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Electrochemical Characteristics of Anthraquinonecyanine and Phthalocyanine Derivatives

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Abstract

Electrochemical characteristics of metal anthraquinonecyanine and cobalt phthalocyanine derivatives in an organic solvent were estimated in detail by the measurement of cyclic voltammograms and potential-step chronocoulometry. Electron transfer properties of metal anthraquinonecyanine and cobalt phthalocyanine derivatives were shown to be similar. Except for the cobalt phthalocyanine octacarboxylic acid, electrode processes of metal anthraquinonecyanine and cobalt phthalocyanine derivative were diffusion controlled at approximately one electron transfer involving some weak adsorption together with the chemical reaction.

Key-words: *Metal Anthraquinonecyanine, Cobalt Phthalocyanine Derivatives, Electrochemical characteristics, Cyclic Voltammetry, Potential - step chronocoulometry*

1. Introduction

In this decade metal phthalocyanines and their derivatives have been employed as functional chromophores in the fields of electronics, sensor, biology and pharmaceuticals since they possess a molecular structure similar to porphyrin which have exhibited high electron transfer abilities¹⁾ owing to their π electron conjugated ring system. Although the functions of metal phthalocyanine derivatives are almost all based on electron transfer reactions, there have been few electrochemical studies on the electron transfer properties in solution of metal phthalocyanine derivatives in

an organic solvent. The authors reported syntheses of metal anthraquinonecyanine²⁾ and metal phthalocyanine derivatives³⁾. Metal anthraquinonecyanine is a novel metal phthalocyanine derivative and has four 9,10-anthraquinone units in the molecule. In general however, metal phthalocyanine derivatives are utilized only in a few fields because of their lower solubility in common organic solvents. Utilization of cobalt phthalocyanine derivatives is much more efficient than metal ones^{4),5)}. An observation of electron transfer is the most valid means for the estimation of functional material. The electron transfer of metal phthalocyanines and their derivatives is estimated by the preparation of a thin layer film and so on.

In this study, we have measured cyclic voltammograms and potential-step chronocoulometry of metal anthraquinonecyanine (1)

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and cobalt octakis(hexoxymethyl)phthalocyanine (2). 1, which are a new class of phthalocyanines, are expected to possess high electron transfer ability, since they have four anthraquinone units which show strong redox property. However, there is little known about the electrochemical characterization for 1. 2 is also a novel compound, it can be used in order to examine the effect of substitution (**Figure 1**). Cobalt phthalocyanine tetrasulfonic acid (3) and cobalt phthalocyanine octacarboxylic acid (4) were also measured as standard compounds in order to estimate their electron transfer ability and mechanism.

2. Experimental

2.1 Equipment

Cyclic voltammetry and potential-step chronoamperometry 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

tetrabutylammonium perchlorate (TBAP). Cyclic voltammograms were recorded by scanning the potential at the rate of 50 mV^{-1} . Then, the scan rate was varied from 50 to 300 mVs^{-1} . The working and counter electrodes were platinum wires and the reference electrode was a silver/silver chloride (Ag/AgCl) saturated sodium chloride electrode. The area of working electrode was $2.0 \cdot 10^{-2} \text{ cm}^2$.

In a reversible process, peak current of cyclic voltammetry is expressed by the following equation;

$$i_p = 2.69n^{3/2} AD^{1/2}Cv^{1/2}$$

where, i_p is the peak current (A), n is the number of electrons transferred per ion or molecule (mol^{-1}), A is the electrode area ($2.0 \cdot 10^{-2} \text{ cm}^2$), D is the diffusion constant (cm^2/s), C is the concentration (mol/cm^3) and v is scanning velocity (V/s).

In the potential-step chronocoulometry, the initial potential in each case was -1200 mV vs. Ag/AgCl and the step width was 250 ms. The

Metal anthraquinonecyanine (1)

Cobalt octakis(hexoxymethyl)phthalocyanine (2)

Cobalt phthalocyanine tetrasulfonic acid (3)

Cobalt phthalocyanine octacarboxylic acid (4)

Fig. 1 Molecular structure of metal anthraquinonecyanine and cobalt phthalocyanine derivatives

step potential was +1600 mV vs. Ag/AgCl. In the potential-step chronocoulometry, reverse steps were attenuated to 0 μC with 70 ms from -1200 to 0 mV vs. Ag/AgCl potential, oxidation side had a linear forward step and a flat reverse step from the 0 to +1600 mV vs. Ag/AgCl step, indicating no faradic activity for all compounds.

