November, 1989] © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***62***, *3469—3474 (1989)* 3469

Tetrakis[3-(diethylamino)propyl]- and Tetrakis[3-(diethylmethylammonio)-propyl]phthalocyanines: The First Amphiphilic Phthalocyanines

Nagao Kobayashi,* Fumihiro Ojima, Tetsuo Osa,* Steve Vigh,† and Clifford C. Leznoff*,†
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980
†Department of Chemistry, York University, 4700 Keele Street, North York, Ontario, Canada M3J 1P3

(Received June 23, 1989)

The first amphiphilic cobalt (**III**) and copper phthalocyanines (**V**) have been prepared and are characterized by UV-absorption and magnetic circular dichroism (MCD) spectra in water and organic solvents and in their mixtures. These phthalocyanines exist as dimers in water and as monomers in some organic solvents. Monomer-dimer equilibrium was affected by solvent polarity (or hydrophobicity); with lower cosolvent polarity favoring formation of monomers. Cyclic voltammetry suggests that **III** adsorbed onto glassy carbon (GC) from an aqueous or acetonitrile (AN) solution in monomeric, irrespective of its state in solution. The $Co^{II/I}$ redox potential of **III** shifts anodically by adsorption onto GC, and this shift is larger when adsorbed from an AN solution than from an aqueous solution. Electroreduction of oxygen occurs at more positive potential at **III**-adsorbed GC in plain solution than at bare GC in **III**-dissolved solution.

Phthalocyanines (Pcs) are a remarkably versatile and robust class of compounds.[1] However, the solubility of the unsubstituted parent molecules is notoriously low, so that the introduction of bulky or long alkyl chains is generally required to increase their solubility in organic solvents.[2] Phthalocyanines containing sulfonyl,[3] carboxyl,[4] and amino groups[5] are, on the other band, water soluble. Phthalocyanines which dissolve in water at all pH values have not been reported to date, although a brief report on compound **I** and its zinc derivatives for use in photodynamic therapy of cancer appeared recently.[6] In view of such considerations, we report here the first example of amphiphilic phthalocyanines, i.e. the cobalt **III** and copper **V** complexes of **I**. These dissolve not only in water at all pH values, but also in many of the common organic solvents such as chloroform, acetone, alcohols, and benzenes. As will be shown below, they are compounds which can bridge the chemistry of phthalocyanines in water and organic solvents.

Experimental

Measurements. Matheson high-purity argon or high-purity nitrogen has passed through concentrated sulfuric acid (H_2SO_4) and preheated copper filings was used to maintain inert atmosphere conditions. Oxygen was purified by passage through concentrated H_2SO_4. Infrared spectra were recorded on a Pye Unicam SP 1000 infrared spectophotometer using KBr discs. Fast-atom-bombardment (FAB) spectra were obtained with a Kratos MS-50 tripic analyzer mass spectrometer equipped with a FAB ion source of standard Kratos design and an Ion Tech atom gun. The number in parentheses after the indicated ion shows the percentage of the base peak represented by that ion. Absorption spectra were collected on a Hewlett Packard HP8451A Diode Array spectrophotometer or on a Shimadzu UV-250 spectrophotometer. In the experiments in the mixed solvent system, the following procedures were adopted in order to minimize concentration differences among each of the samples. Initially, a concentrated phthalocyanine solution was prepared in acetonitrile. From this solution, a fixed small amount was transferred into a 1 cm cuvette using a microsyringe, and the solvent evaporated. To this cuvette was added 3 cm^3 of a mixed solvent of desired composition ratio, and the spectra were recorded. MCD spectra were run on a Jasco J-500 spectropolarimeter equipped with a Jasco electromagnet to produce longitudinal magnetic fields up to 1.1 T. Each measurement was made with both parallel and antiparallel fields.

Cyclic voltammetric (CV) sweeps were generated by an NF circuit design block FG-100 AD function generator in conjunction with a potentiostat which was built by methods recorded in the literature.[7] A glassy carbon (GC) (area 0.070 cm^2), a saturated calomel electrode (SCE), and a platinum foil were used, respectively, as a working electrode, a reference electrode, and a counter electrode. The GC was polished on one side to a bright surface with fine emery paper and alumina powder (final polish with 0.05 μm particle size, Buehler) immediately prior to use.

