTEREST

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ABSTRACT

Electrode reactions are classified on the basis of their mechanisms and characteristics; those which are of analytical interest especially, are utilized for trace analysis and used also for the universal potential scale in different solvents, are considered. Effects of complex-forming substances, surface-active substances, supporting electrolytes and solvents on the mechanisms and characteristics of electrode reactions are discussed.

1. INTRODUCTION

There are a number of electrode reactions which are used for analytical purposes. Some electrode reactions are simple, while others are complex. Some electrode reactions are successfully applied to trace analysis by the alternating current or the square wave polarographic method, but others are not. In some cases, increasing concentrations of supporting electrolyte increase the sensitivity of the determination, while in other cases, there is a decrease. These differences depend to a great extent on the mechanisms and characteristics of electrode reactions.

In this paper, the author intends to classify electrode reactions on the basis of their mechanisms and characteristics and to discuss the effects of complex-forming substances, surface-active substances, supporting electrolytes and solvents on the mechanisms and characteristics of electrode reactions. The electrode reactions which are utilized for trace analysis and for the universal potential scale in different solvents are especially considered.

2. CLASSIFICATION OF ELECTRODE REACTIONS

An electrode reaction is, in general, considered to be composed of (i) the mass transport of reactant and product, (ii) the electron transfer of electro-active reactant at the electrode/solution interface and (iii) the preceding or the succeeding chemical reaction taking place in the vicinity of the electrode. All electrode reactions involve processes (i) and (ii), but there are many electrode reactions which do not involve process (iii). In addition, adsorption and desorption processes take place in some electrode reactions.

For the purpose of the representation of mechanisms of electrode reactions,

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Table 1. Symbols for processes in electrode reactions

Process	Symbol
Mass transport	$T, T', T'' \ldots$
Electron transfer	$E, E', E'' \ldots ;\ \sum_{i=1}^{p} E_i,\ \sum_{i'=1}^{p'} E'_{i''} \ldots$
Chemical reaction (preceding or succeeding)	$C, C', C'' \ldots ;\ \sum_{j=1}^{q} C_j,\ \sum_{j'=1}^{q'} C'_{j''} \ldots$
Adsorption	$A, A', A'' \ldots$
Desorption	$D, D', D'' \ldots$

it seems convenient that electrode processes are denoted with appropriate symbols[1], which are given in *Table 1*. The simplest reaction is one which involves processes (i) and (ii). This is denoted as TET′. Since all electrode reactions involve the mass transport of initial reactant and that of final product, symbols T and T′ may be omitted, so that the simplest electrode reaction is represented with E. Some electrode reactions which involve the mass transport and two or more processes of electron transfer may be denoted as $E_1 E_2 \ldots E_p$.

An electrode reaction which is accompanied by a preceding or a succeeding reaction may be represented, in general, with ECE′ or $E_i C_j E'_{i'}$. *Table 2* gives examples of the electrode reactions of $E_i C_j E'_{i'}$ mechanism. Another type of electrode reaction is one which is catalytic in nature; this is denoted, for example, with (EC)′E′. A typical example of electrode reactions of (EC)′E′ mechanism is the reduction of Fe^{3+} ions in the presence of hydrogen peroxide.

Electrode reactions may be divided into simple and complex reactions from the mechanistic standpoint. The former is a reaction which involves

Table 2. Examples of electrode reactions of $E_i C_j E'_{i'}$ mechanism

$E_i C_j E'_{i'}$			Expression of mechanism	Example of reaction	
i	j	i′		Equation	Detailed expression of mechanism
1	0	0	E	$Cu^{2+} + 2e + Hg = Cu(Hg)$	E(2e)
			$E_1 E_2$	$Cu(NH_3)_4^{2+} + e = Cu(NH_3)_2^{+} + 2NH_3$	$E_1(1e)E_2(1e)$
				$Cu(NH_3)_2^{+} + e + Hg = Cu(Hg) + 2NH_3$	
1	1	0	EC	$Cr(NH_3)_6^{3+} + e = Cr(NH_3)_6^{2+}$	E(1e, irr)-
				$Cr(NH_3)_6^{2+} + 6H_3O^{+} = Cr(H_2O)_6^{2+} + 6NH_4^{+}$	C(diss.)
0	1	1	CE′	$CdNTA^{-} + H^{+} = Cd^{2+} + HNTA^{2-}$	C(diss-
			(or CE)	$Cd^{2+} + 2e + Hg = Cd(Hg)$	E(2e, rev.)
1	1	1	ECE′	$Cr(NH_3)_6^{3+} + e = Cr(NH_3)_6^{2+}$	E(1e, irr.)-
				$Cr(NH_3)_6^{2+} + H_2EDTA^{2-} + 4H_3O^{+}$	C(subst.)-
				$= CrEDTA^{2-} + 6NH_4^{+} + 4H_2O$	E′(1e, rev.)
				$CrEDTA^{2-} = CrEDTA^{-} + e$	

only process E, and the latter, a reaction which involves E and other types of processes. On the other hand, the electrode reactions are customarily classified to reversible and irreversible reactions according to the characteristics of the reaction. These words can be applied to both simple and complex reactions. The distinction between reversible and irreversible electrode reactions is based on the rate of electron transfer at the electrode/solution interface.

