Dyes and Pigments, Vol. 37, No. 4, pp. 291–306, 1998

Printed in Great Britain
PII: S0143-7208(97)00083-1 0143-7208/98 $19.00+0.00

Electrochemical Characterization of Soluble Cobalt Phthalocyanine Derivatives

Keiichi Sakamoto* & Eiko Ohno

Department of Industrial Chemistry, College of Industrial Technology, Nihon University,
1-2-1 Izumi-cho, Narashino, Chiba 275, Japan

(Received 4 July 1997; accepted 8 August 1997)

ABSTRACT

Cyclic voltammograms and chronocoulometry were measured for soluble cobalt phthalocyanine derivatives and cobalt anthraquinocyanine which had been previously synthesized, in order to examine their electron transfer abilities and electrochemical mechanism in an organic solvent. Electron transfer properties were shown to be similar except for the cobalt phthalocyanine octacarboxylic acid. Electrode processes were diffusion controlled at almost one electron transfer involving some weak adsorption and having the following chemical reaction, except for the cobalt phthalocyanine octacarboxylic acid. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: cobalt phthalocyanine derivatives, cobalt anthraquinonecyanine, cyclic voltammetry.

1 INTRODUCTION

Metal phthalocyanines and their derivatives have exhibited high electron transfer abilities [1].

The functions of metal phthalocyanine derivatives are almost all based on electron transfer reactions because of their π electron conjugated ring system. There have been few electrochemical studies on the electron transfer properties of the solid state of metal phthalocyanine derivatives. It is necessary then to examine the electron transfer behavior in the solution of metal phthalocyanine derivatives in an organic solvent in order to study further

---

*Corresponding author.

applications, such as fixing, dyeing and dispersion use. In our previous papers, soluble metal phthalocyanine derivatives [2] were synthesized, and a new metal phthalocyanine derivative (metal anthraquinocyanine) which has four 9,10-anthraquinone units in the molecule was also synthesized [3]. Metal phthalocyanine derivatives are, however, utilized only in a few fields, because of their lower solubility in common organic solvents. It is felt, because of our previous studies, that the application of cobalt phthalocyanine derivatives could be more efficient than other metal ones [4, 5].

Observation of electron transfer is a most valid procedure for the estimation of functional materials. The electron transfer of metal phthalocyanines and their derivatives can be estimated by the preparation of a thin layer film.

We have measured cyclic voltammograms (CVs) and chronocoulometry of cobalt phthalocyanine tetrasulfonie acid (1), and cobalt phthalocyanine octacarboxylic acid (2) as standard compounds. Since cobalt octakis(hexoxymethyl)phthalocyanine (3) and cobalt anthraquinocyanine (4) are novel compounds they could be of value in order to estimate electron transfer ability and mechanisms within this type of compound.

2 EXPERIMENTAL

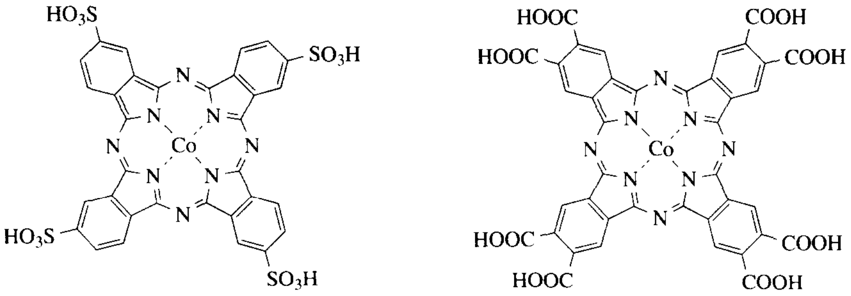
2.1 Equipment

Cyclic voltammetry and chronoamperometry of soluble cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4) were carried out with a BAS CV-50W voltammetric analyzer at room temperature in dimethylsulfoxide (DMSO) containing a 0.10 mol m^{-3} solution of tetrabutylanmonium perchlorate (TBAP). Cyclic voltammograms were recorded by scanning the potential at the rate of 50 mV^{-1}. The working and counter electrodes were platinum wires, and the reference electrode was a silver (Ag)/silver chloride (AgCl) saturated sodium chloride electrode. The area of working electrode was 2.0×10^{-2} cm^{2}.

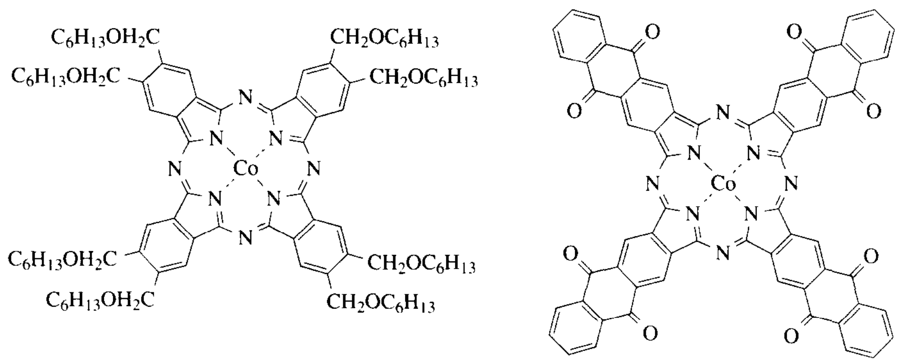
Infrared (IR) spectra were recorded on a Shimadzu IR-435 spectrometer. Electron spectra were measured on a Shimadzu UV-2100 UV-spectrometer. Each sample was prepared in a 0.025 mg m^{-3} pyridine solution. Elemental analyses were carried out using a Perkin–Elmer 2400. Melting points were measured with a Metler FP-5 apparatus.

2.2 Synthesis of soluble cobalt phthalocyanine derivatives (1)–(3) and of cobalt anthraquinocyanine (4)

Figure 1 shows the molecular structures of the cobalt phthalocyanine derivatives (1)–(3) and of the cobalt anthraquinocyanine (4).