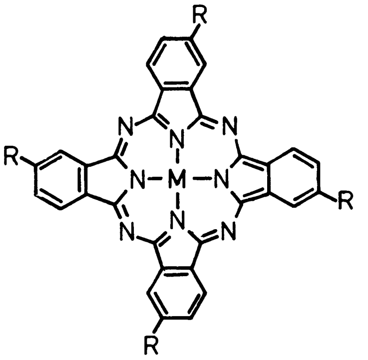
Materials. *o*-Dichlorobenzene (DCB) (Aldrich, Gold Label), acetonitrile (AN) (Wako, spectrograde), dioxane, 2-butoxyethanol, and 2-propanol (Nakarai, Guaranteed reagents) were used as supplied. Measurements at pH 1 or 7 were performed in 0.05 M H_2SO_4 or 0.1 M phosphate buffer (1 M=1 mol dm^{-3}), respectively. The GC electrode was purchased from Tokai Carbon Ltd.

2,9,16,23-Tetrakis[3-(diethylamino)propyl]phthalocyaninatocobalt(II), (II). To a solution of 108 mg (0.11 mmol) of **I**[6] in 10 ml toluene/2-methoxyethanol (1:1 v/v), was added 150 mg (1.15 mmol) of anhydrous cobalt dichloride. The solution was stirred at 120 °C (reflux) under argon for 20 h. The crude reaction mixture was applied directly to a short (10 cm×1 cm) basic alumina column (act 3) and eluted with toluene/2-methoxyethanol (3:1 v/v). Evaporation of the solvent gave **II** as a dark blue shining solid, 110 mg (96.5% yield); mp >300 °C. IR (KBr) 2980, 2800, 1610, 1520, 1340, 1100, 750 cm^{-1}. MS, *m/z* 1025 (M^++1, 75), 1024 (M^+, 57), 995(18), 968(15), 924(20). Analysis was performed on the quaternized methyl iodide salt (**III**).

2, 9, 16, 23-Tetrakis[3-(diethylmethylammonio)propyl]-phthalocyaninatocobalt(II) Tetraiodide, (III). To a solution of 75 mg (0.073 mmol) of **II** in 10 ml toluene was added 0.5 ml (8 mmol) of methyl iodide. This solution was stirred for 20 h at room temperature. The observed blue precipitate was filtered and washed with ether. The yield of the blue powdery solid (**III**) was 94.3 mg (81% yield). Found: C, 48.20; H, 5.39; N, 10.85; Co, 3.60%. Calcd for $C_{64}H_{88}N_{12}CoI_4$: C, 48.28; H, 5.57; N, 10.56; Co, 3.70%. Mp >300 °C. IR (KBr) 2960, 1610, 1520, 1460, 1330, 1100, 820, and 760 cm^{-1}.

2,9,16,23-Tetrakis[3-(diethylamino)propyl]phthalocyaninatocopper(II), (IV). To a solution of 76 mg (0.07 mmol) of **I**[3] in 10 ml of a toluene/2-methoxyethanol (1:1 v/v) mixture was added 150 mg (0.83 mmol) of anhydrous copper(II) acetate. The solution was stirred at 120 °C reflux under an argon atmosphere for 20 h. The crude reaction mixture was applied directly to a short basic alumina (Act 3) column (10×1 cm) and eluted with toluene/2-methoxyethanol (3:1 v/v). Evaporation of the solvent gave **IV** as a dark blue shining solid; 78 mg (96% yield). Mp >300 °C. IR (KBr) 2980, 2800, 1610, 1520, 1330, 1100, 830, and 750 cm^{-1}. MS, *m/z* 1030(10), 1029(M$^+$+1, 15), 1028(M$^+$, 8), and 927(5). Analysis was performed on the quaternized methyl iodide salt (**V**).

2,9,16,23-Tetrakis[3-(diethylmethylammonio)propyl]phthalocyaninatocopper(II) Tetraiodide, (V). To a solution of 35 mg (0.034 mmol) of **IV** in 10 ml of toluene was added 0.5 ml (8 mmol) of methyl iodide. This solution was stirred for 20 h at room temperature. The observed blue precipitate was filtered and washed with ether. The yield of blue powdery solid (**V**), after drying, was 40 mg (74% yield). Found: C, 47.80; H, 5.50; N, 10.94; Cu, 3.66%. Calcd for $C_{64}H_{88}N_{12}CuI_4$: C, 48.14; H, 5.55; N, 10.53; Cu, 3.98%. Mp >300 °C. IR (KBr) 2960, 1610, 1450, 1410, 1330, 1170, 1090, and 750 cm^{-1}.