Infrared spectra were recorded on a Shimadzu FTIR-8100A spectrometer. Electron spectra were measured on a Shimadzu UV-2400PC, ultraviolet-visible spectrometer. Each sample was prepared in a 0.025 mg m^{-3} pyridine solution. Elemental analyses were carried out using a Perkin-Elmer 2400 equipment. Melting points were measured with a Mettler FP-5 apparatus.

2.2 Materials

1 is a new type of phthalocyanine derivative which was synthesized from 9, 10-anthraquinone-2,3-dicarboxylic acid, metal halide and urea²⁾.

2 was synthesized from 1,2-dicyano-4,5-bis(hexoxymethyl)benzene and cobalt halide (CoCl_2)³⁾.

3 was synthesized from 4-sulfophthalic acid, metal halide and urea³⁾.

4 was synthesized from benzene-1,2,4,5-tetracarboxylic dianhydride (pyromellitic dianhydride), metal halide and urea³⁾.

3. Results and Discussion

3.1 Cyclic voltammogram

Cyclic voltammetry can be used to make to use an estimation of electrochemistry. Cyclic voltammetry consists setting up a of cyclic potential with a stationary electrode immersed in a quiescent solution and measuring the resulting current.

The important parameters of a cyclic voltammogram are the magnitudes of the anodic peak current (i_a), the cathodic peak current (i_c), the anodic peak potential, the cathodic peak potential and the mid-point

potential for reversible couple (E_{mid}). In other word, the anodic peak potential means the oxidation potential, and the cathodic peak potential is the reduction potential.

Figure 2 shows cyclic voltammograms and their first differential curves of cobalt complexes of 1, 2, 3 and 4. The reported potentials are the midpoint potential of anodic and cathodic peaks for each couple, E_{mid} , and the peak potential for the irreversible step.

The shape of the cyclic voltammogram for cobalt complex of 1 showed three cathodic peaks and two anodic peaks. Cobalt complex of 1 has one pair of reversible potential.

Cyclic voltammogram of 2 showed four cathodic peaks and three anodic peaks. 2 has two irreversible oxidations and two pairs of reversible reduction potential. Since the substituent hexoxymethyl is the electron-donating group, the negative charge is expected to increase on the phthalocyanine ring. The reported potentials are E_{mid} , and the peak potential for the irreversible step.

The cyclic voltammogram of 3 showed two cathodic peaks and four anodic peaks. The peaks of 3 are attributed to five reduction stages.

Clack⁶⁾ and Rollmann⁷⁾ reported the reduction and oxidation properties of cobalt phthalocyanine and cobalt phthalocyanine tetrasulfonic acid which possessed five redox waves.

The cyclic voltammogram of 4 shows three cathodic peaks and six anodic peaks. The peaks were sorted into three reversible reduction couples, and three irreversible oxidation waves. The reduction and oxidation of metal phthalocyanine derivatives are due to the interaction between the phthalocyanine ring and the central metal^{8),9)}. Sulfonic and carboxylic 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 kind and

number of substituents.

The porphyrazine ring in the molecules of metal phthalocyanine derivatives is influenced by the π electrons about the closed system. The π electron system of metal phthalocyanine derivatives such as compounds 2-4 consists of one porphyrazine and four phenylene rings³⁾.

Substituents influence the π electron environment in metal phthalocyanine derivatives, especially phenylene rings. It is thought that the effect of substituents give rise to changes of electron density of the phenylene rings in the molecule of metal phthalocyanine derivatives. The effect of sulfonic and carboxylic

Fig. 2 Cyclic voltammograms and their first differential curves of cobalt anthraquinonocyanine (1) and cobalt phthalocyanine derivatives (2-4) in DMSO with 0.1M TBAP, at scan rate of 50mV/s

a: First differential curve of upper half of cyclic voltammogram
b: Cyclic voltammogram

c: First differential curve of lower half of cyclic voltammogram

- (1): Cobalt anthraquinonocyanine
- (2): Cobalt octakis(hexoxymethyl)phthalocyanine
- (3): Cobalt phthalocyanine tetrasulfonic acid
- (4): Cobalt phthalocyanine octacarboxylic acid

groups is a very complicated phenomenon.

It is concluded that the irreversible peaks are attributed to the oxidation of the central metal and reversible peaks represent the redox of the anthraquinonecyanine or phthalocyanine ring. The difference of cyclic voltammogram between 1 and 2-4 is attributed to the effect of variation of the interaction between the central metal and the anthraquinone or phthalocyanine ring.

The ΔE values in **Table 1** are the anodic peak to cathodic peak separation located in the oxidation (negative) potential region. The negative potential region represents oxidation reaction. The ΔE values are around 100 mV and the redox processes are the same for these molecules, except for 4. They mean that the electron processes of metal anthraquinonecyanine and cobalt phthalocyanine derivatives involve approximately one electron transfer, except for 4. The ΔE values of 4 showed strange behavior in comparison to the others.