Cobalt phthalocyanine tetrasulfonic acid (1) Cobalt phthalocyanine octacarboxylic acid (2)



Cobalt octakis(hexoxymethyl)phthalocyanine (3) Cobalt anthraquinocyanine (4)

Fig. 1. Molecular structure of cobalt phthalocyanine derivatives and cobalt anthraquinocyanine.

2.2.1 Cobalt phthalocyanine tetrasulfonic acid (1) [2, 6]

Cobalt phthalocyanine-4,4′,4″,4‴-tetrasulfonic acid was synthesized from 4-sulfophthalic acid, cobalt halide and urea.

A 200-ml three-necked flask equipped with a reflux condenser, a thermometer and a motor was charged with 12.3 g (50 mmol) of 4-sulfophthalic acid, 30.0 g (0.50 mol) of urea, 30 mmol of cobalt chloride ($CoCl_2$), 1 g of 1,8-diazabicyclo[5,4,0] undec-7-ene (DBU) as a catalyst, and 150 ml of 1,2,4-trichlorobenzene as a solvent. The reaction mixture was heated to 210°C for 180 min. The product was washed with benzene to fully remove 1,2,4-trichlorobenzene and was then filtered. The resulting solid was dried in vacuum to constant weight: yield 75%. (Found C, 42.91; H, 2.08; N, 19.67. $C_{32}H_{16}N_8O_{12}S_4Co$ requires C, 42.86; H, 1.80; N, 19.45), λ_{max}(pyridine)/nm 688.5, 649.0, 354.0, 213.0; ν_{max}/cm^{-1} 3000(ν_{C-H}) 1720(ν_{C-C}), 1450(δ_{C-H}), 1380(ν_{S-O}), 1050(δ_{C-H}), 770(δ_{C-H}).

2.2.2 Cobalt phthalocyanine octacarboxylic acid (2) [2, 7]

Cobalt phthalocyanine-2,3,9,10,16,17,23,24-octacarboxylic acid was synthesized from benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride), cobalt halide and urea under the reaction conditions for the monomer preparation.

A 100 ml two-necked flask equipped with a reflux condenser and a thermometer was charged with 2.50 g (11.5 mmol) of pyromellitic dianhydride, 13.0 g (0.22 mol) of urea, 23.5 mmol of $CoC1_2$, and 0.1 g of DBU. The flask was heated to 250°C until the reaction mixture was fused. The reaction product was washed with water, acetone and 6N-hydrochloric acid (HCI).

After drying, the solid obtained was hydrolyzed. Thirty grams of crude product, 30 g of potassium hydroxide (KOH) and 90 ml of water were charged in a 300 ml beaker. The beaker was heated for 480 min at 100°C. The mixture was diluted with 200 ml of water and was filtered. The filtrate was acidified to pH 2 with conc. HCl. The product precipitated as a blue color at this point. The blue product was separated from the solution by a centrifuge. The solid was washed with water three times, and was then dried.

The IR spectrum of the cobalt octasubstituted phthalocyanine synthesized from pyromellitic dianhydride gave a characteristic pattern of imide groups in the region of 1600–1800 cm^{-1}. The synthesized metal octasubstituted phthalocyanine changed the functional group from imide to acid by hydrolysis with KOH. It was confirmed that the functional groups were in fact changed to acid after the hydrolysis treatment; yield 30%. (Found C, 57.86; H, 2.14; N, 14.52. $C_{40}H_{16}N_8O_{16}Co$ requires C, 57.44; H 2.14; N, 14.90), λ_{max}(pyridine)/nm 684.0; ν_{max}/cm^{-1} 3390–3000(ν_{C-H}), 1750(ν_{C-O}), 1720(ν_{C-C}) 1480(ν_{C-H}) 1060(δ_{C-O}), 720(δ_{C-O}).

2.2.3 Cobalt octakis(hexoxymethyl)phthalocyanine (3) [2, 8]

Cobalt 2,3,9,10,16,17,23,24-octakis(hexoxymethyl)phthalocyanine was synthesized from 1,2-dicyano-4,5-bis(hexoxymethyl)benzene and cobalt halide.

A 200-ml three-necked flask equipped with a reflux condenser, a thermometer and a motor was charged with 2.00 g (5.61 mmol) of 1,2-dicyano-4,5-bis(hexoxymethyl)benzene, 11.8 mmol of $CoCl_2$, 0.1 g of DBU, and 20 ml of hexanol as solvent. The mixture was refluxed for 600 min at 155°C and then filtered; yield 10%. (Found C,70.18; H, 8.40; N, 7.43. $C_{88}H_{128}N_8O_8Co$ requires C, 70.87; H 8.63; N, 7.51), λ_{max}(pyridine)/nm 665.0; ν_{max}/cm^{-1} 3300(ν_{C-H}), 2900(ν_{C-H}), 1590(ν_{C-C}), 1150(δ_{C-O}), 1090(δ_{C-H}).

2.2.4 Cobalt anthraquinocyanine (4) [2, 3]

Cobalt anthraquinocyanine is a new type of phthalocyanine derivative synthesized from 9, 10-anthraquinone-2,3-dicarboxylic acid, cobalt halide and urea.

A 100-ml two-necked flask equipped with a reflux condenser and thermometer was charged with 1.00 g (3.30 mmol) of 9,10-anthraquinone-2,3-dicarboxylic acid (10), 2 g (34.0 mmol) of urea, 6.75 mmol of $CoCl_2$ and 0.1 g of DBU. The flask was heated to 210°C until the reaction mixture was fused. The reaction product was washed with water and was dried; yield 23%. (Found C,70.17; H, 2.26; N, 10.30. $C_{64}H_{24}N_8O_8Co$ requires C, 70.46; H 2.22; N, 10.27), λ_{max}(pyridine)/nm 688.0; ν_{max}/cm^{-1} 3330(ν_{C-H}), 2900(ν_{C-H}) 1690(ν_{C-O}) 1470(ν_{C-H}), 980(δ_{C-H}), 780(δ_{C-H}). The electronic absorption band of the product showed it to be consistent with the formation of the anthraquinocyanine ring.