(**I**) $R=(Et)_2N(CH_2)_3\text{-}$, $M=H_2$
(**II**) $R=(Et)_2N(CH_2)_3\text{-}$, $M=Co$
(**III**) $R=(Et)_2Me\overset{\oplus}{N}(CH_2)_3\text{-}\overset{\ominus}{I}$, $M=Co$
(**IV**) $R=(Et)_2N(CH_2)_3\text{-}$, $M=Cu$
(**V**) $R=(Et)_2Me\overset{\oplus}{N}(CH_2)_3\text{-}\overset{\ominus}{I}$, $M=Cu$

Table 1. Absorption Spectra of Phthalocyanines (Pcs) (**II**—**V**) in Some Solvents

Pc	Solvent	λ(max)/nm (ε in log)			
II	DCB[a)]	672(5.16)	650(4.63)	610(4.48)	332(4.76)
		292(4.47)			
III	H_2O[b)]	670(4.77)	626(4.82)	320(4.82)	292(4.88)
		226(5.14)			
	AN[c)]	660(5.26)	598(4.61)	326(4.98)	287(4.86)
		244(5.10)			
IV	DCB[a)]	682(5.14)	658(4.60)	650(4.52)	616(4.53)
		346(4.70)	292(4.18)		
V	H_2O[b)]	670(4.57)	630(4.75)	334(4.73)	225(5.01)
	AN[c)]	670(5.24)	607(4.39)	338(4.84)	245(4.89)

a) DCB; *o*-dichlorobenzene. b) Data in water were collected at 4.665×10^{-6} M for **III** and 5.216×10^{-6} M for **V**. c) AN; acetonitrile.

UV data of **II**—**V** in several solvents are summarized in Table 1.

Results and Discussion

Experiments were designed to illustrate the amphiphilic properties of the compounds.

(i) UV-Absorption and MCD Spectroscopy. Figures 1 and 2 show absorption and MCD spectra of **III** and **V**, respectively, in water, AN and in their mixtures. Their absorption spectra in AN are characteristic of monomeric phthalocyanines.[7)] When trace amounts of water were admixed, the spectra changed only in the region higher in energy than 270 nm probably as a result of coordination of water molecule to cobalt or copper. When the water content in the solvent exceeded 50% in each case, the whole spectrum started to change as shown by arrows with sets of isosbestic

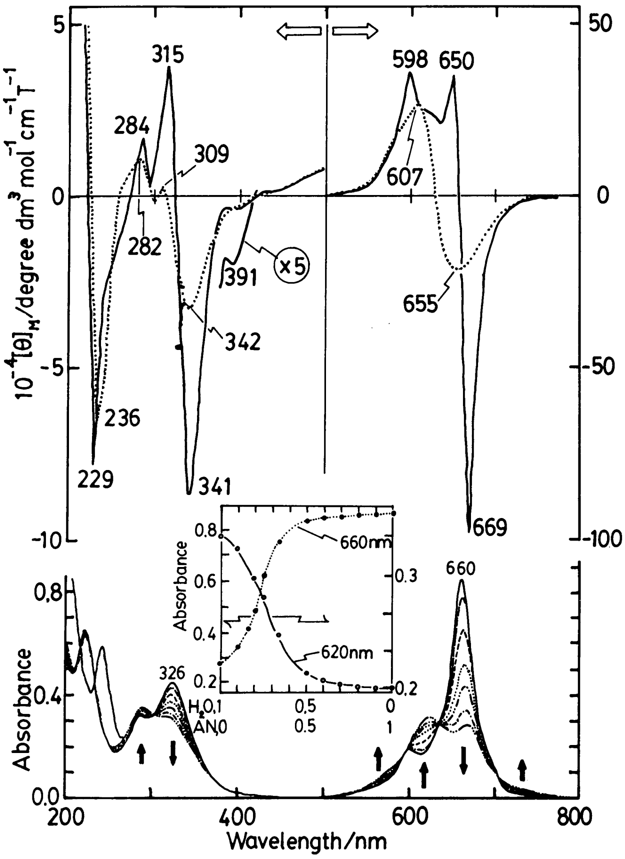


Fig. 1. Absorption (bottom) and MCD (top) spectra of **III** in acetonitrile (solid line), water (dotted line) and in their mixtures. Concentration=4.665×10^{-6} M. Cell path length=10 mm. Magnetic field=1.09 T. The inset shows the absorbance at 660 and 620 nm in acetonitrile-water mixtures.

