

Electrochemical Investigation of N,N'-Propylene-bis-(salicylideneiminato) Mn(III) in Phosphate Buffer Solutions

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Summary. An electrochemical study on N,N'-Propylene-bis-(salicylideneiminato) Mn(III) was performed using cyclic voltammetry with convolution–deconvolution and digital simulation in phosphate buffer solutions of *pH* values ranging from 5–9.5 at a hanging mercury drop electrode (HMDE). The reduction pathway of the investigated complex shows that a moderately fast transfer of one electron is followed by a very fast chemical reaction (E_qC_{irr} scheme). The electrochemical parameters have been determined experimentally and *via* digital simulation experiments.

Keywords. Cyclic voltammetry; Convolution–deconvolution; Digital simulation; Mn(III) complex.

Elektrochemische Untersuchung von N,N'-Propylen-bis-(salicylideniminato)-Mn(III) in Phosphatpufferlösungen

Zusammenfassung. N,N'-Propylen-bis-(salicylideniminato)-Mn(III) wurde in Phosphatpufferlösungen mit *pH*-Werten im Bereich von 5–9.5 an einer Quecksilbertrofelektrode (HMDE) mittels cyclischer Voltammetrie (Konvolution–Dekonvolution, digitale Simulation) elektrochemisch untersucht. Ein mäßig schneller Transfer eines Elektrons wird von einer sehr schnellen chemischen Reaktion gefolgt (E_qC_{irr} -Schema). Die elektrochemischen Parameter wurden experimentell und durch Simulationsexperimente bestimmt.

Introduction

The use of higher valent manganese compounds in photosynthetic water oxidation has prompted wide interest in the chemical and electrochemical properties of various manganese complexes as redox models [1]. The role of manganese in the oxidation process has been based on the availability of higher oxidation states and variable coordination numbers [2–4]. A variety of nitrogen and nitrogen–oxygen donor complexes of manganese, including porphyrin complexes, have been proposed as models for manganese in photosystems, [3, 5, 6].

In the present study, an electrochemical investigation has been undertaken on N,N'-propylene-bis-(salicylideneiminato) Mn(III) utilizing the techniques of cyclic and convolution–deconvolution voltammetry at a HDME and digital simulation. It is focussed on the determination of the different chemical and electrochemical

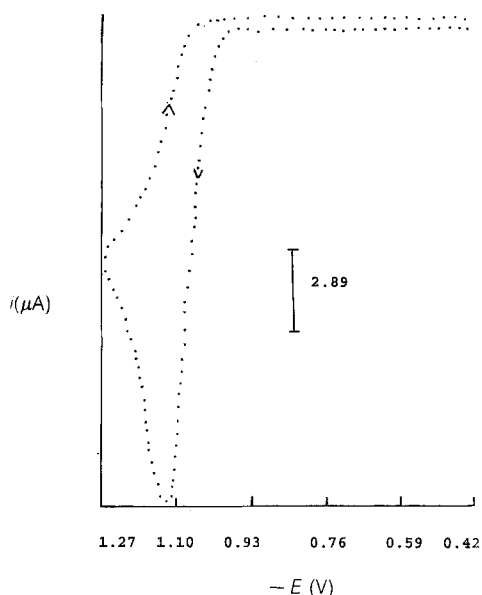


Fig. 1. Cyclic voltammogram of the investigated complex in phosphate buffer at *pH* 5.2 and a scan speed of 0.5 V/s

parameters as well as the mechanism of the electrode reaction of the complex of interest.

Results and Discussion

Figure 1 shows the cyclic voltammogram of the complex under consideration at *pH* 5.2 and at a scan speed of 0.5 V/s. One quasi-reversible reduction wave was observed (HMDE, phosphate buffer solution, room temperature). The reduction peak (E_p) of the cyclic voltammogram shifts to more negative values with increasing scan speed. The absence of an anodic peak up to scan speeds of 5 V/s indicates that a very fast chemical process follows the electron transfer.

The nature of the observed reduction wave was established from the following electrochemical peak characteristics:

i) Potential width of the peak

The asymmetry of the cathodic peak potential of the wave at various *pH* values is represented by the potential width, measured as $E_p - E_{p/2}$ (E_p is the cathodic peak potential, and $E_{p/2}$ is the half peak potential, respectively). The obtained values are listed in Table 1 and range from 60 to 78 mV, indicating the quasi-reversibility of the charge transfer and the fact that one electron is involved in the electrode reaction [9].

ii) Peak current potential vs. logarithm of scan speed

$$E_p = E^0 - \frac{RT}{\alpha n_a F} \left(0.78 - \frac{2.3}{2} \cdot \log \frac{\alpha n_a F D}{k_s^2 RT} \right) - \frac{2.3RT}{2\alpha n_a F} \log v \quad (1)$$