2.2.5 Electron spectra of cobalt phthalocyanine derivatives and cobalt anthraquinocyanine

Cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4) showed strongest absorption peak around the 680 nm region. The strongest absorption peak assignees are the Q band, which can be attributed to the allowed π–π^* transition [9, 10]. The Q band absorption of the soluble metal phthalocyanine derivatives synthesized in this work shifted by 50–80 nm to longer wavelength in comparison with unsubstituted metal phthalocyanines, which appeared around 600 nm. The shift of absorption maxima depends upon the change in electron distribution in the phthalocyanine macrocycle by substituents. The Q band data are summarized in Table 1.

3 RESULTS AND DISCUSSION

3.1 Cyclic voltammogram

Figure 2 shows CVs and the first differential curves of cobalt phthalocyanine tetrasulfonic acid (1), cobalt phthalocyanine octacarboxylic acid (2), cobalt octakis(hexoxymethyl)phthalocyanine (3) and cobalt anthraquinocyanine (4), respectively. The reduction and oxidation potentials of the cobalt phthalocyanine derivatives (1)–(3), and cobalt anthraquinocyanine (4) are

TABLE 1

Adsorption Maximum of Q Band in Electron Absorption Spectrum of Cobalt Phthalocyanine Derivatives and Phthalocyanine Derivatives and Cobalt Anthraquinocyanine

Compound	λ_{max} *in Q band (nm)*
Cobalt phthalocyanine tetrasulfonic acid (1)	649
Cobalt phthalocyanine octacarboxylic acid (2)	684
Cobalt octakis(hexoxymethyl)phthalocyanine (3)	665
Cobalt anthraquinocyanine (4)	688

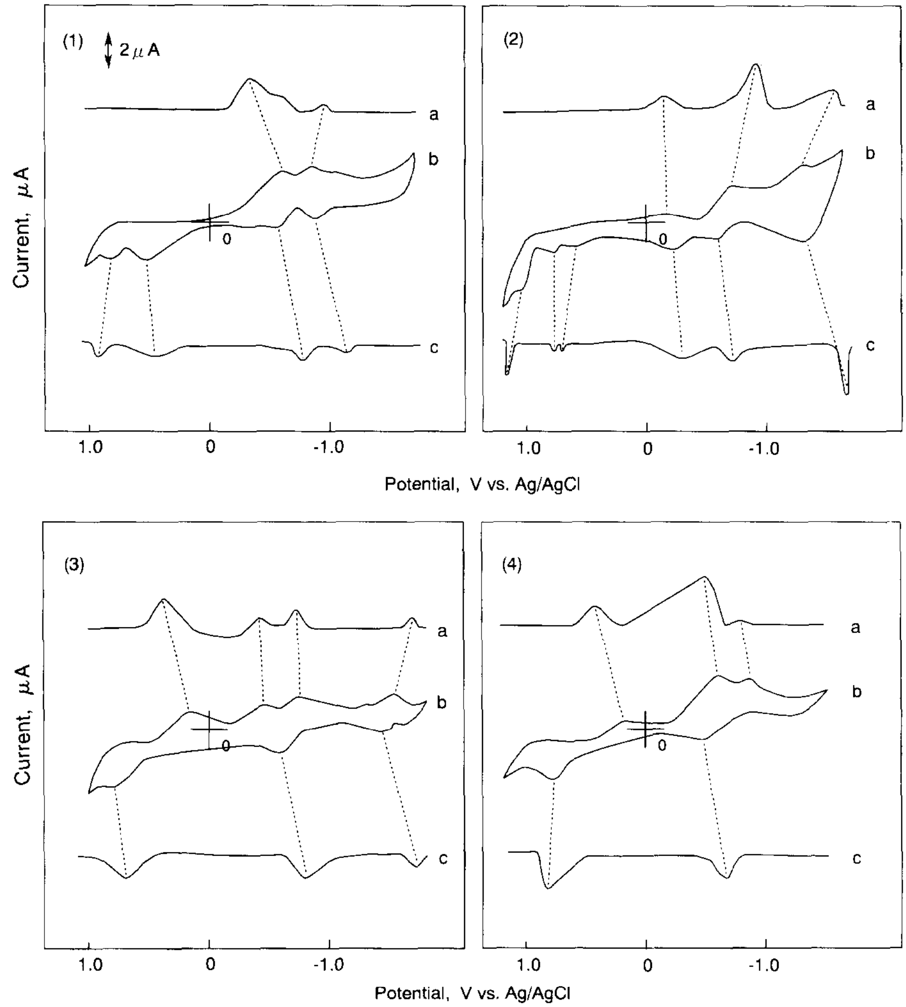


Fig. 2. Cyclic voltammograms and their first differential curves of cobalt phthalocyanine derivatives and cobalt anthraquinocyanine in DMSO with 0.1M TBAP, scan rate: 50 mV/s. (1) Cobalt phthalocyanine tetrasulfonic acid; (2) cobalt phthalocyanine octacarboxylic acid; (3) cobalt octakis(hexoxymethyl)phthalocyanine; (4) cobalt anthraquinocyanine. a: First differential curve of upper half of cyclic voltammogram. b: Cyclic voltammogram. c: First differential curve of lower half of cyclic voltammogram.

summarized in Table 2. The reported potentials are the midpoint potential of the anodic and cathodic peaks for each couple, E_{mid}, and the peak potential for the irreversible step.