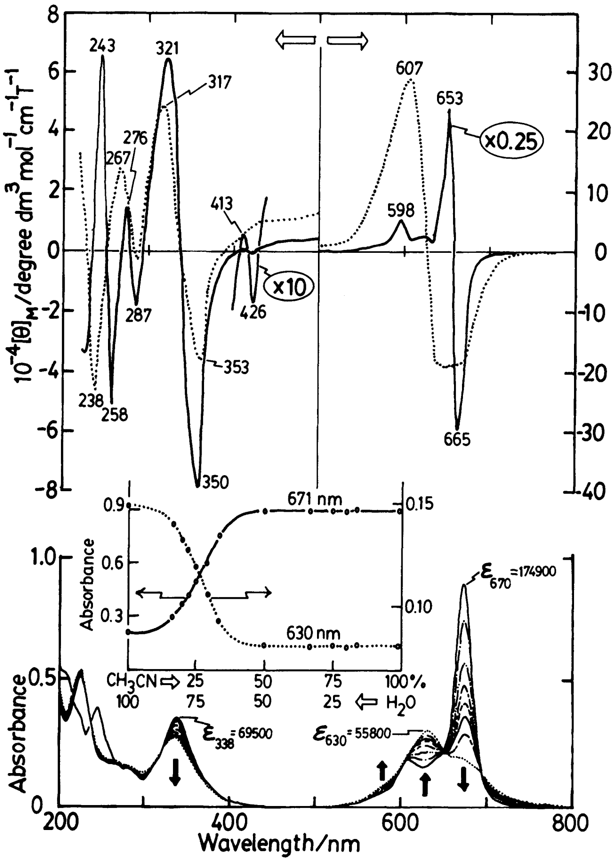


Fig. 2. Absorption (bottom) and MCD spectra (top) of **V** in acetonitrile (solid line), water (dotted line) and in their mixtures. Concentration=5.146×10^{-6} M. Cell path length=10 mm. Magnetic field=1.09 T. The inset shows the absorbance at 671 and 630 nm in acetonitrile–water mixtures.

points, and finally in pure water the spectra shown by the dotted lines were recorded. Although shapes of the spectra in pure water can be classified into those of aggregated phthalocyanines,[7] these are thought to be the spectra of dimeric species, since clear isosbestic points at several positions were observed in each case. The blue shift of the Soret and Q bands observed accompanying the change of solvent from AN to water suggests that the phthalocyanine dimers in water are in a card-pack arrangement.[7–9] This type of aggregation has been formed for tetrasulfonated phthalocyanine in water.[9] It is conceivable that, by the increase of polarity of solvent, the more hydrophobic phthalocyanine moieties approach each other (thereby forming dimers). As can be seen from the inflection points of the two curves in the inset, 50% of the monomeric phthalocyanines have dimerized when the AN:water ratio attains 23:77 (v/v) for **III** or 26.5:73.5 (v/v) for **V**.[10] In order to obtain further information on the state of **III** and **V** in water, the ESR spectrum of **V** was recorded in water. A 3.0×10^{-4} M solution gave an ESR singal at g=2.056 at 77 K, but little hyperfine structure which is observed clearly in

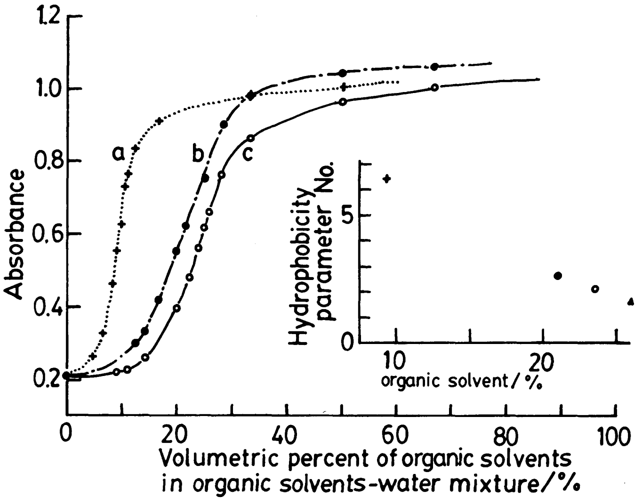


Fig. 3. Absorbance of the Q band of **V** in (a) 2-butoxyethanol–water, (b) dioxane–water, and (c) 2-propanol–water mixtures. Concentration=5.216×10^{-6} M. The inset shows the relationship between the hydrophobicity parameter and the organic solvent percent in organic solvent–water mixtures where 50% of the monomers have formed dimers. These data were obtained from lines a—c and the inset in Fig. 2.

monomeric species[7,11] appeared. Thus, **III** and **V** may exist as somewhat cofacial but slipped and/or staggered type dimers in water.

The MCD spectra of **III** and **V** in both water and AN are typical of phthalocyanines, in that Faraday *A*-terms appeared corresponding to the main absorption maxima.[12] However, though hardly detectable in the absorption spectra, a small but explicit Faraday *A*-term which indicates another degenerate excited state was discerned in the spectrum in AN at around 375—400 nm for **III** and 410—430 nm for **V**. The presence of this *A* term was only recently discovered for the first time for ZnPc[13] by MCD spectroscopy and assigned as a transition to the B state. So far the band at around 300—360 nm has generally been considered to be the B band.[14] However, if we follow the so-called "Four-Orbital Model" by Gouterman,[14,15] the band at 671, ca. 387, and 338 nm of **III** and 659, 420, 341, 282, and 250 nm of **V** in AN can be assigned as transitions to Q, B, N, L, and C states, respectively, in this order.[16] The possibility of a charge-transfer (CT) transition may not be ruled out completely; however, this possibility appears to be small, because an iron phthalocyanine[17] also reveals Faraday *A*-term type MCD signals in the same wavelength region (395—430[17] nm), irrespective of the different central metals. Especially, in the case of copper phthalocyanines, the CT band is not expected theoretically except in the near infrared region.[18]