According to relationship 1 [9], the slope of the plot of E_p vs. $\log v$ was used to examine the electrochemical reversibility of the investigated system [9–11] and to obtain the values of the transfer coefficient α . From the slope (61–72 mV), the

Table 1. Peak characteristics of the investigated complex at different scan speeds

<i>pH</i>	scan speed (V/s)	$-E_p$ (V)	$E_p - E_{p/2}$ (mV)	w_p (mV)
5.2	0.1	0.82	60	96
	0.2	0.84	62	96
	0.5	0.86	64	97
	1	0.88	67	99
	2	0.91	72	99
7.4	0.1	1.06	63	95
	0.2	1.08	65	97
	0.5	1.10	69	98
	1	1.12	74	99
	2	1.14	78	100
9.4	0.1	1.260	65	95
	0.2	1.275	68	96
	0.5	1.300	69	97
	1	1.320	74	99
	2	1.345	78	100

Table 2. Electrochemical parameters of the investigated complex

<i>pH</i>	$k_s \times 10^2$ (cm/s)		$D \times 10^{10}$ (m ² /s)		α		$-E^0$ (V)	k_c
	CV	Sim	CV	Sim	CV	Sim	Decon	Sim
5.2	4.2	4.1	8.21	8.50	0.41	0.42	0.78	18
7.4	3.5	3.7	6.57	6.34	0.42	0.43	1.02	20
9.4	2.8	2.9	4.53	4.25	0.43	0.44	1.22	21

value of α was found to equal 0.42 ± 0.01 (Table 2). The values of the standard heterogeneous rate constant at various *pH* values listed in Table 2 were estimated from the intercept of the plot of E_p vs. $\log v$. The values of the diffusion coefficient at the selected *pH* values were determined from the slope of the plot of i_p vs. $v^{1/2}$ via Eq. (2) [9] and are cited in Table 2. The electron transfer coefficient α was calculated from Eq. (3) [12–15] where n_a is the number of electrons transferred in the electrochemical process, and E_{p2} and E_{p1} are the peak potential values (V) at the corresponding scan speeds v_1 and v_2 (V/s).

$$i_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} A C^{\text{bulk}} D_0 v^{1/2} \quad (2)$$

$$\alpha n_a = \left[\frac{0.0591}{(E_{p2} - E_{p1})} \right] \log \left(\frac{v_1}{v_2} \right)^{1/2} \quad (3)$$

Convolution analysis has been shown to be useful for the analysis of electrochemical data [16–20]. The maximum value of the convolution transform was a linear function of the concentration, whereas the voltammetric peak currents gave a non-linear working curve due to the increasing effects of uncompensated resistance at increasing concentration. The shape of the $I_1 - E$ curve gives important information for a classification of the nature of the electrode reaction. For a fast electrode reaction with no coupled chemical reactions, the shape of the $I_1 - E$ curve is identical to that of the $i - E$ polarogram at a dropping mercury electrode [18, 19]. For moderate fast and slow electrode reactions there is a separation between the forward and backward convolution, whereas in the case of a chemical step following the electron transfer, *i.e.* an *EC* scheme, the backward convolution does not return to the initial value [20].

The convolution of the current data $(\pi t)^{-1/2}$ function is obtained as

$$I_{1(t)} = i_{(t)} * \frac{1}{(\pi)^{1/2}} = \frac{1}{(\pi)^{1/2}} \int_0^t \frac{i(u)}{(t-u)^{1/2}} du \quad (4)$$

where $I_{1(t)}$ is the convoluted current at the total elapsed time t and $i(u)$ is the experimental current at time u [18–20].

The limit of $I_{1(t)}$ as E approaches infinity is known as I_{lim} and defined as Eq. (5) [20]:

$$I_{lim} = nFAC_{OX}^{bulk} D^{1/2} \quad (5)$$

This relation is quite useful for the evaluation of the diffusion coefficient of the starting species *via* C_{OX}^{bulk} and *vice-versa*, irrespective of the rate of electron transfer.

A better method for calculating E^0 by the use of voltammetry is to use a transformation of the current rather than the actual current values [20]. In the case of fast electron transfer, the derivative dI_1/dt consists of two mirror-image peaks with maximum amplitude at E^0 and a half-width of $(2RT/nF) \ln((\sqrt{2} + 1)/(\sqrt{2} - 1))$ mV, *i.e.* $3.526 RT/nF$ or $90.53/n$ mV at 25°C . In the case of slower electron transfer, the mean value of these peak potentials corresponds approximately to E^0 .

Figure 2 shows the $I_{1(t)}$ convolution of the cyclic voltammogram at 1 V/s and indicates that the backward convolution for the reduced species does not return to the initial value, confirming that a chemical process follows the quasi-reversible electron transfer [20]. The diffusion coefficient evaluated *via* I_{lim} using Eq. 5 is given in Table 2. It compares well with the value determined from cyclic voltammetry. Also, the lack of overlay of the backward sweep with the forward sweep as shown in Fig. 2 evidences the quasi-reversibility of the electrode reaction.