The CV of cobalt phthalocyanine tetrasulfonic acid (1) showed two cathodic peaks at −0.63 and −1.00 V vs Ag/AgCl, and four anodic peaks at 0.89, 0.67, −0.60 and −0.90 V vs Ag/AgCl. The peaks of cobalt phthalocyanine tetrasulfonic acid (1) are attributed to a five reduction stage. The

TABLE 2
Reduction and Oxidation Potential of Cobalt Phthalocyanine Derivatives and Cobalt Anthraquinocyanine

Compound	*Potential V (vs Ag/AgCl)*						
	Reduction				*Oxidation*		
Cobalt phthalocyanine tetrasulfonic acid (1)	-1.63^a	-0.95	-0.62		0.67^a	0.89^a	
ΔE^b		0.98	0.34				
Cobalt phthalocyanine octacarboxylic acid (2)	-1.39		-0.66	-0.24	0.67^a	0.87^a	1.06^a
ΔE^b	1.60		2.27	0.84			
Cobalt octakis(hexoxymethyl)-phthalocyanine (3)	-1.50	-1.25^a	-0.67	-0.49^a	0.16^a	0.73^a	
ΔE^b	0.88		1.27				
Cobalt anthraquinocyanine (4)	-0.95^a	-0.63			0.19^a	0.87^a	
ΔE^b		1.07					

Potentials of reversible wave are midpoint potential of anodic and cathodic peaks for each couple, $E_{1/2}$.
[a] Irreversible peak.
[b] The anodic peak to cathodic peak separation for reversible couple ($\times 10^{-2}$).

first reversible reduction potential at −0.62 V vs Ag/AgCl and the first oxidation potential of cobalt phthalocyanine tetrasulfonic acid (1) appeared at 0.67 V vs Ag/AgCl.

Reduction and oxidation properties of cobalt phthalocyanine and cobalt phthalocyanine tetrasulfonic acid have been reported by Clack [11], and Rollmann [12], respectively. They reported that cobalt phthalocyanine and cobalt phthalocyanine tetrasulfonic acid possessed five redox waves. Results in this work are in agreement with previously reported data [11–13].

In the case of cobalt phthalocyanine octacarboxylic acid (2), three cathodic peaks and six anodic peaks appeared. The peaks were sorted into three reversible reduction couples at −0.24, −0.66 and −1.39 V vs Ag/AgCl, and three irreversible oxidation waves at 0.67, 0.87 and 1.06 V vs Ag/AgCl. The reduction and oxidation of metal phthalocyanine derivatives are due to the interaction between the phthalocyanine ring and the central metal [14, 15]. The reduction and oxidation potential of cobalt phthalocyanine derivatives reported by Rollmann [11] and Orihashi [13] showed more negative values than in the case of cobalt phthalocyanine tetrasulfonic acid (1) and cobalt phthalocyanine octacarboxylic acid (2). Carboxylic and sulfonic groups are electron-withdrawing groups, so they are expected to reduce the electron charge in the phthalocyanine ring. The change in the redox potential is due to the nature and number of the substituents.

The cyclic voltammogram of cobalt octakis(hexoxymethyl)phthalocyanine (3) showed four cathodic peaks at 0.16, −0.49, −0.73 and −1.54 V vs Ag/AgCl, and three anodic peaks at 0.73, −0.61 and −1.47 V vs Ag/AgCl.

Cobalt octakis(hexoxymethyl)phthalocyanine (3) has two irreversible oxidations at 0.16 and 0.73 V vs Ag/AgCl, and two pairs of reversible reduction potential. Since the hexoxymethyl substituent is an electron-donating group, the negative charge is expected to increase on the phthalocyanine ring.

The cyclic voltammogram of cobalt anthraquinocyanine (4) showed a unique shape in comparison with the other cobalt phthalocyanine derivatives (1)–(3). The shape of the CV for cobalt anthraquinocyanine (4) showed three cathodic peaks at 0.19, −0.69 and −0.95 V vs Ag/AgCl, and two anodic peaks at 0.87 and −0.58 V vs Ag/AgCl. Cobalt anthraquinocyanine (4) has almost one pair of reversible potential.

The ΔE values in Table 2 are the anodic to cathodic peak separation located in the oxidation (negative) potential region. The ΔE values, except for cobalt phthalocyanine octacarboxylic acid (2), are around 100 mV and the redox processes are the same for these molecules.

Kadish *et al.* [16] suggested that the potential difference between the reduction and oxidation is expressed in the HOMO-LUMO energy gap. This potential difference decreases from 1.36 V for cobalt phthalocyanine octacarboxylic acid (2) to 0.65 V for cobalt octakis(hexoxymethyl)phthalocyanine (3). The values of $\lambda_{\max}$ in the Q band shown in Table 1 correlate with the potential difference between the reduction and oxidation of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4).

Figure 3 shows the change in the ratio of the anodic peak current to the cathodic current of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4) with a scan rate (ν).

Nicholson and Shain studied the relationship between the ratio of anodic to cathodic peak current, i_a/i_c and the scan rate, ν [17]. When the relationship was unity, a reversible or catalytic reaction is involved the system. This relationship between the anodic to cathodic peak current ratio of a reversible couple, i_a/i_c and the scan rate, (ν) serves as a quick test for an electrochemical mechanism associated with a preceding or succeeding reversible or irreversible chemical equilibrium. The scan rate varied from 0.05 to 0.3 Vs^{-1} in this work.

It is shown that the ratio of anodic to cathodic peak current (i_a/i_c) decreased continuously with an increasing scan rate for all reversible couples of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4). The reversible reduction couples of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4) are characterized as a fast reversible electron transfer followed by a reversible chemical reaction. The value of the anodic to cathodic peak current ratio, i_a/i_c, converges when the ratio is extrapolated to zero of scan rate.

The potentials of anodic to cathodic peak potential ΔE are around 100 mV, except for cobalt phthalocyanine octacarboxylic acid (2) (see Table 2). Extrapolated to zero of scan rate the ΔE values approach close to 60 mV. These data suggest that the electrode processes of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4) take place in almost one-electron transfer. The midpoint potential of the cathodic to anodic peak, E_{mid}, is independent of scan rate and has constant values.