3. ELECTRODE REACTIONS UTILIZED FOR TRACE ANALYSIS

3.1. Simple electrode reactions

In direct current polarography, the limiting diffusion current, which is one of the measured quantities, is utilized for the determination of the concentration of electroactive substance. Therefore, the sensitivity of most of the d.c. polarographic methods depends on the rate of mass transport. On the other hand, there are many electrochemical methods in which the quantities measured for the determination of the concentration depend on the rate of electron transfer at the electrode/solution interface. Current/potential curves of square wave polarography which were calculated with various standard rate constants are shown in *Figure 1*[2]. Kinetic parameters including rate constants have been determined for many electrode reactions[3,4], from which the information can be obtained concerning the utility of electrode
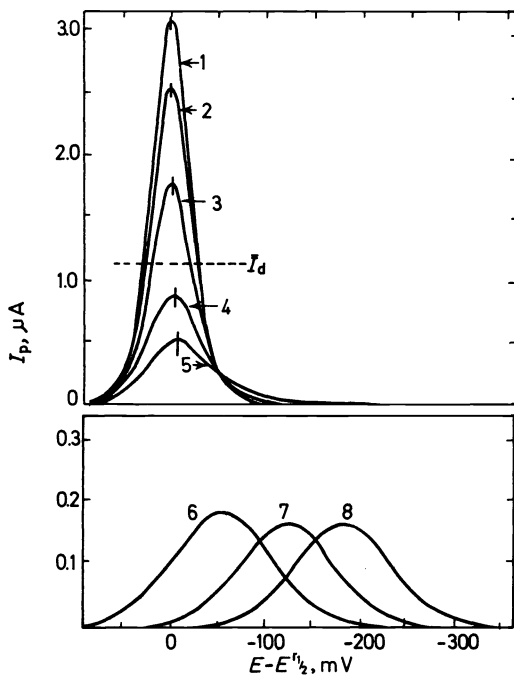
Figure 1. Rate constants and current/potential curves of square wave polarography[2]. ($\alpha = 0.5$) k_s in cm s^{-1}: (1) ∞, (2) 10^{-1}, (3) 3×10^{-2}, (4) 10^{-2}, (5) 5×10^{-3}, (6) 10^{-3}, (7) 10^{-4} and (8) 10^{-5}.

Table 3. Some simple electrode reactions with large rate constants at the mercury electrode

Reactions	Electrode*	Medium	Temp °C	Transfer coefficient		Rate constant $[(k_s)_{ms}]$ cm s^{-1}	Method†	Ref.
				Anodic	Cathodic			
$Cd^{2+} + 2e + Hg = Cd(Hg)$	DME	1 M NaClO$_4$(pH = 3)	25		0.32 ± 0.3	0.46 ± 0.04	fr	5
$Co(III)EDTA + e = Co(II)EDTA$	DME	0.4 M NaNO$_3$ + 0.1 M acetate buffer	25	0.49	0.52	0.029	ps	6
$Cr(III)EDTA + e = Cr(II)EDTA$	SDME	0.4 M NaCl + 0.1 M acetate buffer	25	0.39	0.58	0.21	ps	7
$Cu^{2+} + 2e + Hg = Cu(Hg)$	DME	1 M KNO$_3$	25	0.53	0.43	0.019	ps	8
$Fe(ox)_3^{3-} + e = Fe(ox)_3^{4-}$	DME	1 M K$_2$ox + 0.05 M H$_2$ox	25		0.78 ± 0.04	0.86 ± 0.03	fr	5
$Hg_2^{2+} + 2e = 2Hg$	HMDE	1.00 M HClO$_4$	25		0.32 ± 0.02	0.019 ± 0.002	cir	9
$Pb^{2+} + 2e + Hg = Pb(Hg)$	DME	1 M HClO$_4$	25		0.5 (assumed)	0.9 ± 0.1	fr	10
$Ti(IV) + e = Ti(III)$	DME	0.200 M H$_2$C$_2$O$_4$ + 0.0400 M KClO$_3$	25		0.35 ± 0.03	(4.6 ± 0.02) × 10^{-2}	acp(ϕ)	11
$Tl^+ + e + Hg = Tl(Hg)$	DME	1 M NaClO$_4$ (pH = 2)	22		0.69	1.2	fr	12

* DME means dropping mercury electrode, SDME, slowly dropping mercury electrode and HDME, hanging mercury drop electrode.
† fr means faradaic rectification method, cir—current-impulse-relaxation method, ps—potentiostatic method, fi—faradaic impedance method and acp(ϕ)—a.c. polarography with phase-angle measurement.

reactions in trace analysis. Examples of simple electrode reactions which have large rate constants at the mercury electrode are given in *Table 3*.

3.2 Kinetic parameters of electrode reactions

3.2.1 Kinetic parameters and Marcus theory

Kinetic parameters of electrode reactions have been determined by various methods[3, 4]. Some methods are suitable for the determination of larger rate constants, while others are suitable for the determination of smaller ones. Recently, Senda and his co-workers[13] applied the radio frequency polarographic method to determine the kinetic parameters of some porphyrins and their metal complexes with the result of measured rate constants $[(k_s)_{ms}]$ ranging from $0.64\ cm\,s^{-1}$ to $5.6\ cm\,s^{-1}$. Aoyagui and his co-workers[14, 15] determined the standard rate constants of the electrode reactions of bipyridine complexes of transition metals and compared them with the rate constants of the electron exchange reactions of the corresponding metal complexes in solutions.