It is assumed that the ΔE values are due to kind and number of the substituents, i.e. carboxylic acids.

The potential difference between the reduction and oxidation is expressed in the HOMO

–LUMO energy gap¹⁰⁾. The values of $\lambda_{\max}$ in the Q band correlate with the potential difference between the reduction and oxidation of 1 and 2-4.

Figure 3 shows the change in the ratio of anodic peak current to the cathodic current of 1 and 2-4 with a scan rate, ν . The 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 electrochemical mechanism associated with a preceding or succeeding reversible or irreversible chemical equilibrium. When the relationship between the ratio of anodic to cathodic peak current, i_a/i_c and the scan rate, ν ¹¹⁾ is unity, reversible or catalytic reaction is involved in the system.

It is shown that i_a/i_c decreased continuously with an increasing scan rate, ν for all reversible couples of cobalt complex of 1 and 2-4. The reversible reduction couples of cobalt complex of 1 and 2-4 are characterized as a fast, reversible electron transfer followed by a reversible chemical reaction. The value of anodic to cathodic peak current ratio, i_a/i_c converges when the ratio is extrapolated to zero scan rate, ν , except for the third redox

Table 1 Reduction and oxidation potential of metal anthraquinonecyanine and cobalt phthalocyanine derivatives

Compound	Potential (V vs. Ag/AgCl)					
	Reduction			Oxidation		
Iron complex of 1	-0.76*	-0.63	-0.28*	0.86*		
ΔE^{**}		0.14				
Cobalt complex of 1	-0.95*	-0.63	-0.58	0.19*	0.87*	
ΔE^{**}		0.11				
Zinc complex of 1	-0.73*	-0.60	-0.070*	0.87*		
ΔE^{**}		0.13				
2	-1.50	-1.25*	-0.67	-0.49*	0.16*	0.73*
ΔE^{**}	0.088		0.13			
3	-1.63*	-0.95	-0.62	0.67*	0.89*	
ΔE^{**}		0.098	0.034			
4	-1.39		-0.66	-0.24	0.67*	0.87*
ΔE^{**}	0.16		0.23	0.084		1.06*

Potentials of reversible wave are midpoint potential of anodic and cathodic peaks for each couple, E_{mid}

* Irreversible peak

** The anodic peak to cathodic peak separation for reversible couple

couple of 4.

Extrapolated to zero scan rate, ν , the ΔE values approach close to 60 mV. These data suggest that the electrode processes of cobalt complex of 1 and 2-4 take place with approximately one-electron transfer. The midpoint potential of cathodic to anodic peak, E_{mid} are independent of scan rate, ν and have constant values.

Electron transfer properties of 1 and 2-4 depend on the nature of porphyrazine ring, which is a component of anthraquinonecyanine or phthalocyanine rings, and on the kind and number of substituents. The porphyrazine ring in the molecule of 1 and 2-4 is influenced by the closed conjugated system.

It is thought that the substituents of 2-4 directly influence the porphyrazine ring by

their electron properties. 1 might be expected to have an effect on electron transfer for anthraquinone units. However, anthraquinone units in 1 did not make contribution to electron transfer ability. The anthraquinone units in 1 must be different from substituents of 2-4.

It is concluded that the effect of anthraquinone units in 1 is incorporated into the macrocycle conjugated system.

3.2 Other electrochemical measurements

Another type of electrochemical measurement, potential - step chronoamperometry involves the current-time response to a potential step excitation signal.

The current-time curve for chronoamperometry is expressed by the Cottrell equation¹⁰.

Electron processes in the systems are diffusion - controlled electron transfers as

Fig. 3 Change in the anodic to cathodic current ratio with scan rate for metal anthraquinonecyanine (1) and cobalt phthalocyanine derivatives (2-4)

(1): $\diamond$:Iron complex, $\square$:cobalt complex, and $\circ$:zinc complex

(2)-(4): $\square$ First redox couple, $\diamond$:second redox couple and $\circ$:third redox couple

mentioned above. Relationships between the current and square root of time are considered assuming a finite diffusion for 1 and 2-4.

Table 2 shows the slope of Cottrell plots. The current of the Cottrell plot means the rate of electrolysis which is controlled with mass transfer by diffusion on the electrode surface. Accordingly, the diffusion constant implies the rate of electrolysis and is expressed by the slope of the Cottrell plot in each step (forward step indicates the reduction reaction and the reverse step is oxidation). The oxidation processes of 1 and 2-4 are faster than the reduction.

Potential-step chronocoulometry was taken by one treatment of potential-step chronoamperometry in which the current response was integrated to give a response of the charge¹⁰.