Consequently, it is concluded that these electrode processes are diffusion-controlled complicated electron transfer, involving some weak adsorption with the oxide of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4).

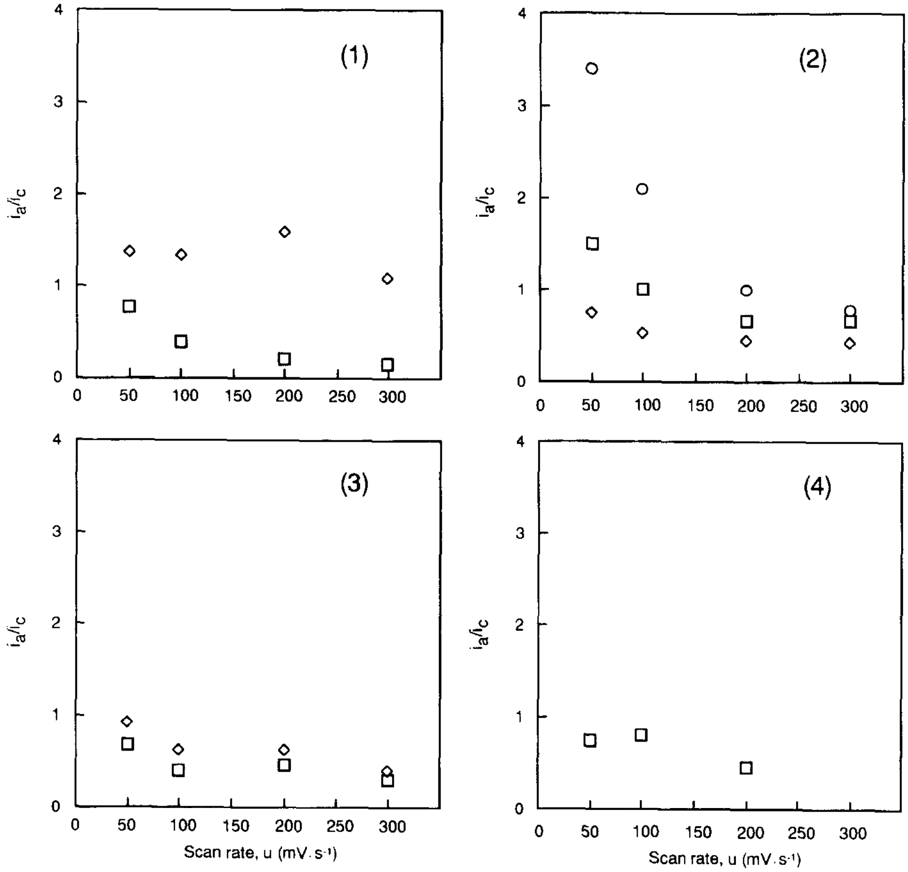


Fig. 3. Change in the anodic to cathodic current ratio with scan rate for cobalt phthalocyanine derivatives and cobalt anthraquinocyanine. (1) Cobalt phthalocyanine tetrasulfonic acid; (2) cobalt phthalocyanine octacarboxylic acid; (3) cobalt octakis(hexoxymethyl)phthalocyanine; (4): cobalt anthraquinocyanine. □ First redox couple; ◇ second redox couple; ○ third redox couple.

3.2 Chronoamperometry and chronocoulometry

Figure 4 shows the chronoamperometry of cobalt octakis(hexoxymethyl)phthalocyanine (3) following applied voltage pulse from −1200 to 0 mV vs Ag/AgCl and from −1200 to +1600 mV vs Ag/AgCl, and the reversible pulse. Chronoamperometry involves the measurement of the current–time response to a potential step excitation signal. A large cathodic current flows immediately when the potential is stepped up from the initial value, after that it slowly attenuates. The reduction step exhibited the same behavior in comparison with both potential steps.

The current–time curve for chronoamperometry is expressed by the Cottrell eqn (1),

$$i = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} = Kt^{-1/2} \qquad (1)$$

where, i: current (A), n: number of electrons transferred per ion or molecule ($\mathrm{mol^{-1}}$), F: Faraday's constant (96,485 $\mathrm{C\,mol^{-1}}$), A: electrode area ($2.0\times10^{-2}\,\mathrm{cm^2}$), C: concentration ($\mathrm{mol\,cm^{-3}}$), D: diffusion constant ($\mathrm{cm\,s^{-1}}$), t: time (s).

Electron processes in the systems are diffusion-controlled electron transfers mentioned above. Relationships between the current and square root of time are considered to be a finite diffusion for cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4).

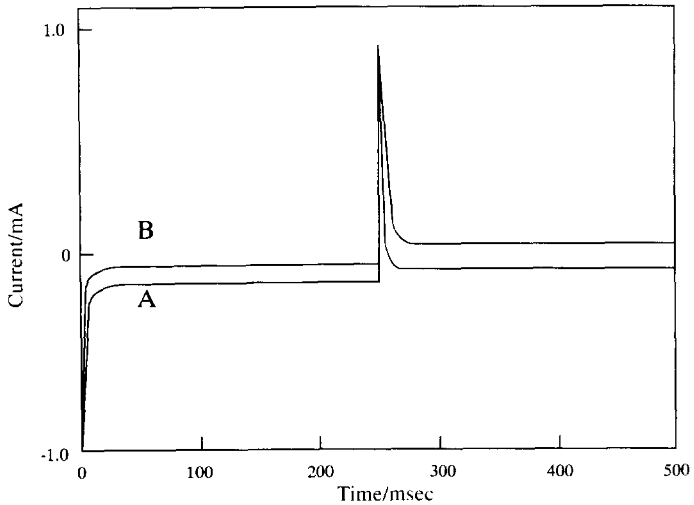


Fig. 4. Chronoamperometry of cobalt octakis(hexoxymethyl)phthalocyanine. A: pulse step −1.2~0 V vs Ag/AgCl, step width 250 ms; B: pulse step −1.2~1.6 V vs Ag/AgCl, step width 250 ms.