The relation between the rate constants of the electron exchange reactions in solution (k_{ex}) and the standard rate constants of the corresponding electron transfer reactions at the electrode/solution interface (k_s) has been studied by Marcus[16], who proposed the relation

$$k_s/A_{el} \leqslant (k_{ex}/A_{ex})^{1/2} \tag{1}$$

where A_{el} and A_{ex} are frequency factors of the electrode reaction and the electron exchange reaction in solution, respectively, and have been assumed to be $10^4\ cm\,s^{-1}$ for A_{el} and $10^{11}\ l\,mol^{-1}\,s^{-1}$ for A_{ex}. Introducing these values into equation (1) and $10^9\ l\,mol^{-1}\,s^{-1}$ for k_{ex}, which is nearly the highest value for the second-order reaction in an aqueous solution, one obtains

$$k_s \leqslant 10^3\ cm\,s^{-1} \tag{2}$$

If the Marcus theory is correct, the standard rate constant of $10^3\ cm\,s^{-1}$ is the upper limit of the electron transfer reaction at the electrode/aqueous solution interface. In square wave polarography[2], the condition that the electrode reaction of standard rate constant k_s can be treated as a reversible system is given by

$$k_s > 0.32\,\theta^{-1/2} \tag{3}$$

where θ denotes the duration of a half cycle of square wave voltage. This means that the electrode reaction whose standard rate constant is $10^3\ cm\,s^{-1}$ can be treated as a reversible one unless the frequency of the square wave exceeds $10^7\ Hz$.

3.2.2 Measured and corrected rate constants and transfer coefficients

Since the rate constant and transfer coefficient of the electrode reaction are affected by the electrical double layer at the electrode/solution interface, the values obtained in the experiment are not the true ones; the effect of the double layer must be corrected. The correction which is widely accepted is one proposed by Frumkin[17].

The determination of the rate constant and the transfer coefficient and the application of the Frumkin correction to the values obtained will be shown using the electrode reaction of Cr(III)CyDTA/Cr(II)CyDTA as an example, where CyDTA stands for *trans*-1,2-cyclohexanediaminetetraacetic acid.

The reduction of Cr(III)CyDTA to Cr(II)CyDTA at the mercury electrode proceeds as a simple reaction of E(1e) mechanism. The cathodic and the anodic rate constants (k_c and k_a) were obtained by the potentiostatic method.

When an electrode reaction is expressed as

$$O + ne \rightleftharpoons R \tag{4}$$
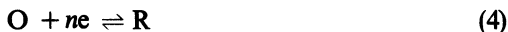
the relation between the cathodic current (I) and the time (t) after the beginning of the electrolysis at a given potential is given by the equation[6, 7]:

$$\left(\frac{I}{I_d}\right)_t \Big/ \left(\frac{I}{I_d}\right)_{t'} = \pi^{\frac{1}{2}} \lambda_{ms} t^{\frac{1}{2}} \exp(\lambda_{ms}^2 t) \, \text{erfc}(\lambda_{ms} t^{\frac{1}{2}}) \tag{5}$$

$$(t')^{\frac{1}{2}} \gg t^{\frac{1}{2}} \tag{6}$$

$$(k_c)_{ms} = \lambda_{ms} \left(\frac{I}{I_d}\right)_{t'} (D_O)^{\frac{1}{2}} \tag{7}$$

$$(k_a)_{ms} = \lambda_{ms} \left\{ 1 - \left(\frac{I}{I_d}\right)_{t'} \right\} (D_R)^{\frac{1}{2}} \tag{8}$$

where

$$\lambda_{ms} = \frac{(k_c)_{ms}}{D_O^{\frac{1}{2}}} + \frac{(k_a)_{ms}}{D_R^{\frac{1}{2}}} \tag{9}$$

D_O and D_R are the diffusion coefficients of oxidant and reductant, respectively, and subscript ms denotes the measured value.

In order to apply the double layer correction, the Frumkin equations were arranged as follows:

$$(k_c)'_{ms} \equiv (k_c)_{ms} \exp\left[\frac{z_O F}{RT} \phi_2\right] = (k_s)_{corr} \exp\left[-\frac{(\alpha_c)_{corr} nF}{RT}(E - \phi_2)\right]$$
$$\times \exp\left[\frac{(\alpha_c)_{corr} nF}{RT}(E_0)_{corr}\right] \tag{10}$$

$$(k_a)'_{ms} \equiv (k_a)_{ms} \exp\left[\frac{z_R F}{RT} \phi_2\right] = (k_s)_{corr} \exp\left[\frac{(\alpha_a)_{corr} nF}{RT}(E - \phi_2)\right]$$
$$\times \exp\left[\frac{(\alpha_a)_{corr} nF}{RT}(E_0)_{corr}\right] \tag{11}$$

where ϕ_2 means the potential at the outer Helmholtz plane of the double layer, and the subscript corr denotes the corrected value. In *Figure 2*[18] are shown the plots of $\log(k_c)'_{ms}$ versus $E - \phi_2$ and those of $\log(k_a)'_{ms}$ versus $E - \phi_2$ obtained for the electrode reaction of Cr(III)CyDTA/Cr(II)CyDTA. Both the plots gave straight lines, the intersection of which gave the corrected standard potential $(E_0)_{corr}$ and the corrected standard rate constant $(k_s)_{corr}$.
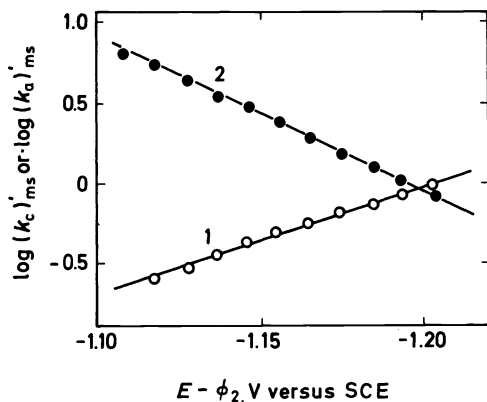
Figure 2. Determination of kinetic parameters of Cr(III) CyDTA/Cr(II) CyDTA. (1) log $(k_c)'_{ms}$ versus $E - \phi_2$ and (2) log $(k_a)'_{ms}$ versus $E - \phi_2$ obtained in the solution of pH 4.7 containing 0.4 M NaCl, 0.1 M acetate buffer and 2×10^{-6} M LEO at 25°C.

