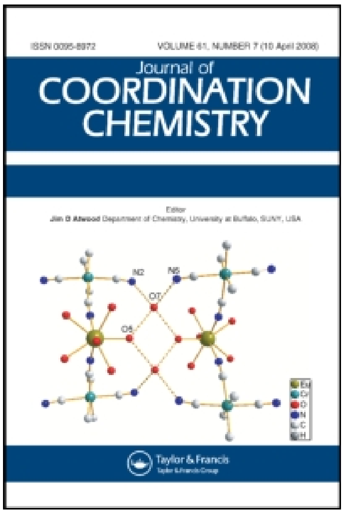

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ELECTROCHEMICAL STUDIES OF TETRACROWN-ETHER SUBSTITUTED PHTHALOCYANINES IN SOLUTION

Ali Riza Özkaya[a]; Ali Ihsan Okur[b]; Ahmet Gül[b]; Özer Bekâroğlu[b]
[a] Department of Chemistry, Faculty of Atatürk Education, Marmara University, Kadiköy, Istanbul, Turkey [b] Department of Chemistry, Technical University of Istanbul, Maslak, Istanbul, Turkey

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ELECTROCHEMICAL STUDIES OF TETRA-CROWN-ETHER SUBSTITUTED PHTHALOCYANINES IN SOLUTION

ALI RIZA ÖZKAYA

Department of Chemistry, Faculty of Atatürk Education, Marmara University, Kadiköy, Istanbul, Turkey

ALI IHSAN OKUR, AHMET GÜL and ÖZER BEKÂROĞLU*

Department of Chemistry, Technical University of Istanbul, Maslak, Istanbul, Turkey

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Cyclic voltammetry of soluble metal-free and copper phthalocyanines with crown ethers attached to the periphery through oxymethyl bridges show two one-electron reduction processes on sweeping to negative potentials. The addition of sodium or potassium ions to the solution results in a decrease in diffusion coefficients, which is a consequence of intermolecular complex formation in the presence of these two cations.

KEYWORDS: phthalocyanines, copper, crown ether, electrochemistry

INTRODUCTION

In recent years, phthalocyanines have been studied extensively with respect to their potential importance for technological applications.[1] These materials are of specific interest for their special properties such as photoconductivity,[2] electrochromism,[3] catalytic[4] and photovoltaic[5] effects. Their sensitivity as photoreceptor materials attracts attention especially for the long wavelengths where they are functional.[6] The attractive and challenging characteristics of the phthalocyanines are their great variety, chemical stability, the relative ease with which they can be prepared and isolated and the strong dependence of their properties upon substitution patterns.

Cyclic voltammetry is the most widely used method to determine electrochemical properties in solution. In the case of phthalocyanines, the disadvantage of insolubility has been overcome either by working with electrodes coated with thin films of these materials[7] or by adding polar or bulky substituents (*e.g.*, *t*-butyl,[8] sulfur[9] or quaternary ammonium groups[10]).

Phthalocyanines appended with macrocyclic substituents bring novel features in addition to those of the parent molecules.[11–17] Among these we may site

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* Author for correspondence.

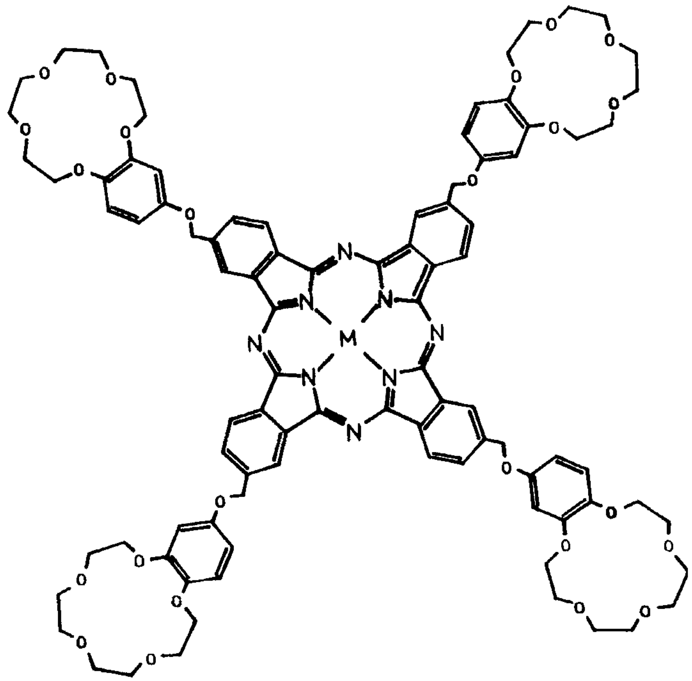
polynuclear complex formation, enhanced solubility, condensed phase interactions (ion channel and mesophase formation[18]) and electroconductivity. While crown-ether substituted species show a high tendency to bind alkali metal ions,[11-13] those with tetraazamacrocycles prefer to coordinate with transition metal ions.[16] Mixed donor macrocyclic substitution has been also accomplished.[15-17]