The monomer-dimer transformatins of **V** were studied further in various organic-water solvent mixtures (Fig. 3). Three organic solvents which mix with water in a wide ratio and have a range of hydrophobicity were selected. These were 2-propanol, dioxane, and 2-butoxyethanol, and have polarity parameters of 2.2, 2.6, and 6.4, respectively[19] (the larger the value, the higher the hydrophobicity). From this figure and the inset, it is found that the higher the hydrophobicity of the organic solvents used, the smaller the organic solvent:water ratio which is required for monomer to dimer transformation. Thus, the hydrophobicity (or polarity) of the solvent does affect the monomer–dimer equilibrium.

(ii) Electrochemistry of III in the Presence or Absence of Oxygen in Water. Cobalt phthalocyanines and porphyrins have been employed as catalysts for the electroreduction of oxygen in systems where the catalysts were homogeneously dissolved[20] in solution or adsorbed[21] onto working electrodes. Although there appears to be a general agreement that mononuclear cobalt complexes promote the O_2 reduction process by two electrons to give H_2O_2, almost no comparison has been made on the catalytic behavior between catalyst-dissolved and -adsorbed systems. The change of solvent on adsorption may also affect catalytic activity, but adsorption of catalysts onto electrodes has always been carried out in a single solvent. No study on the effect of varying the solvent has been reported previously. Since **III** is an amphiphilic cobalt phthalocyanine, we can perform O_2 electroreduction experiments under various conditions and can compare the results mutually.

The adsorption of **III** onto a GC electrode was examined from both 10^{-4} M AN and 10^{-4} M 0.1 M phosphate buffer (pH 7.0) solutions. The electrode was dipped in these solutions for a fixed time, taken out and dried in air, and transferred to a blank solution of 0.05 M H_2SO_4 or 0.1 M phosphate buffer (pH 7.0). The adsorption was saturated within ca. 30 s both in AN and aqueous solutions. Cyclic voltammograms at this prepared electrode are shown in Fig. 4 as curves a and a′ (pH 7, under nitrogen). Clear $Co^{II/I}$ redox couples whose peak currents have a linear relationship with the sweep rate (line b and b′) appeared at ca. −0.3 V vs. SCE, and the amount of the adsorbed catalyst, as deduced from the charge under the area (0.085 μC, i.e. 1.2 μC cm^{-2}) is approximately the same in both cases. The redox couple at the modified GC prepared in aqueous solution appears at a slightly (ca. 30 mV) negative potential than that prepared in AN. The relatively symmetrical redox patterns suggest the absence of significant interaction among the adsorbed species,[22] and imply that although **III** exists as a dimer in water (Fig. 1), the dimer structure may not be retained when it is immobilized onto GC by adsorption.

Figure 4, curves c and c′ are cyclic voltammetric curves at these modified electrodes in the presence of oxygen. Oxygen is reduced catalytically[23] at a much more positive potential than the $Co^{II/I}$ redox couple in curve a or a′, but there is no difference in the peak height between the two types of modified electrodes even over a sweep range of 20 to 200 mV s^{-1}. The peak height was linearly proportional to the square root of the sweep rate (lines d and d′), confirming a diffusion limited process, and to O_2 concentration (line e and e′). The difference in the potentials of O_2 reduction peaks of the two electrodes increases to ca. 50 mV compared with 30 mV for the $Co^{II/I}$ redox couple (curves a and a′). Oxygen reduction at the modified electrode in AN occurs at more anodic potentials than that at the electrode prepared in water. Thus the electrode modified in AN may be slightly better from the standpoint of the O_2 reduction potential.