The corrected transfer coefficients $(\alpha_c)_{corr}$ and $(\alpha_a)_{corr}$ are calculated from the slopes of the respective straight lines.

Kinetic parameters obtained for the electrode reactions of Cr(III/II)EDTA and Cr(III/II)CyDTA are shown in *Table 4* as an example.

3.3 Increase of rate constant

3.3.1 Complexation reactions

There are many complexation reactions which increase the rate constant of the electrode reactions, although many other complexation reactions decrease the rate constants. A typical example of the former case is the electrode reaction of Cr(III)EDTA/Cr(II)EDTA. The corrected standard rate constant of hydrated Cr^{3+} ions in a 1.0 M sodium perchlorate solution was found[19] to be 2.8×10^{-7} cm s^{-1}, whereas Cr(III)EDTA complex gives the corrected standard rate constant of 17 cm s^{-1} as shown in *Table 4*. The complexation with EDTA increases the standard rate constant of Cr(III) by more than 10^8 and made the Cr(III)/Cr(II) system completely reversible even in alternating current and square wave polarography. Many similar cases

Table 4. Kinetic parameters of the electrode reactions of Cr(III/II)EDTA[7] and Cr(III/II)CyDTA[18].

	Cr(III)EDTA/Cr(II)EDTA	Cr(III)CyDTA/Cr(II)CyDTA
$(E_0)_{ms}$, V versus SCE	-1.220	-1.198
$(k_s)_{ms}$, cm s^{-1}	0.21	0.029
$(\alpha_c)_{ms}$	0.58	0.33
$(\alpha_a)_{ms}$	0.39	0.67
$(E_0)_{corr}$, V versus SCE	-1.220	-1.198
$(k_s)_{corr}$, cm s^{-1}	17	0.93
$(\alpha_c)_{corr}$	0.54	0.40
$(\alpha_a)_{corr}$	0.43	0.57

Table 5. Effect of complexation on standard rate constants of electrode reactions

Reaction	Electrode*	Medium	Temp. °C	Rate constant $[(k_s)_{m.s.}]$ cm s^{-1}	Method†	Ref.
Bi(III) + 3e + Hg = Bi(Hg)	DME	1 N HClO$_4$	26 ± 0.5	0.39 × 10^{-3}	fi	19
	DME	0.6 N HClO$_4$ + 0.4 N HNO$_3$	26 ± 0.5	(1.7–1.8) × 10^{-3}	fi	19
	DME	1 N HNO$_3$	26 ± 0.5	(2.8–4.2) × 10^{-3}	fi	19
Eu(III) + e = Eu(II)	DME	10^{-3} N HClO$_4$ + 0.02–1.00 M NaClO$_4$	25	2 × 10^{-5}	dcp	20
Fe^{3+} + e = Fe^{2+}	Hg	1 M KCl	20	2.1 × 10^{-4}	fi	21
	Hg	1 M KI	20	1.6 × 10^{-3}	fi	21
	Hg	1 M KSCN	20	8.0 × 10^{-3}	fi	21
Fe(CN)$_6^{3-}$ + e = Fe(CN)$_6^{4-}$	Pt	1 M HClO$_4$	25	2.2 × 10^{-3}	cp	3
Fe(ox)$_3^{3-}$ + e = Fe(ox)$_3^{4-}$	Pt	1 M KCl	25	0.052	cp	3
In^{3+} + 3e + Hg = In(Hg)	DME	1 M K$_2$ox + 0.05 M H$_2$ox	25	0.86 ± 0.03	fr	22
In(III) + 3e + Hg = In(Hg)	DME	0.5 M ClO$_4^-$	26.5°C	3.1 × 10^{-8} (estimated)	dcp	23–25
	DME	1 M NaCl	25	0.034	fi	26
	DME	1 M NaBr	25	0.65	fi	26
	DME	1 M NaN$_3$	25	0.053	fi	26
Zn(II) + 2e + Hg = Zn(Hg)	DME	1 M NaClO$_4$ + 0.1 mM HClO$_4$ + 2 μM LEO	25	2.6$_0$ × 10^{-3}	dcp	27
	DME	1 M NaCl	25	3.9 × 10^{-3}	fi	26
	DME	1 M NaN$_3$	25	(7.4–7.5) × 10^{-3}	fi.	26
	DME	1 M NaBr	25	(7.6–7.8) × 10^{-3}	fi	26
	SDME	1 M NaSCN	25	2.9$_5$ × 10^{-2}	ps	28
	SDME	1 M NaI	25	7.7$_6$ × 10^{-2}	ps	28

* Pt means Pt electrode. Hg is the mercury electrode and the others are the same as described in *Table 3*.
† cp means current/potential curve and the others are the same as described in *Table 3*.

are found with various metal ions and many inorganic and organic ligands. Some examples are given in *Table 5*.

3.3.2 Adsorption of surface-active substances on the electrode surface

The increase of the rate constant can be attained by the adsorption of an appropriate surface-active substance on the electrode surface. Surface-active substances usually retard the electron transfer at the electrode/solution interface but some surface-active substances accelerate the electron transfer. A typical example of this kind of increase is the effect of thiocyanate ions on the reduction of In^{3+} ions.