There are relatively few studies of the electrochemistry of phthalocyanines with macrocyclic substituents; the crown-ether-substituted diphthalocyanine complex of lutetium showed two, reversible, one-electron steps with K^+ and Na^+ ions;[19] the solvent effect was investigated in the case of Cu^{II} and Co^{II} phthalocyanines carrying 17-membered diazatrioxamacrocyclic substituents.[20]

In the present work, the cyclic voltammetry of Cu^{II} and metal-free phthalocyanines substituted with four crown ethers through oxymethyl bridges has been investigated in dimethylsulphoxide (DMSO) and the effect of alkali cations (Na^+ and K^+) on their CV has been examined.

EXPERIMENTAL

The synthesis of the tetracrown metal-free and Cu^{II} phthalocyanines ($TCRPcH_2$ and TCRPcCu) was previously reported[21] (Scheme 1). Spectrosol grade DMSO, dried over 4A molecular sieves, was used in the voltammetric experiments. Tetrabutylammonium perchlorate (TBAP) was employed as the supporting electrolyte at a 0.1



Scheme I Phthalocyanines used in this work; $TCRPcH_2$ (M = 2H) TCRPcCu (M = Cu).

mol dm^{-3} concentration. Solutions were deaerated by bubbling nitrogen for at least 30 minutes prior to each voltammetric measurement.

Cyclic voltammograms were performed with an instrument (CV EG and G PARC model 273 controlled by an external computer) utilizing a three-electrode configuration. A platinium wire served as counter electrode and a commercial saturated calomel electrode (SCE) was employed as the reference electrode. The working electrode was a platinium plate having an area of 0.55 cm^2. The surface of the working electrode was polished with a water suspension of Al_2O_3 before every experiment. The last polish was performed with a particle size of 50 nm. Voltammograms were recorded using an X-Y recorder (RE 0091). Coulometric measurements were carried out at constant potentials corresponding to the CV peak potentials of the phthalocyanines with bulk electrolysis of 5×10^{-4} mol dm^{-3} solutions at the platinium electrode, and afforded two, one-electron, redox waves.

RESULTS AND DISCUSSION

Cyclic Voltammetry of $TCRPcH_2$ and TCRPcCu

For each of the phthalocyanines, two, one-electron, reduction peaks were observed on sweeping to negative potentials with the corresponding anodic waves on the reverse sweep. The first wave for $TCRPcH_2$ shows irreversible behaviour, anodic to cathodic peak separation being 160 mV even at the slowest scan rate, 0.010 V/s. The second wave indicates a reversible wave with a peak separation of 60 mV at sweep rates 0.010–0.100 V/s. However, the peak separation increases considerably with sweep rate at the higher scan rates, resulting in a slow electron transfer process. Therefore, the variation of E_p with sweep rate for the second wave of $TCRPcH_2$ changes from the reversible case to the charge transfer rate-determining case.

On the other hand, the first electrode process for TCRPcCu shows a *quasi*-reversible character with a peak separation of 75 mV at a scan rate of 0.010 V/s, but becomes irreversible at higher scan rates. The second wave of TCRPcCu also indicates reversible behaviour and becomes irreversible with increasing scan rate.

The voltammetric data for $TCRPcH_2$ and TCRPcCu are shown in Table 1. The value of i_{pc}/i_{pa} for each wave is highly different from unity at all scan rates studied and the ratio $i_{pc}(1)/i_{pc}(2)$ decreases with sweep rate for each phthalocyanine. This may be attributed to instability of the reduced species or to a chemical reaction following each electron transfer for both $TCRPcH_2$ and TCRPcCu.