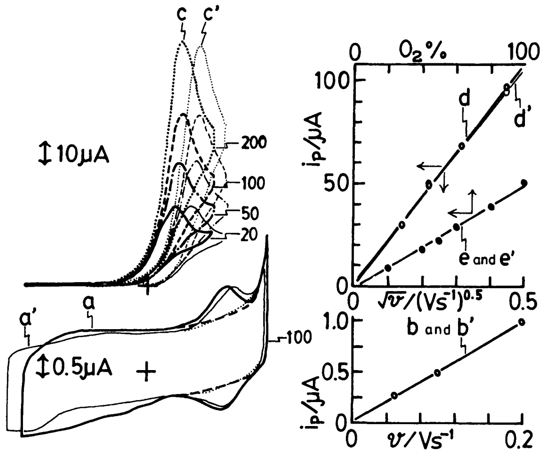


Fig. 4. Cyclic voltammograms at **III**-adsorbed GC electrodes (area, 0.070 cm^2) in water of pH 7.0. Adsorption was carried out either in 10^{-4} M acetonitrile solutions (bolder curves and lines, denoted by alphabet without prime) or in 10^{-4} M aqueous solutions (finer curves and lines denoted by alphabet with prime) for 10 min. Numbers on curves indicate scan rate in mV s^{-1}. Curve a and a′, responses in deaerated solution, and curves c and c′, in O_2-saturated solution. Line b and b′ indicates relationship between peak currents in curve a or a′ (ca. −0.31 or ca. −0.33 V) and scan rate. Lines d and d′ show relationship between peak currents in curves c or c′ and the square root of scan rate, and line e and e′ demonstrates catalytic O_2 reduction peak current vs. O_2 concentration relationship obtained at a sweep rate of 50 mV s^{-1}.

Potentials for the $Co^{II/I}$ couple and O_2 reduction peak at the modified electrodes at pH 1 are summarized together with the data at pH 7 in Table 2. As for other cobalt phthalocyanine systems,[24] the $Co^{II/I}$ redox potentials of **III** at pH 1 lie at much more anodic potentials than at pH 7, but the O_2 reduction potentials at pH 1 do not greatly shift from those at pH 7 and are equal to $Co^{II/I}$ redox potentials of **III** at pH 1. Since the $Co^{II/I}$ and O_2 potentials are similar for the catalyst-adsorbed system at pH 1, the O_2 reduction process can be explained by an electrochemical (EC)

Table 2. Some Potentials at Modified- or Bare Glassy Carbon Electrode

	Electrode with adsorbed **III** from 10^{-4} M AN solution		Electrode with adsorbed **III** from 10^{-4} M 0.1 M phosphate buffer		**III**-dissolved system	
	pH 1	pH 7	pH 1	pH 7	pH 1	pH 7
$Co^{II/I}$potential/V[a]	−0.12	−0.31	−0.15	−0.33	−0.43	−0.38
O_2 reduction Potential/V	−0.12	−0.12	−0.15	−0.17	−0.17	−0.22

a) Defined as (cathodic peak potential+anodic peak potential)/2.

catalytic regeneration mechanism (Eqs. 1 and 2).

$$Co^{II}Pc + e \longrightarrow Co^{I}Pc \qquad E' \tag{1}$$

$$Co^{I}Pc + 0.5O_2 + H^+ \longrightarrow Co^{II}Pc + 0.5H_2O_2 \tag{2}$$

where Pc stands for the phthalocyaninato dianion. The mechanism at the catalyst-adsorbed system at pH 7, on the other band, may be different, since the potential difference between the $Co^{II/I}$ redox couple and O_2 reduction is very large (ca. 200 mV[25]). A reaction mechanism such as a CE (chemical step followed by electron transfer) mechanism (Eqs. 3 and 4) might be considered.[24b)]

$$Co^{II}Pc + O_2 \longrightarrow Co^{II}PcO_2 \tag{3}$$

$$Co^{II}PcO_2 + 2e + 2H^+ \longrightarrow Co^{II}Pc + H_2O_2 \tag{4}$$

Some responses in the catalyst-dissolved system in aqueous solution at pH 1 are displayed in Fig. 5. In deaerated solutions, the bare GC electrode detected aggregated[22)] electroactive species (curves a and b). When O_2 was admitted, the amount of catalytic O_2 reduction current (curve c), which is proportional to the square root of scan rate (curve d), is approximately the same as that in the catalyst-adsorbed systems, and its potential is much more positive than the $Co^{II/I}$ redox couple. Results at the catalyst-dissolved system at pH 7 are similar to those at pH 1 (Table 2). Since the potential difference between the $Co^{II/I}$ redox couple and O_2 reduction is large, it appears difficult to expalin the mechanism as an EC process which has frequently been adopted for O_2 reduction in catalyst-dissolved systems in the past.[20,26)] The reduction mechanisms may be affected by pH value, by the kind of solvents used for adsorption of catalysts and so on. However, we can extract at least the following information based on the data in Table 2 and the above mentioned experimental observations. i) The O_2 reduction potential at GC electrode modified in AN is slightly (20—50 mV) more positive than that prepared in water. ii) The $Co^{II/I}$ redox couple shifts anodically by adsorption onto electrodes, by about 300 mV at pH 1 and 50—70 mV at pH 7. iii) O_2 reduction occurs at more positive potential in the catalyst-adsorbed system than in the catalyst-dissolved system by ca. 20—100 mV. iv) Both monomeric and aggregated forms of the catalyst have catalytic activity toward O_2 electroreduction.

