

TEMPERATURE-DEPENDENCE
OF ELECTROCHEMICAL KINETIC PARAMETERS:
ELECTRODE REACTION OF THE Zn(Hg)/Zn(II) SYSTEM*

S. KANG**, K. MATSUDA and R. TAMAMUSHI

*Institute of Physical and Chemical Research,
2-1 Hirosawa, Wako, Saitama, 351 Japan*

Received February 12th, 1981

The electrochemical kinetic parameters of the D.M.E./Zn(II) electrode reaction in aqueous solutions containing perchlorate, nitrate, chloride and bromide ions were measured at different temperatures (5–50°C) by the modified square-wave polarographic technique. The Arrhenius activation parameters and thermodynamic quantities of the electrode reaction were determined from the temperature dependence of the rate constant and conditional potential, respectively. Empirical correlations were observed between some pairs of kinetic and thermodynamic quantities.

Electrode reactions are influenced by temperature in a similar manner to conventional chemical reactions, and the activation quantities determined from the temperature dependence of electrochemical kinetic parameters are useful adjuncts to the knowledge on the mechanism of electrode reactions^{1,2}. Since the pioneering work by Randles and Somerton³ activation energies have been reported for a number of electrode reactions^{4,5}; among those studies Blackledge and Hush⁶ determined the activation energies for electrode reactions of Zn(II) ion at a dropping mercury electrode (D.M.E.) and observed a linear relationship between the enthalpy and entropy of activation. The information on activation quantities available in the literature, however, does not seem sufficient to make any mechanistic discussion.

This paper concerns the determination of kinetic parameters of the D.M.E./Zn(II) electrode reaction in different supporting electrolyte solutions in the temperature range from 5 to 50 °C at intervals of 5 °C. Activation and thermodynamic quantities are determined from the temperature dependence of electrochemical kinetic parameters, and relationships between pairs of kinetic and thermodynamic quantities are examined.

EXPERIMENTAL

The electrochemical kinetic parameters were determined by the modified square-wave polarography⁷. The electrode potential of the D.M.E. was varied linearly with time at a rate of 0.2 to

* Presented at the J. Heyrovský Memorial Congress on Polarography in Prague, 1980.

** Present address: Department of Metallurgy, Faculty of Engineering, Korea University, 1-700 Ogawa, Kodaira, Tokyo, 187 Japan.

0.5 mV s^{-1} and was modulated by a square-wave signal of amplitude $\Delta E = 5 \text{ mV}$ and half-period $\theta = 3 \text{ ms}$ by using a Potentiostat Model 361 (Fuso Seisakusho). The periodical component of current at the moment of $\theta/2$ was sampled and measured by using a Square Wave Unit Model 903 (Fuso Seisakusho). Conventional d.c. polarographic measurements were carried out in parallel with the square-wave polarography.

The cell construction was similar to that described in the previous paper⁷. The glass capillary tubing of the D.M.E. was immersed deeply into the electrolysis solution so that the temperature of the mercury drop was equilibrated with the solution temperature. The drop time of the D.M.E. was electromechanically controlled at 6.0 s by a Drop Controller Model 329 (Fuso Seisakusho) and the flow rate of mercury was measured at each experimental temperature ($m = 0.59 - 0.9 \text{ mg s}^{-1}$ in redistilled water at open circuit and at 25°C). The counter electrode was a bright Pt-spiral placed in the electrolysis solution. The reference electrode was a saturated calomel electrode at room temperature, this electrode being connected to the electrolysis solution by a salt bridge. Temperature of the cell compartment containing the D.M.E., Pt-counter electrode, and electrolysis solution was regulated with the accuracy of $\pm 0.1^\circ\text{C}$ by means of a water thermostat.

The solutions were prepared by using analytical reagent chemicals and redistilled water, the molar concentration of Zn(II) was 0.2–1.0 mM and calibrated at each temperature. The dissolved oxygen was expelled by passing nitrogen through and over the solution.