The reduction of In^{3+} ions in a sodium perchlorate solution is completely irreversible at the dropping mercury electrode[23-25]. Upon the addition of a small concentration of thiocyanate ions, the electron transfer is clearly accelerated as shown in *Figure 3* (curve 2)[29], although curve 1 indicates a
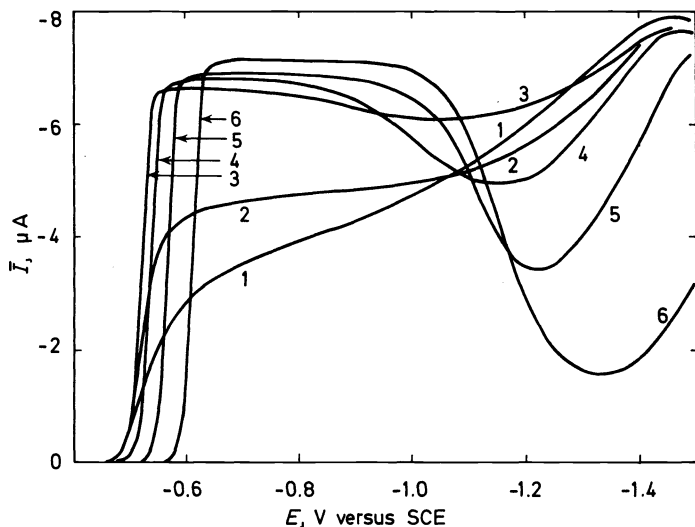
Figure 3. D.c. polarograms of 1.0 mM In $(NO_3)_3$ at ionic strength 1.0 $(NaNO_3)$. Concentrations of KSCN: (1) 0, (2) 0.0001, (3) 0.002, (4) 0.04, (5) 0.20 and (6) 1.00 M.

certain degree of acceleration caused by the presence of nitrate ions. The acceleration of electron transfer by thiocyanate ions is apparently caused by the bridging action of thiocyanate ions which are adsorbed on the electrode surface, because it is estimated from the stability constant that the presence of 0.0001 M thiocyanate ions forms $InSCN^{2+}$ ions by only four per cent of total In(III) in solution and the rest of In(III) (96 per cent) is in the form of hydrated In^{3+} ions. Unfortunately, the standard rate constant has not been determined in the presence of a small amount of thiocyanate, but that of In(III) in the presence of 1 M NaCl, 1 M NaN_3 and 1 M NaBr were determined to be 3.4×10^{-2}, 5.3×10^{-2} and 6.5×10^{-1} cm s^{-1}, respectively[26]. They are much greater than the k_s value of 3.1×10^{-8} cm s^{-1} in perchlorate media, which was estimated from the rate constant at 0 V versus NHE, the αn value and the standard potential of the In^{3+}/In couple. The increase of

the standard rate constant is considered to be attributed not only to complexation with halide or azide ions, but also to the adsorption of these ions on the electrode surface, which facilitates the electron transfer at the electrode/solution interface. The mechanism of this kind of reaction may be denoted as ACE, which is one of the reaction mechanisms of analytical interest.

3.3.3 Effects of double layer and non-complexing supporting electrolyte

The standard rate constant of the electrode reaction is affected by the concentration of a non-complexing supporting electrolyte. This effect is considered to be due to the change of the ϕ_2 potential of the double layer caused by the change of the concentration of the supporting electrolyte. *Table 6*[27, 30] gives examples which indicate that the measured standard rate

Table 6. Effect of supporting electrolyte on the standard rate constant of electrode reaction of Zn(II)/Zn(Hg) (25°C)[27, 30].

Supporting electrolyte	Concentration M	$(k_s)_{ms} \times 10^3$ cm s^{-1}	$(k_s)_{corr} \times 10^4$ cm s^{-1}
NaClO$_4$	1.00	2.6	2.9
	0.75	3.4	3.1
	0.50	5.4	3.0
	0.30	8.0	2.5
	0.10	17	1.4
Mg(ClO$_4$)$_2$	0.33	2.1	4.0
	0.17	3.0	4.0
	0.083	4.2	3.4
	0.033	6.9	3.2
Al(ClO$_4$)$_3$	0.17	2.1	4.0
	0.05	2.6	3.0
	0.017	3.1	2.1

constants increase with decreasing concentrations of supporting electrolyte, but the corrected standard rate constants calculated according to the Frumkin equation are almost constant independent of the concentration of supporting electrolyte except that obtained at a lower ionic strength. It should be noticed that in the reduction of cation in a potential region where the electrode is negatively charged, the measured standard rate constants increase with increasing concentrations of non-complexing supporting electrolyte.

In some cases, the Frumkin correction cannot give the constant standard rate constant. The standard rate constants of the Cr(III)CyDTA/Cr(II)CyDTA reaction which were obtained in various ionic strengths are given in *Table 7*[31]. The measured standard rate constants increase with increasing concentrations of supporting electrolyte, but the corrected standard rate constants decrease under the same conditions. In the case of the reduction of anion at the negatively charged electrode, the larger concentration of non-complexing supporting electrolyte seems to increase the sensitivity of the determination because of the increase of the measured standard rate constant of the electrode reaction.

Table 7. Effect of supporting electrolyte on the standard rate constant of electrode reaction of Cr(III)CyDTA/Cr(II)CyDTA (25°C)[31].