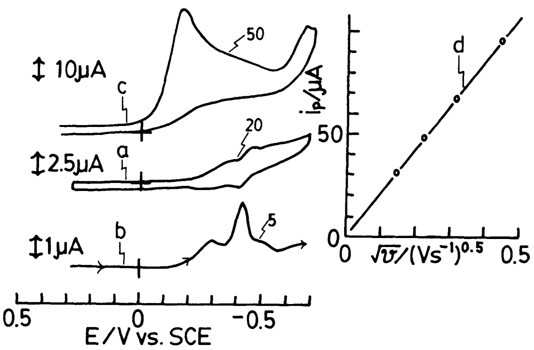


Fig. 5. Cyclic- and differential pulse voltammetric responses at bare GC electrodes in 0.05 M H_2SO_4 solution containing 0.5 mM of **III**. Curves a and b, in deaerated solution, and curve c in O_2-saturated solution. Line d shows the relationship between peak currents in curve c and the square root of the scan rate. Numbers on curves indicate scan rate in mV s^{-1}.

In trying to elucidate reasons for the above observations, and especially iii), we attempted scanning electron microscopy and surface enhanced Raman scattering spectroscopy. However, the amount of adsorbed catalyst was too small for the former spectroscopy and the GC surface was too dark for the latter spectroscopy.

In conclusion, although we cannot yet give a rationale for all the newly observed phenomena, the preparation of amphiphilic phthalocyanines has enabled us to connect and compare phthalocyanine chemistry in organic solvents and in water, which has not previously been possible. Thus, monomer–dimer transformation of phthalocyanines in water–organic solvent mixtures was found to depend on the polarity of organic solvents used. And, although no clear rationale could be given, electroreduction of oxygen at modified electrode was found to be affected not only by the pH value of solution but also by the solvents used for adsorption of catalysts.

We thank Dr. W. A. Nevin for critically reading this manuscript.

References

1) A. B. P. Lever, *Adv. Chem. Radiochem.*, **7**, 27 (1965); F. H. Moser and A. L. Thomas, "The Phthalocyanines," CRC Press, New York, Florida (1983).

2) G. Pawlowski and M. Hanack, *Synthesis*, **1987**, 287; T. W. Hall, S. Greenberg, C. R. McArthur, B. Khouw, and C. C. Leznoff, *Nouv. J. Chim.*, **6**, 653 (1982); H. Shirai, K. Hanabusa, M. Kitamura, E. Masuda, O. Hirabaru, and N. Hojo, *Makromol. Chem.*, **185**, 2537 (1984); D. Wohrle and G. Krawczyk, *Polym. Bull.*, **15**, 193 (1986).

3) J. H. Weber and D. H. Busch, *Inorg. Chem.*, **4**, 469 (1965).

4) D. R. Boston and J. C. Bailor, Jr., *Inorg. Chem.*, **11**, 1578 (1972); N. Kobayashi, H. Shirai, and N. Hojo, *J. Chem. Soc., Dalton Trans.*, **1984**, 2107.

5) V. M. Derkacheva, N. I. Bundina, N. G. Mekhryakova, O. L. Kaliya, T. Yu. Gulinat, and E. A. Luk'yanets, *Russ. J. Inorg. Chem. Engl. Ed.*, **26**, 911 (1981).

6) C. C. Leznoff, S. Vigh, P. I. Svirskaya, S. Greenberg, D. M. Drew, E. Ben-Hur, and I. Rosenthal, *Photochem. Photobiol.*, **49**, 279 (1989).

7) N. Kobayashi and A. B. P. Lever, *J. Am. Chem. Soc.*, **109**, 7433 (1987) and some references therein.

8) A. R. Monahan, J. A. Brado, and A. F. DeLuka, *J. Phys. Chem.*, **76**, 446 (1972); J. H. Sharp and M. Lardon, *ibid.*, **72**, 3230 (1968).

9) S. E. Sheppard and A. L. Geddes, *J. Am. Chem. Soc.*, **66**, 1995 (1944); Z. A. Schelly, R. D. Farina, and E. M. Eyring, *J. Phys. Chem.*, **74**, 617 (1970).

10) Thus, **V** forms a dimer more easily than **III**, since it requires a lower amount of dimer-forming solvent (water). Since there are no structural differences between **III** and **V**, this furhter indicates that copper(II) has a higher tendency toward dimerization than cobalt(II).

11) R. Neiman and D. Kivelson, *J. Chem. Phys.*, **35**, 156 (1961); C. M. Gusy, J. B. Raynor, and M. C. R. Simons, *J. Chem. Soc. A*, **1961**, 2299; S. S. Eaton, K. M. More, B. M. Sawant, and G. R. Eaton, *J. Am. Chem. Soc.*, **105**, 6560 (1983); M. Chikira, H. Yokoi, and T. Isobe, *Bull. Chem. Soc. Jpn.*, **47**, 2208 (1974).