RESULTS

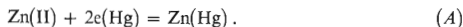
The diffusion-controlled limiting current and reversible half-wave potential $E_{1/2}^r$ were determined by the analysis of d.c. polarographic waves⁸. The electrochemical rate parameter λ_c^0 and cathodic transfer coefficient α_c were obtained from square-

TABLE I

Kinetic parameters for the D.M.E./Zn(II) electrode reaction in 1M-NaClO₄ solution containing 0.01M-HClO₄

Temp. °C	$-E_{1/2}^r$ V vs S.C.E.	$-E^{0'}$ V vs S.C.E.	$10^6 D_0$ $\text{cm}^2 \text{ s}^{-1}$	$\alpha_c = a + b\zeta$		λ_c^0 $\text{s}^{-1/2}$	$10^3 k_c^0$ cm s^{-1}
				a	b		
5	1.013	1.019	5.3	0.27	—	0.41	1.1
10	1.009	1.014	6.1	0.24	0.01	0.55	1.5
15	1.001	1.006	7.0	0.28	0.01	0.75	2.2
20	1.000	1.004	8.7	0.28	0.01	0.94	3.0
25	0.996	0.999	10.0	0.28	0.01	1.17	4.0
30	0.990	0.992	11.5	0.31	0.01	1.50	5.4
35	0.986	0.988	13.3	0.29	—	1.77	6.7
40	0.976	0.980	14.4	0.32	0.01	2.30	9.1
45	0.974	0.975	16.4	0.26	—	2.73	11.3
50	0.969	0.970	19.0	0.29	0.01	3.20	14.0

wave polarograms by using the analytical method described earlier^{7,9}; in this analysis the electrode reaction was assumed to be a one-step two-electron transfer as represented by



Diffusion coefficient of Zn(II), D_0 , was estimated from the diffusion-controlled limiting current by the Ilkovič equation, and that of Zn(Hg), D_R , from the experimental data reported by Bond and coworkers¹⁰. Conditional potential $E^{0'}$ and conditional rate constant k_c^0 were calculated according to the following equations:

$$E^{0'} = E_{1/2}^r + \frac{RT}{2nF} \ln \frac{D_0}{D_R} \quad (1)$$

$$k_c^0 = \lambda_c^0 D_0^{(1-\alpha_c)/2} D_R^{\alpha_c/2}. \quad (2)$$

The cathodic transfer coefficient α_c was analysed by assuming a linear function of electrode potential as represented by⁹

$$\alpha_c = a + b\zeta, \quad \zeta = \frac{nF}{RT}(E - E_{1/2}^r). \quad (3), (4)$$

The results are presented in Tables I–V.

The activation energy of electrode reaction at the conditional potential is defined by Eq. (5) in terms of the temperature dependence of conditional rate constant¹¹:

$$U^* = -R \left(\frac{\partial \ln k_c^0}{\partial T^{-1}} \right)_p. \quad (5)$$

The plot of $\ln k_c^0$ against T^{-1} (Arrhenius plot) gave a reasonably good straight line which indicates that the rate constant satisfies the Arrhenius-type equation

$$k_c^0 = A \exp \left(- \frac{U^*}{RT} \right), \quad (6)$$

where A is the pre-exponential frequency factor.

Similarly the temperature dependence of diffusion coefficients can be represented by the Arrhenius-type equation; the activation energy for diffusion of Zn(II) in solution was determined from the slope of $\ln D_0$ vs T^{-1} plot.