For each phthalocyanine, only the first cathodic peak current is directly proportional to the square root of scan rate. In other words, the value $i_p/v^{1/2}$ has a constant value at the all scan rates studied only for the first cathodic peak (Figs. 1 and 2). The other peak currents appear to be affected by coupled chemical reactions or decomposition of the species produced by the electrochemical reactions. On the basis of this result, the diffusion coefficient of each phthalocyanine was calculated from the cathdodic peak current of the first wave recorded at the highest scan rate (0.750 V/s) by using the Randles-Sevcik equation[22] for the irreversible case. The diffusion coefficient associated with the second cathodic wave was assumed to have the same value as that associated with the first.

The standard heterogeneous rate constant (k_o) and the value of αn for each redox process was determined from the slope and intercept (at logv = 0) of E_{pc} *versus* logv

Table 1 Voltammetric data for $TCRPcH_2$ and TCRPcCu.

Substrate	v/Vs^{-1}		E_{pc}/-V *vs* SCE	$i_{pc}/\mu A$	i_{pc}/i_{pa}	$\Delta E_p/V$
$TCRPcH_2$	0.010	1	0.770	1.60	2.13	0.170
		2	1.020	0.60	0.86	0.060
	0.050	1	0.795	3.50	1.89	0.205
		2	1.020	1.55	0.74	0.060
	0.100	1	0.805	5.20	1.82	0.215
		2	1.020	2.70	0.73	0.060
	0.250	1	0.820	7.80	1.73	0.240
		2	1.045	4.25	0.67	0.105
	0.500	1	0.830	11.20	1.63	0.255
		2	1.060	6.25	0.64	0.135
	0.750	1	0.835	14.10	1.49	0.260
		2	1.070	8.30	0.62	0.160
TCRPcCu	0.010	1	0.835	1.60	7.27	0.075
		2	1.100	0.75	1.50	0.060
	0.050	1	0.860	3.70	5.69	0.120
		2	1.120	1.85	1.28	0.090
	0.100	1	0.870	5.00	5.55	0.140
		2	1.130	2.95	1.64	0.105
	0.250	1	0.885	8.00	4.90	0.165
		2	1.145	5.00	1.43	0.125
	0.500	1	0.900	11.25	4.50	0.195
		2	1.160	7.00	1.75	0.145
	0.750	1	0.910	13.75	4.30	0.210
		2	1.170	9.50	1.73	0.155

plots[23–25] (Fig. 3). The standard potential, E°, for each wave was calculated by averaging the pair of cathodic and anodic peak potentials associated with the voltammograms recorded at the slowest scan rate at which the waves are reversible in general. Therefore, it was not necessary to correct the value of E° for

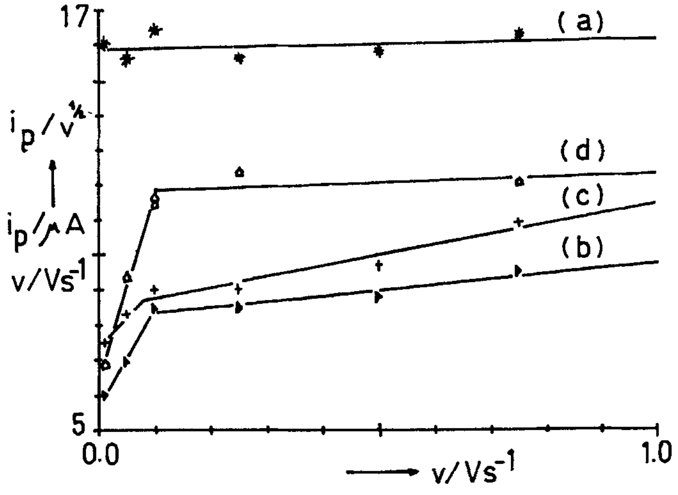


Figure 1 $i_p/v^{1/2}$ *vs* v for $TCRPcH_2$ [a for $i_{pc}(1)$, b for $i_{pc}(2)$, c for $i_{pa}(1)$, d for $i_{pa}(2)$].