The deconvolution of the current-potential data with $1/\sqrt{\pi t}$ is shown in Fig. 3. It was found that the maximum peak position of the forward and backward deconvolution is displaced from the mean value of the reduction potential E^0 . The value of the reduction potential at the selected *pH* values was taken as the mean value of the maximum deconvoluted peak for forward and backward deconvoluted current (Table 2). The difference of height for the forward and backward sweep as shown in Fig. 3 may be due to the difference of the diffusion coefficients of the oxidized and reduced species in the aqueous electrolyte and at the mercury surface and/or to the presence of the fast chemical step after the moderate fast transfer of one electron in the electrode reaction. The measured values of peak width (w_p) of the deconvolution

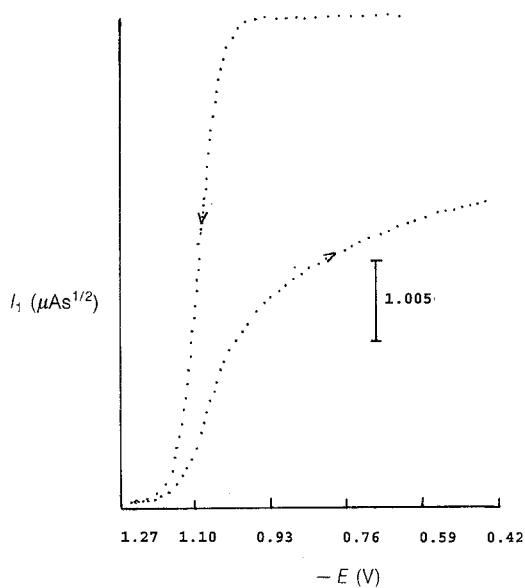


Fig. 2. I_1 convolution at a scan speed of 1 V/s

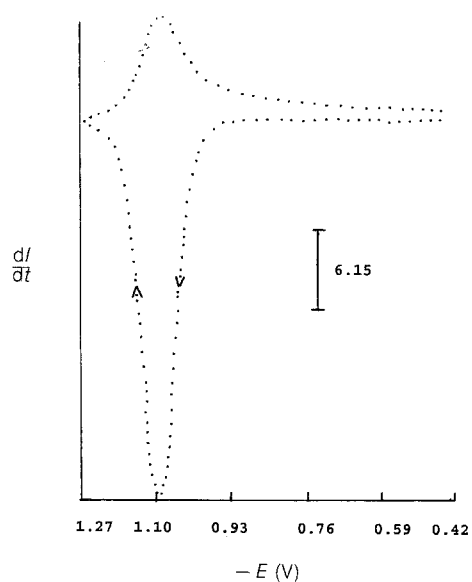


Fig. 3. Deconvoluted current (dI/dt) at a scan speed of 1 V/s

voltammetry were equal to 95–100 mV (Table 1), indicating the quasireversibility of the investigated system proposed from CV [20].

Inspection of Table 2 reveals that the electrochemical parameters are not much different and independent of the method of determination.

Digital Simulation

The major application of digital simulation is the determination of kinetic parameters for systems where the theoretical equations cannot be derived analytically, *e.g.* those involving second or higher order effects, coupled homogeneous reactions, and complex reaction sequences.

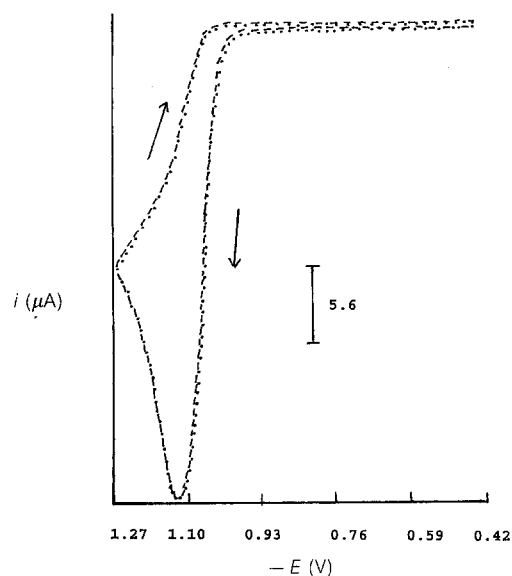
Table 3. Experimental and theoretical values of the peak characteristics at scan speeds 0.2 and 0.5 V/s

pH	scan speed (V/s)	$E_p - E_{p/2}$ (mV)		$-E_p$ (V)		w_p (mV)	
		CV	Sim	CV	Sim	CV	Sim
5.2	0.2	62	63	0.84	0.84	96	95
	0.5	64	65	0.86	0.855	97	96
7.4	0.2	65	66	1.08	1.084	97	95.8
	0.5	69	68	1.10	1.105	98	97.2
9.4	0.2	68	68	1.225	1.228	96	96.2
	0.5	69	70	1.300	1.303	97	98.0