Besides the activation parameters mentioned above, the enthalpy and entropy of the electrode reaction, ΔH^θ and ΔS^θ , were calculated from the temperature

TABLE II
Kinetic parameters for the D.M.E./Zn(II) electrode reaction in LiNO₃ solutions

Temp. °C	$-E_{1/2}^r$ V vs S.C.E.	$-E^{0'}$ V vs S.C.E.	$10^6 D_0$ cm ² s ⁻¹	$\alpha_c = a + b\zeta$		λ_c^0 s ^{-1/2}	$10^3 k_c^0$ cm s ⁻¹
				a	b		
1M-LiNO ₃							
5	1.010	1.016	5.1	0.25	—	0.47	1.2
10	1.006	1.011	6.0	0.25	—	0.61	1.7
15	1.000	1.005	7.0	0.26	0.01	0.80	2.4
20	0.995	0.999	8.1	0.26	0.01	1.02	3.2
25	0.991	0.994	9.8	0.26	—	1.23	4.1
30	0.985	0.988	10.8	0.27	—	1.50	5.2
35	0.980	0.983	11.9	0.27	—	1.98	7.2
40	0.975	0.977	13.8	0.28	—	2.45	9.5
45	0.969	0.970	15.5	0.29	—	3.02	12.2
50	0.964	0.965	17.9	0.28	—	3.65	15.7
2M-LiNO ₃							
5	0.999	1.006	4.6	0.22	—	0.37	0.9
10	0.994	1.000	5.4	0.21	—	0.49	1.3
15	0.989	0.994	6.5	0.21	—	0.62	1.7
20	0.984	0.989	7.1	0.22	—	0.82	2.4
25	0.979	0.983	8.5	0.23	—	1.01	3.2
30	0.974	0.978	9.7	0.24	—	1.31	4.4
35	0.969	0.972	11.1	0.28	0.01	1.62	5.8
40	0.964	0.967	12.5	0.24	—	1.90	7.1
45	0.959	0.961	14.7	0.24	—	2.31	9.1
50	0.954	0.955	16.3	0.25	—	2.97	12.3
4M-LiNO ₃							
5	0.976	0.982	5.2	0.19	—	0.64	1.6
10	0.970	0.975	6.2	0.20	—	0.84	2.3
15	0.966	0.971	7.2	0.19	—	1.06	3.1
20	0.960	0.964	8.3	0.21	—	1.37	4.2
25	0.954	0.957	9.7	0.21	-0.01	1.93	6.3
30	0.949	0.952	10.8	0.22	-0.01	2.31	8.0
35	0.944	0.946	12.5	0.23	-0.01	2.77	10.2
40	0.939	0.941	14.0	0.21	-0.01	3.49	13.4
45	0.934	0.935	15.7	0.21	-0.01	4.05	16.4
50	0.928	0.929	17.3	0.26	—	4.85	20.5

TABLE II
(Continued)

Temp. C°	$-E_{1/2}^I$ V vs S.C.E.	$-E^{0'}$ V vs S.C.E.	$10^6 D_0$ cm ² s ⁻¹	$\alpha_c = a + b\zeta$		λ_c^0 s ^{-1/2}	$10^3 k_c^0$ cm s ⁻¹
				a	b		
6M-LiNO ₃							
5.8	0.949	0.958	2.9	0.19	—	1.7	3.3
10	0.943	0.952	3.5	0.21	—	2.2	4.8
15	0.938	0.946	3.9	0.22	—	2.7	6.3
20	0.933	0.941	4.6	0.21	—	3.3	8.1
25	0.927	0.934	5.3	0.23	—	4.2	10.9
30	0.922	0.929	5.9	0.28	—	6.0	16.9
35	0.917	0.923	6.7	0.29	0.01	7.0	20.9
40	0.912	0.918	7.4	0.30	—	9.1	28.5
45	0.907	0.912	8.7	0.33	-0.01	10.3	34.5
50	0.902	0.907	9.4	0.50	—	11.5	42.2

dependence of the conditional potential $E^{0'}$ according to the well-known relationships:

$$\Delta H^0 = -nFE^{0'} + nFT \frac{\partial E^{0'}}{\partial T} \quad (7)$$

$$\Delta S^0 = nF \frac{\partial E^{0'}}{\partial T} \quad (8)$$

These thermodynamic parameters, ΔH^0 and ΔS^0 , are conditional quantities and do not refer to the standard state of the electrode reaction.