Supporting electrolyte	Concentration M	$(k_s)_{ms}$ cm s^{-1}	$(k_s)_{corr}$ cm s^{-1}
LiCl + LiOAc	1.0	0.025	0.32
	0.5	0.018	0.46
	0.2	0.0096	0.78
	0.1	0.0066	1.2
NaCl + NaOAc	1.0	0.037	0.51
	0.5	0.029	0.93
	0.2	0.011	1.3
	0.1	0.0059	2.5
KCl + KOAc	1.0	0.058	0.81
	0.5	0.034	0.89
	0.2	0.017	1.4
	0.1	0.0085	1.7
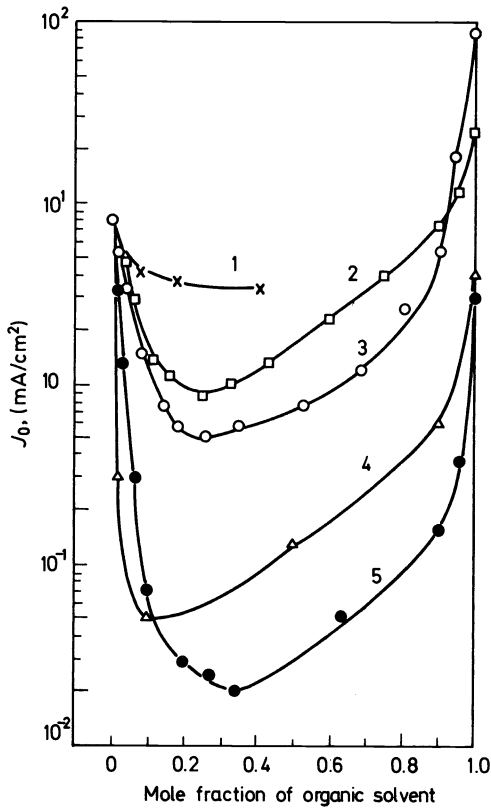
Figure 4. Exchange current densities of Zn^{2+}/Zn (Hg) in mixtures of water and organic solvents. (1) Dioxane, (2) ethanol, (3) acetonitrile, (4) tetrahydrofuran and (5) acetone.

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3.4 Solvent effects

3.4.1 Effect on reaction rates

Solvent effects on the kinetic parameters of electrode reactions have been studied mainly from the experimental standpoint. Jaenicke and Schweitzer[32] determined exchange current densities of the $Zn^{2+}/Zn(Hg)$ reaction in various mixed and pure organic solvents. The variation of exchange current densities with the mole fraction of organic solvent is reproduced in *Figure 4*. In most solvents investigated, the exchange current densities give minimum values at certain mole fractions of solvents. The exchange current densities obtained in ethanol and acetonitrile were found to be greater than that in an aqueous solution. Somewhat conflicting results that the standard rate constants of the $Zn^{2+}/Zn(Hg)$ reaction in water–ethanol mixtures decrease with the increasing concentrations of ethanol were obtained in the range of ethanol concentrations up to 50 vol. %[30].

The standard rate constants of the $Cr(III)CyDTA/Cr(II)CyDTA$ reaction were determined by the coulostatic method in mixed solvents of water and various alcohols[33]. In water–ethanol mixtures, the $Cr(III)CyDTA/Cr(II)$-CyDTA reaction gave a minimum standard rate constant when the mole fraction of ethanol was nearly 0.2. This value is almost identical with the mole fraction of ethanol at which the $Zn^{2+}/Zn(Hg)$ reaction gives a minimum exchange current density. In water–n-propanol mixtures, a minimum standard rate constant was obtained at a lower concentration of alcohol, i.e. at nearly 0.1 mole fraction of n-propanol. From the results mentioned above, it may be concluded that the addition of alcohols or other organic solvents to form mixed solvents seems to have no advantage, as far as the increase of sensitivity of the method is concerned.

3.4.2 Stabilization of extraordinary valence state of metal ions

The reduction of Cu^{2+} ions at the mercury electrode proceeds as

$$Cu^{2+} + 2e + Hg = Cu(Hg) \tag{12}$$

in aqueous solutions containing no complex-forming substance, but in acetonitrile, it proceeds by two steps as given by

$$Cu^{2+} + e = Cu^+ \tag{13}$$

$$Cu^+ + e + Hg = Cu(Hg) \tag{14}$$

This is because the oxidation state of Cu(I) is stabilized in acetonitrile. A similar phenomenon was observed with tris(2,2'-bipyridine)iron(II) complex, which gives a one-step reduction from Fe(II) to Fe(0) in aqueous solutions, but a two-step reduction from Fe(II) to Fe(I) and from Fe(I) to Fe(0) in acetonitrile. Although the oxidation state I is stabilized in both cases, the cause of stabilization seems not to be the same. In the case of Cu(I) its acetonitrile complex, $Cu(CH_3CN)_x^+$, may be stable, while in the case of $Fe(bipy)_3^+$ the rate of dissociation of bipyridine is considered to be much slower in acetonitrile than in aqueous solution. In both of these cases, the solvent effect on reversibility of the electrode reaction has been realized.

In addition to the above two cases, the stabilization of extraordinary valence state in non-aqueous solvents has been found in the formation of

metal complexes of lower oxidation state. For example, it is reported that $Fe(bipy)_3^{2+}$ is reduced to $Fe(bipy)_3^-$ in acetonitrile[34, 35] and other organic solvents[36] which have less oxidizing power, and that many other bipyridine and phenanthroline complexes of transition metals behave similarly. The importance of the electrode reactions of metal complexes of lower oxidation states has been recognized[37].