In the present study, the electrochemical parameters of the investigated complex were determined directly *via* digital simulation by fitting the simulated cyclic voltammogram to the experimental one, using the average values calculated experimentally. To obtain knowledge of the true electrochemical process, the following four different mechanisms were proposed and the simulated curves were compared with the experimental voltammograms:

- i) E_{irr} mechanism, $n = 1$
- ii) E_{irr} mechanism, $n = 2$
- iii) $E_q C_{irr}$ mechanism, $n = 1$
- iv) $E_q C_{irr}$ mechanism, $n = 2$

Table 3 shows the peak characteristics measured experimentally and obtained theoretically for the $E_q C_{irr}$ scheme (type iii). The data prove that the number of

**Fig. 4.** Comparison of digital simulation (...) and experimental voltammogram (---) at a scan speed of 1 V/s

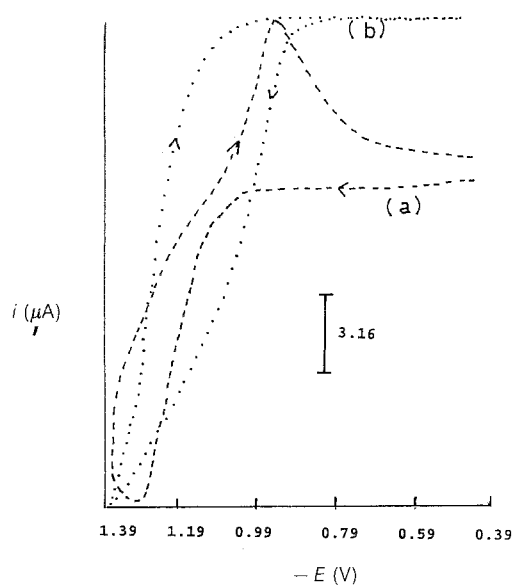
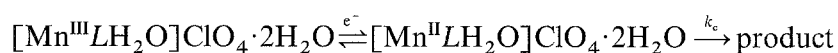


Fig. 5. Simulated voltammogram of E_{irr} mechanism (a) and convoluted current (b) at a scan speed of 1 V/s

electrons involved in the reduction step is one and that the electrode mechanism proceeds according to the $E_{\text{q}}C_{\text{irr}}$ scheme. Figure 4 shows the agreement between the experimental and simulated voltammograms of the system $E_{\text{q}}C_{\text{irr}}$ using the average values of the parameters estimated from the experimental data at pH 7.4 and a scan speed of 1 V/s. The homogeneous rate constant (k_c) for the chemical reaction was determined by simulation and its values at the selected pH values are given in Table 2. Figure 5 shows as an example the simulated voltammogram and its convoluted current for the E_{irr} mechanism (type i) which confirms the proposed $E_{\text{q}}C_{\text{irr}}$ mechanism.

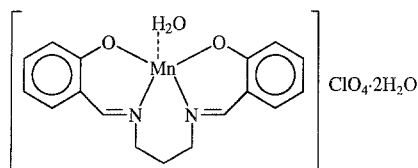
According to our results, we can propose the electrode pathway of the complex as follows:



Experimental

Reagents

The investigated N,N' -propylene-*bis*-(salicylideneiminato) Mn(III) complex ($[\text{Mn}^{\text{III}}\text{LH}_2\text{O}]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$) was prepared according to the method described in the literature [7]. The complex has the following structure [8]:



An alcoholic solution (40% v/v) of the complex in phosphate buffer as supporting electrolyte was investigated. The reagents were generally of laboratory grade. Triply distilled mercury was employed.

Apparatus

To provide i , I_1 , and dI_1/dt vs. E curves directly, the following arrangements were used: (i) a Princeton Applied Research (PAR) Potentiostat Model 264A (from EG&G) which was modified in our laboratory to be connected with computer; (ii) the EG&G Condecon software package; (iii) an electrode assembly Model 303A.

The double layer charging current was minimized by subtracting the background data from the experimental data. The electrodes used were a hanging mercury drop electrode (HMDE) with an area of $2.61 \times 10^{-2} \text{ cm}^2$ as working electrode and Ag/AgCl and Pt-wire as reference and counter electrodes, respectively.

Cyclic voltammetric experiments were carried out at scan speeds ranging from 0.05 to 5 V/s at $25 \pm 2^\circ \text{C}$. Simulation of the data was performed on an IBM computer using the EG&G Condesim package. Air was removed from the cell solution by passing nitrogen through the solution for twenty minutes; the measurements were performed in an N_2 atmosphere.

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