The activation and thermodynamic parameters mentioned above are summarized in Table VI.

DISCUSSION

The theory of electrode reaction¹² gives approximate expression (9) for the pre-exponential frequency factor A

$$\ln A = \ln Z + \ln \kappa + \Delta S^*/R, \quad (9)$$

TABLE III
Kinetic parameters for the D.M.E./Zn(II) electrode reaction in NaNO₃ solutions

Temp. °C	$-E_{1/2}^f$ V vs S.C.E.	$-E^{0'}$ V vs S.C.E.	$10^6 D_0$ cm ² s ⁻¹	$\alpha_c = a + b\zeta$		λ_c^0 s ^{-1/2}	$10^3 k_c^0$ cm s ⁻¹
				a	b		
1M-NaNO ₃							
5	1.019	1.025	4.5	0.22	—	0.42	1.0
10	1.011	1.017	5.4	0.26	—	0.56	1.5
15	1.006	1.011	6.3	0.25	—	0.73	2.1
20	1.003	1.008	7.2	0.24	—	0.96	2.8
25	0.995	1.000	8.5	0.26	—	1.14	3.6
30	0.991	0.995	9.5	0.31	—	1.53	5.2
35	0.984	0.987	10.8	0.26	—	2.24	7.9
40	0.982	0.985	12.1	0.25	—	2.34	8.6
45	0.977	0.979	14.0	0.27	—	2.72	10.6
50	0.971	0.973	15.5	0.30	—	3.22	13.1
2M-NaNO ₃							
5	1.010	1.017	4.5	0.22	—	0.34	0.8
10	1.004	1.010	5.5	0.22	—	0.46	1.2
15	0.999	1.004	6.3	0.23	—	0.60	1.7
20	0.994	0.999	7.6	0.24	—	0.78	2.3
25	0.990	0.994	8.6	0.25	—	0.98	3.1
30	0.985	0.989	9.5	0.25	—	1.28	4.2
35	0.980	0.983	10.6	0.24	—	1.55	5.4
40	0.975	0.978	12.5	0.25	—	1.84	6.8
45	0.969	0.971	14.3	0.26	—	2.29	9.0
50	0.964	0.966	15.4	0.24	-0.01	2.68	10.8
4M-NaNO ₃							
5	0.992	1.001	4.2	0.22	0.01	0.48	1.1
10	0.986	0.993	4.9	0.21	—	0.66	1.6
15	0.982	0.998	5.6	0.22	0.01	0.82	2.2
20	0.976	0.981	6.7	0.21	0.01	1.04	3.0
25	0.972	0.977	7.4	0.20	—	1.30	3.8
30	0.967	0.971	8.6	0.21	—	1.72	5.4
35	0.962	0.966	9.5	0.21	—	2.26	7.4
40	0.957	0.960	11.0	0.20	-0.01	2.80	9.8
45	0.951	0.954	12.0	0.19	-0.01	3.29	11.9
50	0.947	0.950	13.5	0.24	-0.01	4.39	16.9

where ΔS^{\ddagger} is the entropy of activation, κ is the transmission coefficient whose value is assumed equal to unity, and Z is the collision number for electrode reaction, being about 10^4 cm s^{-1} . Under this approximation, the entropies of activation for the Zn(II)/Zn(Hg) electrode reactions are calculated to be nearly $20\text{--}40 \text{ J mol}^{-1} \text{ K}^{-1}$ from the experimental values of A .