Table 3 shows the slope of the relationships between the current and square root of time (Cottrell plots). The current of the Cottrell plot is a measure of the rate for electrolysis at the electrode surface. Electrolysis is controlled with a mass transfer by diffusion on the electrode, so that the diffusion constant implies the rate of electrolysis. In this table, the slope means the diffusion constant in each step, and the forward step indicates the reduction reaction and the reverse step is oxidation. The oxidation processes of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4) are faster than the reduction. The oxidation decreased in the following order: cobalt phthalocyanine octacarboxylic acid (2), cobalt phthalocyanine tetrasulfonic acid (1), cobalt anthraquinocyanine (4) and cobalt octakis(hexoxymethyl)phthalocyanine (3). On the other hand, reduction decreased in the following order: cobalt octakis(hexoxymethyl)phthalocyanine (3), cobalt phthalocyanine tetrasulfonic acid (1) cobalt phthalocyanine octacarboxylic acid (2) and cobalt anthraquinocyanine (4).

Chronocoulometry was taken by one treatment of chronoamperometry in which the current response was integrated to give a response of the charge. The charge–time curve of the forward step for chronocoulometry is the integral of eqn (1):

$$Q = \frac{2n\mathrm{F}AC\mathrm{D}^{1/2}t^{1/2}}{\pi^{1/2}} = 2Kt^{1/2} \qquad (2)$$

This is the Anson equation (2).

The reverse step is expressed by the following equation:

$$Q_r = \frac{2n\mathrm{F}AC\mathrm{D}^{1/2}}{\pi^{1/2}}\left\{\tau^{1/2} + (t - r)^{1/2} - t^{1/2}\right\} \qquad (3)$$

Figure 5 shows the chronocoulometry of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4). The initial potential in each case was −1200 mV vs Ag/AgCl and the step width was 250 ms. The step potential was + 1600 mV vs Ag/AgCl.

TABLE 3
The Slope and Intercept of Cottrell Plot for Cobalt Phthalocyanine Derivatives and Cobalt Anthraquinocyanine

Compound	*Forward step (mA)*		*Reverse step (mA)*	
	Slope	*Intercept*	*Slope*	*Intercept*
Cobalt phthalocyanine tetrasulfonic acid (1)	−0.531	−0.0631	1.020	0.00596
Cobalt phthalocyanine octacarboxylic acid (2)	−0.358	−0.106	1.100	−0.00274
Cobalt octakis(hexoxymethyl)phthalocyanine (3)	−0.525	−0.0360	0.670	−0.000172
Cobalt anthraquinocyanine (4)	−0.322	−0.0632	0.698	0.00547

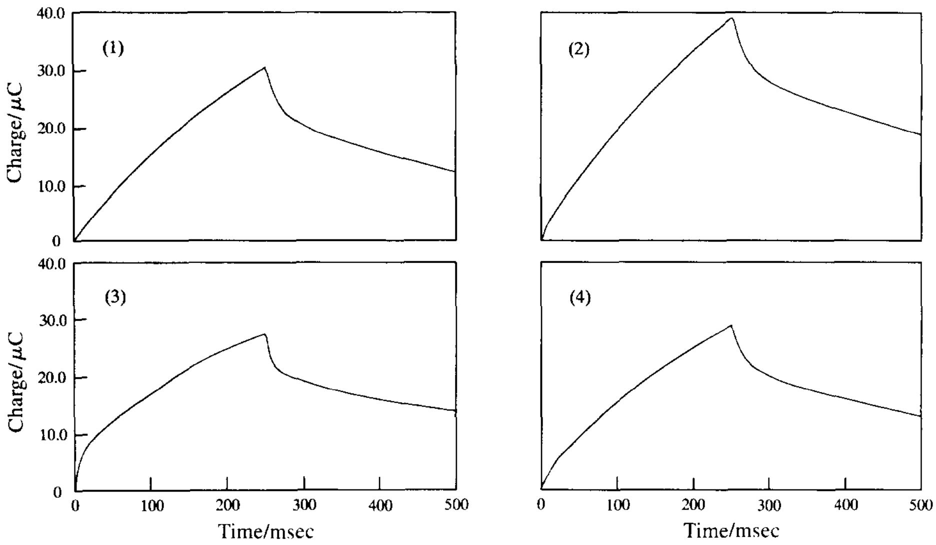


Fig. 5. Chronocoulometry of cobalt phthalocyanine derivatives and cobalt anthraquinocyanine. Potential step: −1.2 ~ 1.6 V vs Ag/AgCl, step width: 250 ms. (1) Cobalt phthalocyanine tetrasulfonic acid; (2) cobalt phthalocyanine octacarboxylic acid; (3) cobalt octakis(hexoxymethyl)phthalocyanine; (4) cobalt anthraquinocyanine.

For cobalt phthalocyanine derivatives (1)–(3), and cobalt anthraquinocyanine (4), the extent of diffusion control increases systematically as the standard potential becomes positive. The electron charge was reached at about 30 μC in the forward step and was decreased to 15 μC, except for cobalt phthalocyanine octacarboxylic acid (2). In the chronocoulometry of the reduction side from −1200 to 0 mV vs Ag/AgCl potential, reverse steps were attenuated to 0 μC with 70 ms, except for cobalt phthalocyanine octacarboxylic acid (2). In the oxidation side from the 0 to +1600 mV vs Ag/AgCl step, chronocoulometry had a linear forward step and a flat reverse step, indicating no faradic activity for all compounds.

It is thought that reduction and oxidation take place in different pathways, where especially a cobalt phthalocyanine octacarboxylic acid (2) exhibits a characteristic behavior.