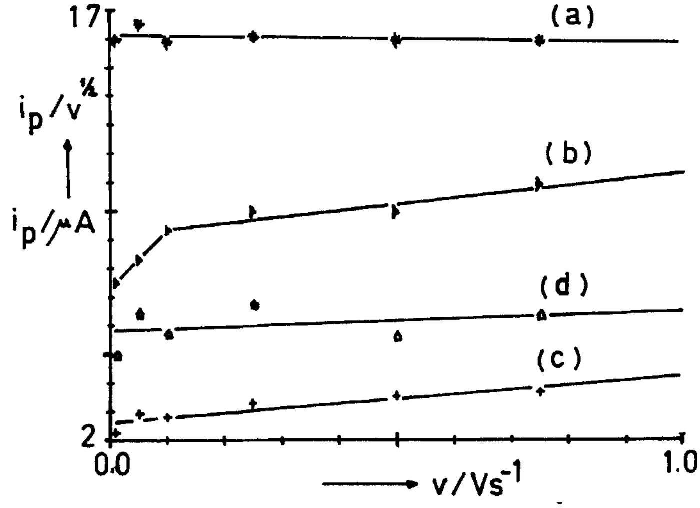


Figure 2 $i_p/v^{1/2}$ *vs* v for TCRPcCu [a for $i_{pc}(1)$, b for $i_{pc}(2)$, c for $i_{pa}(1)$, d for i_{pa} (2)].

irreversibility, using the method given by Matsuda and Ayabe.[26] However, the standard potential for the first redox process of $TCRPcH_2$ was corrected by this method because the process was irreversible even at a scan rate of 0.010 V/s. The data obtained from the evaluation of voltammograms as explained are presented in Table 2, with the relevant equations appended there.

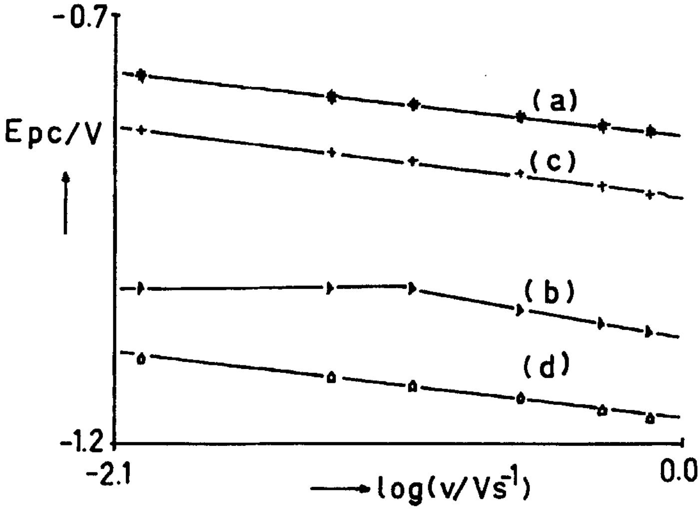


Figure 3 Cathodic peak potentials *vs* log v for $TCRPcH_2$ [a for $E_{pc}(1)$, b for $E_{pc}(2)$] and TCRPcCu [a for $E_{pc}(1)$, b for $E_{pc}(2)$].

Table 2 Diffusion coefficients, standard potentials and electron transfer rate constants for $TCRPcH_2$ and TCRPcCu on Pt in DMSO.

Substrate		E°/ − V *vs* SCE[a]	ΔC[b]	α	$10^{12}D/m^2s^{-1}$ [c]	E_{pc} at logv = 0/ − V *vs* SCE	$10^7k_o/ms^{-1}$ [d]
$TCRPcH_2$	1	0.678	0.035	0.84	3.46	0.840	1.15
	2	0.990	0.057	0.53	3.46[e]	1.077	31.7
TCRPcCu	1	0.797	0.039	0.75	3.68	0.911	8.05
	2	1.070	0.037	0.80	3.68[e]	1.170	10.3

[a] $E^o = \frac{E_{pc} + E_{pa}}{2}$. [b] $\Delta C = \frac{\partial E_{pc}}{\partial \log v} = 0.0295/\alpha n$; hence α. [c] $i_p = 2.98 \times 10^5 n (\alpha n)^{1/2} A c D^{1/2}$; hence D when αn is known for v = 0.750 V/s. [e] $E_p = E^o - b [0.52 - 1/2 \log (b/D) - \log k_o + 1/2 \log v]$; hence k_o when intercept at log v = O, D, αn and E°are known, b = 2.303 RT/αn F. [e] Assumed values for D.