The electrochemical entropy of activation due to rearrangement of the outer solvation spheres of reactants (outer-sphere rearrangement entropy) may be given by the expression^{12,13},

$$\frac{\Delta S_{\text{sol}}^{\ddagger}}{\text{kJ mol}^{-1} \text{ K}^{-1}} = \frac{89n^2}{(a/10^{-8} \text{ cm})} \left(\frac{2}{n_D^3} \frac{dn_D}{dT} - \frac{1}{\epsilon_r^2} \frac{d\epsilon_r}{dT} \right), \quad (10)$$

where a is the radius of the reactant, and ϵ_r and n_D are the relative permittivity and refractive index (D-line), respectively, of the medium. For $\Delta S_{\text{sol}}^{\ddagger}$ in aqueous solutions at 25°C we obtain

$$\frac{\Delta S_{\text{sol}}^{\ddagger}}{\text{J mol}^{-1} \text{ K}^{-1}} \approx - \frac{5.6n^2}{(a/10^{-8} \text{ cm})} \quad (11)$$

using the following numerical values: $n_D = 1.33$ (25°C), $dn_D/dT = -0.00014 \text{ K}^{-1}$ ($15\text{--}60^\circ \text{C}$), $\epsilon_r = 78.5$ (25°C), and $d\epsilon_r/dT = -0.344$ ($10\text{--}60^\circ \text{C}$). Equation (11) shows that $\Delta S_{\text{sol}}^{\ddagger}$ in aqueous solutions should be negative and may be about -20 to $-30 \text{ J mol}^{-1} \text{ K}^{-1}$ for a two-electron process ($n = 2$).

TABLE IV

Kinetic parameters for the D.M.E./Zn(II) electrode reaction in 1M-KCl solution

Temp. $^\circ \text{C}$	$-E_{1/2}^{\ddagger}$ V vs S.C.E.	$-E^{0'}$ V vs S.C.E.	$10^6 D_0$ $\text{cm}^2 \text{ s}^{-1}$	$\alpha_c = a + b\zeta$		λ_c^0 $\text{s}^{-1/2}$	$10^3 k_c^0$ cm s^{-1}
				a	b		
5	1.029	1.034	5.8	0.24	0.02	0.62	1.7
10	1.024	1.029	6.7	0.26	0.02	0.81	2.3
15	1.019	1.023	7.7	0.27	0.02	1.05	3.2
20	1.016	1.020	9.2	0.28	0.02	1.32	4.3
25	1.012	1.015	11.0	0.29	0.01	1.54	5.4
30	1.008	1.010	12.3	0.33	0.02	2.02	7.5
35	1.004	1.005	15.6	0.36	0.02	2.37	9.6
40	0.999	1.000	16.4	0.36	0.01	2.97	12.3
45	0.997	0.997	18.6	0.36	0.02	3.16	13.7
50	0.994	0.993	21.7	0.35	0.02	3.52	16.1

It is important to note that the theoretical value of $\Delta S_{\text{sol}}^{\ddagger}$ is opposite in its sign to ΔS^{\ddagger} calculated from the experimental frequency factor. The difference between $\Delta S_{\text{sol}}^{\ddagger}$ and ΔS^{\ddagger} suggests that the outer-sphere rearrangement is not the only process which operates on the activation quantities of Zn(II)/Zn(Hg) electrode reaction. Instead of making further discussions on the mechanism of the electrode reaction, we are going to examine some phenomenological relationships among the kinetic and thermodynamic quantities.

In the field of electrode kinetics, a linear correlation between the enthalpy and entropy of activation, *i.e.* the isokinetic relationship, was observed first by Blackledge

TABLE V
Kinetic parameters for the D.M.E. Zn(II) electrode reaction in 1M-KBr solution