12) P. J. Stephens, *Ann. Rev. Phys. Chem.*, **25**, 201 (1974).

13) T. Nyokong, Z. Gasyna, and M. J. Stillman, *Inorg. Chem.*, **26**, 1087 (1987).

14) M. Gouterman, "The Porphyrins," ed. by D. Dolphin, Vol. III, Chap. 1, Academic Press, New York, London (1978).

15) M. Gouterman, *J. Chem. Phys.*, **30**, 1139 (1959).

16) A. J. McHugh, M. Gouterman, and C. Weiss, *Theor. Chim. Acta*, **24**, 346 (1972).

17) N. Kobayashi, M. Koshiyama, Y. Ishikawa, T. Osa, H. Shirai, and N. Hojo, *Chem. Lett.*, **1984**, 1633.

18) A. B. P. Lever, S. R. Pickens, P. C. Minor, S. Licoccia, B. S. Ramaswamy, and K. Magnell, *J. Am. Chem. Soc.*, **103**, 6805 (1981).

19) J. R. Haak and J. B. F. N. Engburts, *Recl. Trav. Chim. Pays-Bas*, **105**, 307 (1986); K. Dimroth, C. Reichardt, T. Siepman, and F. Bohlman, *Justus Liebigs Ann. Chem.*, **661**, 1 (1963).

20) a) T. Kuwana and A. Bettelheim, *Anal. Chem.*, **51**, 2257 (1979); b) T. Kuwana and P. A. Forschey, *Inorg. Chem.*, **20**, 693 (1981); **22**, 699 (1983); c) T. Kuwana, P. A. Forschey, N. Kobayashi, and T. Osa, *Adv. Chem. Ser.*, **No. 201**, 601 (1982); d) N. Kobayashi, M. Fujihira, T. Matsue, and T. Osa, *J. Electroanal. Chem.*, **103**, 427 (1979); e) N. Kobayashi, M. Fujihira, T. Osa, and T. Kuwana, *Bull. Chem. Soc. Jpn.*, **53**, 2195 (1980); f) N. Kobayashi and T. Osa, *J. Electroanal. Chem.*, **157**, 269 (1983); g) N. Kobayashi, M. Koshiyama, T. Osa, and T. Kuwana, *Inorg. Chem.*, **22**, 3608 (1983); h) N. Kobayashi and Y. Nishiyama, *J. Phys. Chem.*, **89**, 1167 (1985).

21) R. Jasinski, *Nature (London)*, **201**, 1212 (1964); H. Jahnke, M. Schonborn, and G. Zimmermann, *Topics in Current Chemistry*, **61**, 133 (1976); M. R. Tarasevish and K. A. Radyushkina, *Russ. Chem. Rev. Eng. Trans.*, **49**, 1498 (1980); F. van den Brink, E. Barendrecht, and W. Visscher, *Recl. Trav. Chim. Pays-Bas*, **99**, 253 (1980); J. A. R. van Veen and J. F. van Baar, *Rev. Inorg. Chem.*, **4**, 293 (1982); D. J. Schiffrin, *Electrochemistry*, **8**, 126 (1983); E. Yeager, *Electrochim. Acta*, **29**, 1527 (1984); *J. Mol. Catal.*, **38**, 5 (1986).

22) M. R. Hempstead, C. C. Leznoff, and A. B. P. Lever, *Can. J. Chem.*, **65**, 2677 (1987).

23) O_2 reduction at bare GC electrode occurs at ca. −0.58 V vs. SCE in water.[20b,c]

24) a) S. Zecevic, B. Simic-Glavaski, E. Yeager, A. B. P. Lever, and P. C. Minor, *J. Electroanal. Chem.*, **196**, 339 (1985); b) P. Janda, N. Kobayashi, H. Lam, P. R. Auburn, C. C. Leznoff, and A. B. P. Lever, *Can. J. Chem.*, **67**, 1109 (1989).

25) C. P. Andrieux, C. Blocman, J. M. Bouchiat-Dumas, F. M'Halla, and J. M. Saveant, *J. Electroanal. Chem.*, **119**, 19 (1980); C. P. Andrieux and J. M. Saveant, *ibid.*, **134**, 163 (1982); **142**, 1 (1982); F. C. Anson, *J. Phys. Chem.*, **84**, 3336 (1980).

26) D. O. R. Parash, F. Broitman, U. Mor, and A. Bettelheim, *J. Chem. Soc., Faraday Trans. 1*, **80**, 1139 (1984).