3.5 Complex electrode reactions

3.5.1 ECE' mechanism

The electrode reactions of the ECE' mechanism have been utilized for the analysis of substitution-inert metal complexes. One of the typical examples is the a.c. or square wave polarographic determination of chromium which exists in the form of chromate, dichromate or other substitution-inert chromium complexes in the supporting electrolyte solution containing EDTA. In the case of hexaamminechromium(III) ions, the electrode reaction proceeds as[38–41]
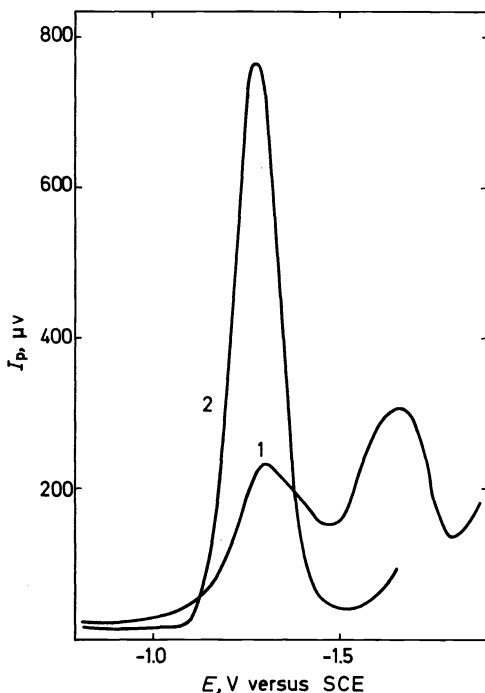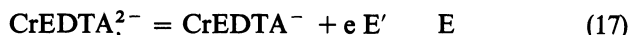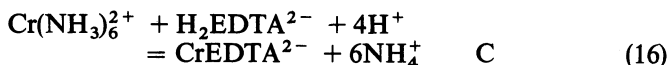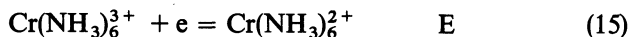
$$Cr(NH_3)_6^{3+} + e = Cr(NH_3)_6^{2+} \qquad E \qquad (15)$$

$$Cr(NH_3)_6^{2+} + H_2EDTA^{2-} + 4H^+$$
$$= CrEDTA^{2-} + 6NH_4^+ \qquad C \qquad (16)$$

$$CrEDTA^{2-} = CrEDTA^- + e \; E' \qquad E \qquad (17)$$

Figure 5. A.c. polarograms of 1 mM $K_2Cr_2O_7$ obtained in the absence (1) and the presence of 4 mM EDTA in 0.4 M NH_4Cl–0.1 M acetate buffer (2).

The reduction of $Cr(NH_6)_6^{3+}$ ions, which do not react with EDTA in solution, is irreversible at the mercury electrode. At the electrode, $Cr(NH_3)_6^{3+}$ ions are reduced to $Cr(NH_3)_6^{2+}$ ions, which are substitution-labile and react quickly with EDTA to form the Cr(II)EDTA complex. The reversibility of the electrode reaction of the Cr(II)EDTA complex is demonstrated with the value of the standard rate constant given in *Table 4*. The same mechanism is expected for the reduction of dichromate ions. An example of an a.c. polarogram of dichromate ions obtained in the absence and the presence of EDTA is shown in *Figure 5*.

The application of the electrode reactions of ECE' mechanism to trace analysis seems to be worth exploiting.

3.5.2 (EC)'E and EC(C'E)'' mechanisms
The electrode reaction of (EC)'E mechanism such as,

$$O + ne \rightarrow R \tag{18}$$

$$R + Z \xrightarrow{k} O \tag{19}$$

has been used for the d.c. polarographic determination of small quantities of metal ions. The r value is considered to indicate the number of repetitions of the combination of electrochemical [equation (18)] and chemical [equation (19)] reactions, and may be given by

$$r = (\bar{I}_t - \bar{I}_d)/\bar{I}_d \tag{20}$$

where $\bar{I}_t$ represents the total limiting current and $\bar{I}_d$, the limiting diffusion current obtained in the absence of Z, both being the average current.
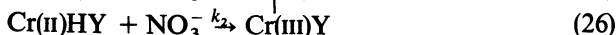
When Z exists in excess over O, the ratio $\bar{I}_t/\bar{I}_d$ is expressed approximately as[42-44]

$$\bar{I}_t/\bar{I}_d = 0.812\,\chi^{\frac{1}{2}} + 1.92\,\chi^{-\frac{1}{2}} \quad (\chi > 10) \tag{21}$$

$$\chi = \alpha k C_Z t_d \tag{22}$$

where α is the stoichiometric ratio of R to Z in reaction (19) and t_d, the drop time of the dropping mercury electrode. Equations (21) and (22) show that increase of current depends on the rate constant of chemical reaction (19).

An example of the electrode reaction of (EC)'E mechanism is the reduction of Cr(III)Y complexes taking place in the presence of nitrate ions, where Y represents an anion of EDTA, CyDTA, TRDTA(trimethylenediaminetetraacetic acid) or HEDTA (hydroxyethylethylenediaminetriacetic acid). Since the $\bar{I}_t/\bar{I}_d$ value depends on the concentration of hydrogen ions, the reaction mechanism is considered as:
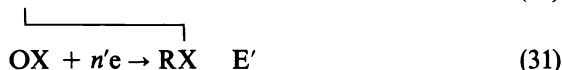
$$Cr(III)Y + e \rightarrow Cr(II)Y \tag{23}$$

$$Cr(II)Y + H^+ \overset{k}{\rightleftharpoons} Cr(II)HY \tag{24}$$

$$Cr(II)Y + NO_3^- \xrightarrow{k_1} Cr(III)Y \tag{25}$$

$$Cr(II)HY + NO_3^- \xrightarrow{k_2} Cr(III)Y \tag{26}$$

The apparent rate constant k in equation (19) is expressed as

$$k = \{k_1 + k_2 K[H^+]\}/\{1 + K[H^+]\} \qquad (27)$$

In the cases of EDTA and CyDTA complexes, k_2 is much larger than k_1 and consequently $\bar{I}_t/\bar{I}_d$ increases with increase of the hydrogen ion concentration.