Cyclic voltammograms of $TCRPcH_2$ and TCRPcCu have similar shapes and characteristics. This indicates that each redox process for TCRPcCu involves the phthalocyanine ligand rather than metal centre. However, the transfer of each electron to TCRPcCu occurs at more negative potentials with respect to $TCRPcH_2$.

The standard rate constants for each of the phthalocyanines have small values in the range of *quasi*-reversibility. However, the second electrode process for $TCRPcH_2$ ($k_o = 3.17 \times 10^{-6}$ m/s) occurs much faster than the first electron transfer ($k_o = 1.15 \times 10^{-7}$ m/s). On the other hand, each electron transfer occurs approximately at the same rate in the case of TCRPcCu. In addition, the rate constant for the first electrode process of TCRPcCu is larger than that of $TCRPcH_2$.

The Effect of Alkali Cations (Na^+ and K^+) on the Cyclic Voltammetry of $TCRPcH_2$ and TCRPcCu

Cyclic voltammograms of $TCRPcH_2$ and TCRPcCu recorded in the presence of Na+ and K+ (2×10^{-3} M) were analyzed in the same way by using the method of Nicholson and Shain.[23] Data are given in Table 3.

Addition of K^+ or Na^+ to each phthalocyanine does not have an important effect on peak potential and anodic to cathodic peak separation. In general, voltammetric waves are still reversible or *quasi*-reversible at slow scan rates and irreversible at higher scan rates. Only the cathodic peak current of the first wave is diffusion controlled. However, the presence of K^+ or Na^+ causes a considerable decrease in

Table 3 Diffusion coefficients, standard potentials and electron transfer rate constants for $TCRPcH_2$ and TCRPcPCu in the presence of Na+ and K+ (2×10^{-3} M) on Pt in DMSO.

Substrate		E°/ − V *vs* SCE[a]	ΔC	α	$10^{12}D/m^2s^{-1}$	E_{pc} at logv = O/ − V *vs* SCE	$10^7k_o/ms^{-1}$
$TCRPcH_2$ +	1	0.675	0.035	0.84	2.75	0.847	0.74
$NaClO_4$	2	0.990	0.058	0.51	2.75[a]	1.073	31.0
$TCRPcH_2$ +	1	0.678	0.037	0.80	1.15	0.845	0.71
$KClO_4$	2	0.990	0.059	0.50	1.15[a]	1.073	20.5
TCRPcCu +	1	0.775	0.039	0.75	2.95	0.890	7.00
$NaClO_4$	2	1.093	0.037	0.80	2.95[a]	1.190	10.1
TCRPcCu +	1	0.780	0.040	0.73	2.58	0.930	2.61
$KClO_4$	2	1.100	0.038	0.77	2.58[a]	1.200	9.53

[a] Assumed values for D.

the first cathodic peak current of each phthalocyanine. This results in a decrease of diffusion coefficients and therefore of standard rate constants for the first electrode process. These results may be attributed to the formation of intermolecular, sandwich-type, complexes with alkali cations, as detected previously.[21] It is obvious that the diffusion of sandwich-type phthalocyanines to the electrode surface would be relatively slow and that slow diffusion to the electrode would decrease the rate constant of the first electrode process (which is diffusion controlled).

Although the cyclic voltammograms of $TCRPcH_2$ and TCRPcCu have similar shapes and characteristics, the nature of the redox reactions involving ligand-based, one-electron, transfer is influenced by the presence of the metal ion. In the case of TCRPcCu, the first electron transfer is relatively much more reversible whereas the second process becomes somewhat more irreversible.

The presence of Na^+ or K^+ strongly affects the first cathodic peak current, resulting in a decrease in diffusion coefficients and standard rate constants of the first electrode process. These data closely follow spectroscopic evidence indicating intermolecular complex formation in the presence of these two alkali cations.[21] The standard rate constants for each of the phthalocyanines are in the range of *quasi*-reversibility and considerably small approaching the irreversible case, both in the presence and absence of alkali cations (Na^+ and K^+).