Temp. °C	$-E_{1/2}^{\ddagger}$ V vs S.C.E.	$-E^{0r}$ V vs S.C.E.	$10^6 D_0$ $\text{cm}^2 \text{s}^{-1}$	$\alpha_c = a + b\zeta^r$		j_c^0 $\text{s}^{-1/2}$	$10^3 k_c^0$ cm s^{-1}
				a	b		
5	1.024	1.029	5.3 4.8 ^a	0.19	0.01	1.2	3.0
10	1.019	1.024	6.4 5.7 ^a	0.22	0.02	1.6	4.4
15	1.013	1.018	7.4 6.4 ^a	0.23	0.01	2.1	6.1
20	1.009	1.013	8.8 7.5 ^a	0.24	0.02	2.8	8.8
25	1.005	1.008	10.1 8.6 ^a	0.25	0.02	3.5	11.8
30	1.001	1.004	12.1 10.0 ^a	0.26	0.01	4.3	15.7
35	0.996	0.997	13.2 11.2 ^a	0.46	0.04	5.8	22.4
40	0.991	0.993	15.6 14.0 ^a	0.20	—	6.9	27.7
45	0.989	0.990	16.9 14.6 ^a	0.21	—	8.4	35.0
50	0.981	0.981	18.2 15.7 ^a	0.34	—	10.1	43.5

^a Determined by normal pulse polarography.

and Hush⁶ by using the activation parameters measured by Randles and Somerton³. One of the present authors (R.T.)⁵ has re-examined the electrochemical isokinetic relationship using 64 sets of data available in literature, and has demonstrated the existence of an empirical correlation between U^\ddagger and $\ln A$ with a correlation coefficient $r = 0.879$ and isokinetic compensation temperature $T_c = 271$ K. The activation parameters for the D.M.E./Zn(II) electrode reactions determined in the present study are compatible with the above-mentioned finding as shown in Fig. 1. Although the isokinetic relationship appears to be useful information in considering the mechanism of electrode reaction, we still have to doubt that the relationship may be spurious and we shall not make further discussion on the physical significance of the relationship.

In aqueous solutions containing nitrate or perchlorate ions, the rate parameters of the D.M.E./Zn(II) electrode reaction were found first by Behr and Malyszko¹⁴ and later by Jindal and coworkers¹⁵ to be influenced by the activity of water. This finding suggests the existence of some correlations between pairs of the kinetic and thermodynamic parameters in perchlorate and nitrate solutions. The statistical

TABLE VI

Activation and thermodynamic parameters for the D.M.E./Zn(II) electrode reaction in different electrolyte solutions (5–50°C)

Medium	Activation parameter			Thermodynamic parameter	
	U^\ddagger kJ mol ⁻¹	$\ln A$ cm s ⁻¹	U_D^\ddagger kJ mol ^{-1a}	ΔH^θ kJ mol ⁻¹	ΔS^θ J mol ⁻¹ K ⁻¹
1M-NaClO ₄	42.7	11.7	12.3	209	210
1M-LiNO ₃	42.3	11.6	20.5	211	221
2M-LiNO ₃	43.1	11.6	21.1	208	216
4M-LiNO ₃	42.8	12.1	20.1	206	226
6M-LiNO ₃	43.3	13.0	19.5	199	219
1M-NaNO ₃	42.6	11.6	20.4	212	221
2M-NaNO ₃	43.0	11.5	20.2	209	215
4M-NaNO ₃	44.4	12.4	19.6	206	214
1M-KCl	38.4	10.3	22.3	202	176
1M-KBr	44.8	13.6	20.9	207	198
			20.4 ± 0.6^b		

^a Arrhenius activation energy for the diffusion of Zn(II) ion. ^b Calculated from the D -values determined by normal pulse polarography.

analysis of the parameters in Table VI gave the result as represented by Fig. 2, where a pair of parameters connected by a straight line exhibits a correlation with a correlation coefficient given beside each line.