In some cases, the rate constant k of a chemical reaction is not large enough to increase the limiting current; the r value is close to zero even when Z exists at a large concentration. The reduction of chromate or $Cr(NH_3)_6^{3+}$ ions in solutions containing no complex-forming substances is such a case; aquachromium(II) ions react with nitrate ions only very slowly[45].

The electrode reaction of $EC(C'E')^{r'}$ mechanism,

$$O + ne \rightarrow R \qquad E \qquad (28)$$

$$R + X \rightarrow RX \qquad C \qquad (29)$$

$$RX + Z \rightarrow OX \qquad C' \qquad (30)$$

$$OX + n'e \rightarrow RX \qquad E' \qquad (31)$$

is effective in this case. One of the examples of $EC(C'E')^{r'}$ mechanism is the reduction of chromate or $Cr(NH_3)_6^{3+}$ ions in the presence of EDTA and nitrate ions[46]. If the d.c. polarographic method is preferable to a.c. or square wave polarography or other similar techniques, the electrode reaction of $EC(C'E')^{r'}$ mechanism is worth considering instead of that of ECE' mechanism.

3.6 Complex procedures

Anodic stripping or cathodic stripping techniques have been considered to be extremely important for trace analysis. It is desirable that the electrode reaction which is utilized for stripping has a large standard rate constant, so that the alternating current or square wave polarographic techniques can be applied to give a high sensitivity. Mechanisms and characteristics of such reactions have been described previously.

4. ELECTRODE REACTIONS UTILIZED FOR THE UNIVERSAL POTENTIAL SCALE IN DIFFERENT SOLVENTS

The establishment of the universal potential scale in different solvents is a long-standing problem in the field of electroanalytical chemistry as well as in electrochemistry. Several attempts to use an appropriate substance as a reference electrode have been reported. For example, electrode reactions of rubidium ion–rubidium amalgam[47], ferricinium ion–ferrocene[48] or tris(1,10-phenanthroline)iron(III)–tris(1,10-phenanthroline)iron(II)[49] have been proposed. Neither of these ions, however, has the same solvation energy in different solvents because of different ion–solvent interactions. The correction for the solvation energy, therefore, was suggested by Koepp, Wendt and Strehlow[48] and Coetzee and his co-workers[50, 51] to be made for each solvent

when these ions were used as reference ions. Since the values of solvation energy are not always available, however, it seems desirable to discover a reference ion which has the least variation of solvation energy with different solvents and therefore is able to be used as a reference without correction for the solvation.

The present author[37] proposed recently the use of $[Fe(bipy)_3]^+-[Fe(bipy)_3]$ couple as a reference electrode. Tris(2,2'-bipyridine)iron(II) gives several polarographic waves in acetonitrile(AN), N,N'-dimethylformamide(DMF) and propylene carbonate (PC) solutions containing tetraethylammonium perchlorate as supporting electrolyte. In the presence of free 2,2'-bipyridine, which is added to prevent the complex from ligand dissociaton, each of the first three waves is of a reversible one-electron reduction. The electrode processes of $[Fe(bipy)_3]^{2+}$ complex, therefore, are considered to proceed as:

$$[Fe(bipy)_3]^{2+} + e = [Fe(bipy)_3]^+$$

$$[Fe(bipy)_3]^+ + e = [Fe(bipy)_3]$$

$$[Fe(bipy)_3] + e = [Fe(bipy)_3]^-$$
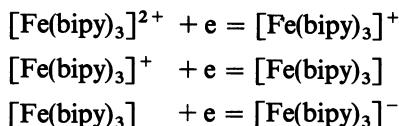
From the calculation of the solvation energy of cations, the relationship between the R_+ value and donor number(DN) of the solvent was revealed, where R_+ is the effective increment of the crystallographic radius to account for dielectric saturation, ion–solvent interaction and so on. The relationship is expressed as

$$(DN - a)(R_+ - b) = c \tag{32}$$

where a, b and c are constants. When $a = 9.7, b = 0.63$ and $c = 0.80$, equation (32) satisfied most the experimental results, that is

$$(DN - 9.7)(R_+ - 0.63) = 0.80 \tag{33}$$

Table 8. Calculated values of the difference in the relative standard potential $(\Delta E°)$[37]

Solvent	$\Delta E°/V$*	
	Rb^+	$[Fe(bipy)_3]^+$
Benzonitrile, C_6H_5CN	0.33	0.07
Acetonitrile, CH_3CN	0.16	0.04
Propylene carbonate	0.07	0·01
Methylacetate, CH_3COOCH_3	0.47	0.18
Acetone, $(CH_3)_2CO$	0.13	0.05
Ethylacetate, $CH_3COOC_2H_5$	0.51	0.20
Water, H_2O	0.00	0.00
Diethyl ether, $(C_2H_5)_2O$	0.71	0.28
N,N-dimethylformamide, $HCON(CH_3)_2$	−0.03	0.01
N,N-dimethylacetamide, $CH_3CON(CH_3)_2$	−0.04	0.01
Dimethylsulphoxide, $(CH_3)_2SO$	−0.07	0.00
Pyridine	0.14	0.08
Hexamethylphosphoramide, $[(CH_3)_2N]_3PO$	−0.04	0.01

* $\Delta E° = E°_{solv.} - E°_{H_2O}$.

Equation (33) can be used to calculate the $\Delta E°(=E°_{solv.} - E°_{H_2O})$ of a reference ion. In *Table 8* are given the $\Delta E°$ values of rubidium and $[Fe(bipy)_3]^+$ ions in several solvents, which were calculated with the aid of equation (33). The $\Delta E°$ values in *Table 8* show clearly that $[Fe(bipy)_3]^+$ ion is superior to the Rb^+ ion as a reference ion. The same is expected of tris(1,10-phenanthroline)-iron(I) complex.

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