Chronocoulometry gives rise to a double layer charging (Q_{dl}), and electrolysis of adsorbed (Q_{ads}) and solution species (Q) in the initial potential step.

$$Q_{\mathrm{total}} = \frac{2n\mathrm{F}ACD^{1/2}t^{1/2}}{\pi^{1/2}} + Q_{\mathrm{dl}} + Q_{\mathrm{abs}} \tag{4}$$

$$Q_{\mathrm{abs}} = n\mathrm{F}A\Gamma \tag{5}$$

where, Q_{dl}: double layer charge (C), Q_{abs}: absorbed species charge (C), Γ: amount of adsorbed (mol cm^{-3}),

The chronocoulometry of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4) show that the reactant is adsorbed, but not the product. With regard to the adsorption using eqn (2) and eqn (3), the charge (Q_{abs}) was found from calculation to be 7.40, 8.92, 2.81 and 7.07 μC for cobalt phthalocyanine tetrasulfonic acid (1), cobalt phthalocyanine octacarboxylic acid (2), cobalt octakis(hexoxymethyl)phthalocyanine (3), and cobalt anthraquinocyanine (4), respectively. Hence, the double layer charge (Q_{dl}) was estimated to be 0.53 μC at 0 ms of the chronocoulometry for cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4).

Figure 6 shows the relationships between Q_r/Q_f, the baseline for the measurement of the reverse step charge Q_r divided by the final value of the forward step Q_f, and the square root of time. This relationship can be estimated by the mechanism and rate of the subsequent chemical reaction. It is found that the following chemical reaction obeyed first-order kinetics. The kinetic constants were found from calculation to be 0.20, 0.26, 0.30 and 0.30 s^{-1} for cobalt phthalocyanine tetrasulfonic acid (1), cobalt phthalocyanine octacarboxylic acid (2), cobalt octakis(hexoxymethyl)phthalocyanine (3) and cobalt anthraquinocyanine (4), respectively.

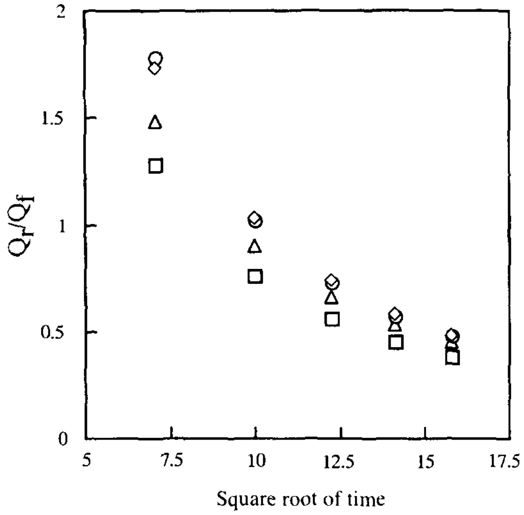


Fig. 6. Variation of Q_r/Q_f with square root of time for cobalt phthalocyanine derivatives and cobalt anthraquinocyanine. Potential step: −1.2~1.6 V vs Ag/AgCl, step width: 250 ms Qf forward step of chronocoulometry; Q_r reverse step of Chronocoulometry. □ Cobalt phthalocyanine tetrasulfonic acid; ◇ cobalt phthalocyanine octacarboxylic acid; ○ cobalt octakis(hexoxymethyl)phthalocyanine; △ cobalt anthraquinocyanine.

The oxidation of metal phthalocyanine derivatives having transition metal are electrochemically irreversible [14, 18, 19] and electrons are added to the orbital of the phthalocyanine ring or the central metal depending on the redox potential for reduction process [19, 20].

Consequently, it is considered that the electron transfer mechanisms can be proposed as follows:

(i) For cobalt phthalocyanine tetrasulfonic acid (1):

oxidation step is,

$$\mathrm{Co(II)\text{-}PC(SO_3H)_4} \rightarrow \mathrm{[Co(III)\text{-}PC(SO_3H)_4]^{+}} + \mathrm{e}$$

reduction steps are,

$$\mathrm{Co(II)\text{-}PC(SO_3H)_4} + \mathrm{e} \rightleftarrows \mathrm{[Co(II)\text{-}PC(SO_3H)_4]^{-}}$$

$$\mathrm{[Co(II)\text{-}PC(SO_3H)_4]^{-}} + \mathrm{e} \rightleftarrows \mathrm{[Co(II)\text{-}PC(SO_3H)_4]^{2-}}$$

$$\mathrm{[Co(II)\text{-}PC(S0_3H)_4]^{2-}} + \mathrm{e} \rightarrow \mathrm{[Co(I)\text{-}PC(SO_3H)_4]^{3-}}$$

(ii) For cobalt phthalocyanine octacarboxylic acid (2):

oxidation steps are,

$$\mathrm{Co(II)\text{-}PC(COOH)_8} \rightarrow \mathrm{[Co(III)\text{-}PC(COOH)_8]^{+}} + \mathrm{e}$$

$$\mathrm{[Co(III)\text{-}PC(COOH)_8]^{+}} \rightarrow \mathrm{[Co(III)\text{-}PC(COOH)_8]^{2+}} + \mathrm{e}$$

$$\mathrm{[Co(III)\text{-}PC(COOH)_8]^{2+}} \rightarrow \mathrm{[Co(IV)\text{-}PC(COOH)]^{3+}} + \mathrm{e}$$

reduction steps are,

$$\mathrm{Co(II)\text{-}PC(COOH)_8} + \mathrm{e} \rightarrow \mathrm{[Co(II)\text{-}PC(COOH)_8]^{-}}$$

$$\mathrm{[Co(II)\text{-}PC(COOH)_8]^{-}} + \mathrm{e} \rightleftarrows \mathrm{[Co(II)\text{-}PC(COOH)_8]^{2-}}$$

$$\mathrm{[Co(II)\text{-}PC(COOH)_8]^{2-}} + \mathrm{e} \rightleftarrows \mathrm{[Co(I)\text{-}PC(COOH)_8]^{3-}}$$