In conclusion, following observations can be made from the present study on the variation of kinetic and thermodynamic parameters for D.M.E./Zn(II) electrode reaction with the composition of solution: 1) Rearrangement of the outer solvation spheres of reactants is not the only process which determines the entropy of activation. 2) The activation parameters, U^\ddagger and $\ln A$, satisfy the isokinetic relationship. 3) The variation of $\ln k_c^\ominus$ (corresponding to the Gibbs energy of activation) is more strongly affected by the entropic term $\ln A$ than by the enthalpic term U^\ddagger . 4) In perchlorate and nitrate solutions, significant correlations were observed for the following pairs of parameters: ΔG^\ominus vs ΔH^\ominus , $\ln k_c^\ominus$ vs ΔG^\ominus (ΔH^\ominus), and $\ln A$ vs ΔG^\ominus (ΔH^\ominus). These correlations became less significant if the electrode reactions in halide solutions were included in the analysis; this difference between the correlations may be understood by considering the complexation of Zn(II) ion in halide solutions.

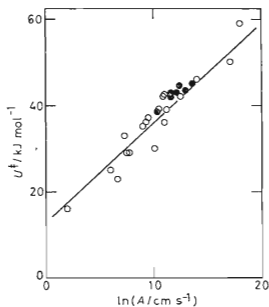


FIG. 1

Isokinetic (enthalpy-entropy) relationship for the Zn(Hg)/Zn(II) electrode reaction in solutions of various compositions: solid circles represent the values obtained in this study, open circles the values given in literature, and the straight line represents the isokinetic relationship⁴ determined by using all the data available in literature

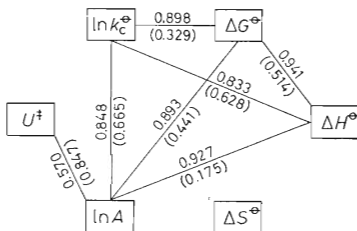


FIG. 2

Correlations between pairs of the kinetic and thermodynamic parameters of the D.M.E./Zn(II) electrode reactions in perchlorate and nitrate solutions. Figures beside each line give the corresponding correlation coefficients; figures in parenthesis are the correlation coefficients calculated by including the reactions in halide solutions

REFERENCES

1. Tamamushi R.: *Rev. Polarog. (Japan)* 10, 1 (1962).
2. Weaver M. J.: *J. Phys. Chem.* 80, 2645 (1976).
3. Randles J. E. B., Somerton K. W.: *Trans. Faraday Soc.* 48, 951 (1952).
4. Tamamushi R.: *Kinetic Parameters of Electrode Reactions of Metallic Compounds*. Butterworths, London 1975.
5. Tamamushi R.: *Denki Kagaku* 48, 603 (1980).
6. Blackledge J., Hush N. S.: *J. Electroanal. Chem. Interfacial Electrochem.* 5, 435 (1963).
7. Tamamushi R., Matsuda K.: *J. Electroanal. Chem. Interfacial Electrochem.* 80, 201 (1977).
8. Tamamushi R., Sato Gen P. in the book: *Progress in Polarography* (P. Zuman, L. Meites, I. M. Kolthoff, Eds.), Vol. III, p. 16. Wiley-Interscience, New York 1972.
9. Matsuda K., Tamamushi R.: *J. Electroanal. Chem. Interfacial Electrochem* 100, 831 (1979).
10. Bond A. M., Grabaric B. S., Jones R. D., Rumble N. W.: *J. Electroanal. Chem. Interfacial Electrochem.* 100, 625 (1979).
11. Parsons R.: *Pure Appl. Chem.* 37, No 4 (1974).
12. Marcus R. A.: *J. Chem. Phys.* 43, 679 (1965); *Electrochim. Acta* 13, 995 (1968).
13. Reynolds W. L., Lumry R. W.: *Mechanisms of Electron Transfer*, Chap. 6 and 7. The Ronald Press Company, New York 1966.
14. Behr B., Malyszko J.: *Bull. Acad. Pol. Sci.* XIII, 747 (1965).
15. Jindal H. L., Matsuda K., Tamamushi R.: *J. Electroanal. Chem. Interfacial Electrochem.* 90, 185 (1978).