Figure 4 shows the potential - step chronocoulometry of cobalt complex of 1 and 2-4. The extent of diffusion control increases systematically as the standard potential becomes positive for 1 and 2-4. The electron charge reached about 30 μC in the forward step and decreased to 15 μC .

It is thought that reduction and oxidation take place by different pathways, where especially 4 exhibits characteristic behavior.

Potential-step chronocoulometry means a sum of double layer charging, electrolysis of

adsorbed and solution species in the initial potential step.

The potential-step chronocoulometry of 1 and 2-4 show that the reactant is adsorbed but not the product. The adsorbed charge was found from calculation to be 7.07, 2.81, 7.40 and 8.92 μC for cobalt complexes of 1, 2, 3 and 4, respectively. Hence, the double layer charge was estimated to be 0.53 μC at 0 ms of the potential-step chronocoulometry for 1 and 2-4.

Figure 5 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 used to estimate the mechanism and rate of the following chemical reaction. It is found that the following chemical reaction obeyed first-order kinetics. The kinetic constants are found from calculation to be 0.30, 0.30, 0.20 and 0.26 s^{-1} for 1, 2, 3 and 4, respectively.

The oxidation of metal phthalocyanine derivatives containing transition metal are electrochemically irreversible^{8),12),13)}. Then, electrons are added either to the orbital of the phthalocyanine ring or the central metal, depending on the redox potential for reduction process^{13),14)}.

Table 2 The slope and intercept of Cottrell plot^{*)} for metal anthraquinonecyanine and cobalt phthalocyanine derivatives

Compound	Forward step (mA)		Reverse step (mA)	
	slope	intercept	slope	intercept
Iron complex of 1	-0.358	-0.0106	1.10	0.00274
Cobalt complex of 1	-0.322	-0.0632	0.698	0.00547
Zinc complex of 1	-0.525	-0.0360	0.670	0.00172
2	-0.525	-0.0360	0.670	-0.000170
3	-0.531	-0.0631	1.02	0.00596
4	-0.358	-0.106	1.10	-0.00274

^{*)} The current-time curve for chronoamperometry is expressed by the Cottrell equation,

$$i = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}}$$

where, i : current (A), n : number of electrons transferred per ion or molecule (mol-1), F : Faraday's constant (96, 485 C/mol), A : electrode area ($2.0 \cdot 10^{-2} \text{cm}^2$), C : concentration (mol/ cm^3), D : diffusion constant (cm/s), t : time(s).

Fig. 4 Chronocoulometry of cobalt anthraquinonecyanine (1) and cobalt phthalocyanine derivatives (2-4) potential step:-1.2~1.6V vs.Ag/AgCl, step width:250ms

Fig. 5 Variation of Q_r/Q_f with square root of time for cobalt anthraquinonecyanine (1:Δ) and cobalt phthalocyanine derivatives (2:○, 3:□ and 4:◇) potential step:-1.2~1.6V vs.Ag/AgCl, step width:250ms
 Q_f :Forward step of Chronocoulometry
 Q_r :Reverse step of Chronocoulometry

4. Conclusion

Electron transfer properties of 1 and 2-4 depend on the nature of porphyrine ring in the molecule, and on the kind and number of substituents.

Electrode processes of 1 and 2-4 are diffusion controlled to approximately one electron transfer involving some weak absorption and are followed by a chemical reaction. The oxidation processes were slower than the reduction ones.

In the electrode processes, the absorbed charge was found from calculation to be close to eight (except for compound 4), and the double layer charge was estimated to be $0.53 \mu\text{C}$.

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

The oxidation reactions are electrochemically irreversible, while the reduction reactions

are reversible for the phthalocyanine ring and irreversible for the central metal atom.

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アントラキノシアンとフタロシアニン誘導体の電気化学的性質

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要 旨

アントラキノシアンおよび金属アントラキノシアンは、その分子中にアントラキノン骨格を有する新規のフタロシアニン誘導体である。この新規のフタロシアニン誘導体は通常のフタロシアニン誘導体よりも大きい酸化還元能力が期待されるが、金属フタロシアニン誘導体を含めて電気化学的に詳細な報告はない。そこで、金属アントラキノシアンとコバルトフタロシアニン誘導体とを合成し、サイクリックボルタンメトリおよびクロノクーロンメトリーを測定することで電気化学的性質を評価した。金属アントラキノシアンおよびコバルトフタロシアニン誘導体は類似した電子移動能力を有することが解った。金属アントラキノシアンとコバルトフタロシアニン誘導体の電極反応は弱い吸着を伴う拡散支配の一電子反応であり、後続化学反応を有することが解った。