(iii) For cobalt octakis(hexoxymethyl)phthalocyanine (3):

oxidation steps are,

$$\mathrm{Co(II)\text{-}PC(CH_2OC_6H_{13})_8} \rightarrow \mathrm{[Co(III)\text{-}PC(CH_2OC_6H_{13})_8]^{+}} + \mathrm{e}$$

$$\mathrm{[Co(II)\text{-}PC(CH_2OC_6H_{13})_8]^{+}} \rightarrow \mathrm{[Co(III)\text{-}PC(CH_2OC_6H_{13})_8]^{2+}} + \mathrm{e}$$

reduction steps are,

$$\begin{gathered}
\mathrm{Co(II)\text{-}PC(CH_2OC_6H_{13})_8} \rightarrow \mathrm{[Co(I)\text{-}Pc(CH_2OC_6H_{13})_8]^-} \\
\mathrm{[Co(I)\text{-}PC(CH_2OC_6H_{13})_8]^-} + \mathrm{e} \rightleftarrows \mathrm{[Co(I)\text{-}PC(CH_2O_6H_{13})_8]^{2-}} \\
\mathrm{[Co(I)\text{-}PC(CH_2OC_6H_{13})_8]^{2-}} + \mathrm{e} \rightleftarrows \mathrm{[Co(I)\text{-}PC(CH_2OC_6H_{13})_8]^{3-}}
\end{gathered}$$

(IV) For cobalt anthraquinocyanine (4):
oxidation steps are,

$$\begin{gathered}
\mathrm{Co(II)\text{-}AQC} \rightarrow \mathrm{[Co(III)\text{-}AQC]^+} + \mathrm{e} \\
\mathrm{[Co(III)\text{-}AQC]^+} \rightarrow \mathrm{[Co(III)\text{-}AQC]^{2+}} + \mathrm{e}
\end{gathered}$$

reduction steps are,

$$\begin{gathered}
\mathrm{Co(II)\text{-}AQC} + \mathrm{e} \rightleftarrows \mathrm{[Co(II)\text{-}AQC]^-} \\
\mathrm{[Co(II)\text{-}AQC]^-} + \mathrm{e} \rightleftarrows \mathrm{[Co(I)\text{-}AQC]^2-}
\end{gathered}$$

The following chemical reaction after reversible redox process is an interaction between the anion of the phthalocyanine ring and the solvent molecule.

4 CONCLUSION

Electrode processes of cobalt phthalocyanine derivatives (1)–(3) and cobalt anthraquinocyanine (4) are diffusion controlled to almost one electron transfer involving some weak absorption and having the following chemical reaction. The oxidation processes were slower than the reduction.

In the electrode processes, the absorbed charge (Q_{abs}) was found from calculation to be close to eight, except for cobalt phthalocyanine octaearboxylic acid (2), and the double layer charge (Q_{dl}) was estimated to be $0.53\,\mu$C.

The subsequent chemical reactions obeyed first-ordered kinetics and their constants were almost 0.3 $\mathrm{s^{-1}}$.

The oxidation reactions are electrochemically irreversible, while the reduction reactions are reversible for the phthalocyanine ring and irreversible for the central metal.

REFERENCES

1. Lezonoff, C. C and Laver, A. B. P., *Phthalocyanine Properties and Applications*, VHC Publishers, 1993.

2. Sakamoto, K. and Ohno, E., *J. Soc. Dyers and Colourists*, 1996, **112**, 368.
3. Ohno, E. and Sakamoto, K., *J. Chem. Soc. Jpn., (Nippon Kagakukai-shi)*, 1995, 730.
4. Sakamoto, K. and Shibamiya, F., *J. Jpn. Petro. Inst., (Sekiyu Gakkaishi)*, 1991, **34**, 557.
5. Sakamoto, K., *J. Jpn. Soc. Colour mater.*, 1995, **68**, 67.
6. Weber, J. H. and Busch, D. H., *Inorg. Chem.*, 1965, **4**, 469.
7. Boston, D. R. and Bai, J. C., *Inorg. Chem.*, 1972, **11**, 1578.
8. Powlowski, G. and Hanack, M., *Synthesis*, 1980, 287.
9. Khatib, N. E. L., Boudjema, B., Maitrot, M., Chermette, H. and Pote, L., *Can. J. Chem.*, 1988, **66**, 2313.
10. Fierro, C., Anderson, A. B., and Scherson, D. A., *J. Phys. Chem.*, 1988, **92**, 6902.
11. Clack, D. W., Hush, N. S. and Wolsey, I. S., *Inorg, Chem.*, 1976, **19**, 133.
12. Rollmann, L. D. and Iwamoto, R. T., *J. Am. Chem. Soc.*, 1968, **90**, 1455.
13. Orihara, Y., Nishikawa, M., Ohno, H., Tsuchida, E. and Matsuda, H., *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3731.
14. Kasuga, K. and Tsutsui, M., *Coordination Chem. Rev.*, 1980, **32**, 67.
15. Lever, A. B. P., Licoccis, S., Magrell, K. and Ramanamy, B. S., *Adv. Chem. Ser.*, 1982, **210**, 237.
16. Kadish, K. M., Moninot, G., Hu, Y., Dubois, D., Ibnlfassi, A., Barbe, J-M. and Guilard, R., *J. Am. Chem. Soc.*, 1993, **115**, 8153.
17. Nicholson, R. S. and Shain, I., *Anal. Chem.*, 1964, **36**, 706.
18. Lexa, D. and Reix, M., *J. Chem, Phys.*, 1974, **71**, 511.
19. Wolberg, A. and Manassen, J., *J. Am. Chem. Soc.*, 1970, **92**, 2982.
20. Giraudean, A., Fan, F-R. F. and Bard, A. J., *J. Am. Chem. Soc.*, 1980, **102**, 5137.