References

1. C.C. Leznoff and A.B.P. Lever (Eds.), *Phthalocyanines: Properties and Applications* (VCH, Weinheim, 1989).
2. H. Meier, W. Albrecht, D. Wöhrle and A. Jahn, *J. Phys. Chem.*, **90**, 6349 (1986).
3. M.M. Nicholson, *Ind. Eng. Chem. Prod. Res. Dev.*, **21**, 261 (1982).
4. B.R. Eggins, J.T.S. Irvine and J. Grimshaw, *J. Electronal. Chem.*, **266**, 125 (1989).
5. S.C. Dohlberg and M.E. Musser, *J. Chem. Phys.* **72**, 6706 (1980).
6. W.E. Ford, B.D. Rihter, M.E. Kenney and M.A.J. Rodgers, *Photochem. Photobiol.*, **50**, 277 (1989).
7. A. Elzing, A. Van der Putten, W. Visscher and E. Barendrecht, *J. Electroanal. Chem.*, **200**, 313 (1986).
8. J. Metz, G. Pawlowski and M. Hanack, *Z. Naturforsch.*, **38b**, 378 (1983).
9. J.T.S. Irvine, B.R. Eggins and J. Grimshaw, *J. Electroanal. Chem.*, **271**, 161 (1989).
10. C.C. Leznoff, S. Vigh, P.I. Svirskaya, S. Greenberg, D.M. Drew, E. Ben Hur and I. Rosenthal, *Photochem. Photobiol.*, **49**, 279 (1989).
11. A.R. Koray, V. Ahsen and Ö. Bekâroğlu, *J. Chem. Soc., Chem. Commun.*, 932 (1986); V. Ahsen, E. Yilmazer, M. Ertas and Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.*, 401 (1988).
12. V. Ahsen, E. Yilmazer, A. Gül and Ö. Bekâroğlu, *Macromal Chem. Rapid Commun.*, **8**, 243 (1987); V. Ahsen, E. Yilmazer and Ö. Bekâroğlu, *Macromol. Chem.*, **189**, 2533 (1988).
13. V. Ahsen, E. Yilmazer, A. Gürek, A. Gül and Ö. Bekâroğlu, *Helv. Chim. Acta*, **71**, 1616 (1988).
14. S. Sarigül and Ö. Bekâroğlu, *Chem. Ber.*, **122**, 291 (1989).
15. V. Ahsen, A. Gürek, E. Musluoğlu and Ö. Bekâroğlu, *Chem. Ber.*, **122**, 1073 (1989); E. Musluoğlu, V. Ahsen, A. Gül and Ö. Bekâroğlu, *Chem. Ber.*, **124**, 2531 (1991).
16. M. Koçak, A. Cihan, A.I. Okur and Ö. Bekâroğlu *J. Chem. Soc., Chem. Commun.*, 578 (1991); A. Gürek, V. Ahsen, A. Gül and Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.*, 3367 (1991).
17. G. Gümüs, Z.Z. Öztürk, V. Ahsen, A. Gül and Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.*, 2485 (1992).
18. C. Sirlin, L. Bosio, J. Simon, V. Ahsen, E. Yilmazer and Ö. Bekâroğlu, *Chem. Phys. Lett.*, **139**, 362 (1987).
19. M. Bardin, E. Bertounesque, V. Plichon, J. Simon, V. Ahsen and Ö. Bekâroğlu, *J. Electroanal. Chem.*, **271**, 173 (1989).
20. N. Tan, Ö. Bekâroğlu and F. Kadirgan, *J. Electroanal. Chem.*, in press.
21. A.I. Okur, A. Gül, A. Cihan, N. Tan and Ö. Bekâroğlu, *Synth. React. Inorg. Met.-Org. Chem.*, **20**, 1399 (1990).

22. A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, (Wiley, New York, 1980).
23. R.S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
24. E. Gileadi, E. Kirowa-Eisner and J. Penciner. *Interfacial Electrochemistry* (Addison-Wesley, Massachusetts, 1975).
25. E. Yeager and A.J. Salkind, *Techniques of Electrochemistry*, (Wiley, New York, 1972).
26. H. Matsuda and Y. Ayabe, *Z. Electrochem.*, **59**, 494 (1955).