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Polarographic Studies of Some Porphyrins and Metalloporphyrins in *N*,*N*-Dimethylformamide

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Electrochemical behavior of protoporphyrin IX dimethylester (PPDM), mesoporphyrin IX dimethylester(MPDM), Fe(III)Cl-protoporphyrin, Ni(II)-, Cu(II)-, Co(II)-, Zn(II)- and Mn(III)Cl·H_2O–PPDM was investigated in dimethylformamide by use of AC polarography, cyclic voltammetry and DC polarography. These porphyrins and divalent metal complexes of PPDM gave, for the most part, three reduction waves. The first and second waves were reversible one-electron steps in each case, but the third step was an irreversible one. Mn(III)-complex gave four reduction waves and one oxidation wave. The first three reduction waves were one-electron steps and the oxidation wave was identified as that due to chloride anion. Fe(III)-complex gave five reduction waves and one oxidation wave. The first two reduction waves were one-electron steps. All these compounds showed specific adsorption at the potential more positive than −1.1 V *vs.* SCE. Assignment of the reduction steps of the metalloporphyrins is described. The observed order of increasing negative half-wave potentials is discussed in terms of Zerner and Gouterman's molecular orbital calculation.

Nonaqueous electrochemistry of porphyrins and metalloporphyrins has been studied by several authors. Electrochemical measurements have been accompanied by ESR and absorption spectral data, and the correlation of half-wave potentials with molecular structures has been discussed.[1–6] The electrode processes have also been studied in detail.[7,8]

In this study, the polarographic reduction of some porphyrins and metalloporphyrins in aprotic solvent, *N*,*N*-dimethylformamide(DMF), was examined in detail by use of DC polarography, cyclic voltammetry and AC polarography.

Experimental

Materials. Hemine(Fe(III)Cl-PP), protoporphyrin IX dimethylester (PPDM) and mesoporphyrin IX dimethylester (MPDM) were prepared from cow blood by established methods[9–11] and purified by repeated column chromatography on neutral alumina with 200 : 1 chloroform–methanol and by recrystallization from chloroform–methanol mixture. Ni(II)-, Cu(II)-, Co(II)- and Zn(II)-PPDM were prepared from the free base by standard procedures[11] and separated from unreacted ligand by repeated column chromatography on neutral alumina with benzene. The solids were recrystallized from chloroform–methanol (or petroleum ether) and dried under vacuum. The absence of metal-free and altered porphyrin impurities in the metalloporphyrins was confirmed by thin layer chromatography on silica gel and absorption spectrophotometry. Mn(III)Cl·H_2O-PPDM was prepared by Boucher's procedures.[12]

DMF(reagent grade) was shaken with potassium hydroxide (about 30 g/l of solvent) for a few hours, decanted, and after bubbling nitrogen gas for thirty minutes, shaken with phosphorus pentoxide (about 40 g/l of solvent) for a few hours. After decanting, the solvent was distilled under reduced pressure (at 45—55 °C) with nitrogen passing through a Widmer's fractional distillation column. The central 60% fraction was collected and stored under dried nitrogen gas. Tetraethylammonium perchlorate(TEAP) was prepared and purified by the methods previously described.[13] Nitrogen gas was dried by passing through a washing bottle containing concd. sulfuric acid and a U-tube containing calcium chloride.

Electrochemical Measurements. DC polarograms and cyclic voltammograms were measured with a potentiostat, Yanaco PE-21-TB2S, equipped with a function generator, YHP 3310 B. AC polarograms were measured with the aid of a lock-in amplifier, NF LI-572B. A polarographic H-cell was used with dropping mercury electrode and platinum wire electrode coiled around the tip of the DME in the same arm. The other arm of the cell was filled with a supporting electrolyte solution(DMF containing 0.1 M TEAP) and connected with a nonaqueous salt bridge(DMF-methylcellulose-0.5 M TEAP) to an aqueous saturated calomel electrode(SCE). The liquid junction was by-passed for alternating current by a "pool" capacitor[16] of 2000 μF between the coiled platinum wire electrode and SCE. The cell was immersed in a water thermostat controlled at 25±0.1 °C. Measurements were carried out under dried nitrogen atmosphere.

The capillary characteristics were $m=1.07_8$ mg/sec and $t=5.8$ s at $h=70$ cmHg in DMF containing 0.1 M TEAP at −0.5 V *vs.* SCE. Cyclic voltammograms were recorded with a very slowly dropping mercury electrode[14] (usually at $t=90$ or 120 s), whose capillary characteristics were $m=4.56\times10^{-2}$ mg/s and $t=345.1$ s at $h=50$ cmHg in DMF containing 0.1 M TEAP at −0.5 V *vs.* SCE.

The porphyrins and their metal complexes were generally sparingly soluble in DMF, and usually their saturated solutions (for the most part, approximately 4×10^{-4} M) were used.

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[11] J. E. Falk, "Porphyrins and metalloporphyrins," Elsevier Publishing Co., New York (1964), p. 125.

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Results

Reduction of PPDM, MPDM, Cu(II)-PPDM and Zn(II)-PPDM. These compounds in DMF gave three well-defined polarographic waves, as shown in Fig. 1. In this figure dotted lines indicate the base currents. By addition of the depolarizer a lowering of the residual current was observed at the potential more positive than about −0.7 V. This can be ascribed to the adsorption[15] of depolarizer on the electrode surface, a fact which was confirmed also by AC polarography and electrocapillary studies, as described below. All three waves gave limiting currents which are proportional to the concentration of depolarizer over the range from 5×10^{-5} to 4×10^{-4} M. Upon variation of the mercury column height, h, from 40 to 80 cm, all limiting currents of these three steps were proportional to $h^{1/2}$. The half-wave potentials of the first two steps were found to be independent of the concentration of depolarizer and of the mercury column over the range studied. The temperature coefficient of the limiting current was, for example, 0.7% at 25 °C for the first two steps of PPDM. These results are typical of a diffusion-controlled electrode process at the d.m.e.. When corrected for drop time, the three waves were in the ratio of 1 : 1 : 1.8 for PPDM and MPDM, and 1 : 1 : 1.5 for Cu(II)-PPDM and Zn(II)-PPDM. The polarographic data and analysis for these compounds are summarized in Table 1. Analysis of the rising portion of the waves indicated that the first two steps were reversible one-electron reduction process. The third step appeared irreversible.

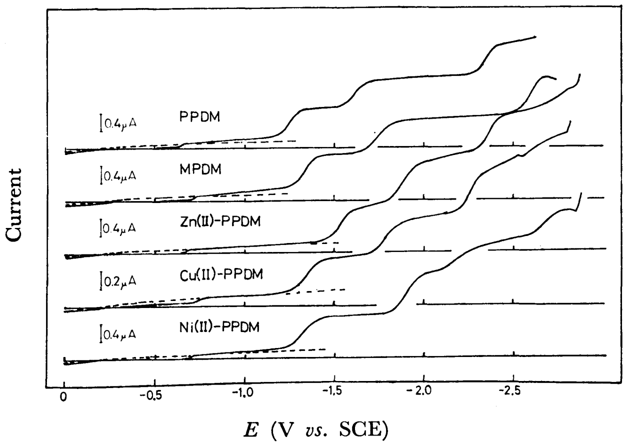

Fig. 1. DC polarograms of PPDM, MPDM, Zn(II)-PPDM, Cu(II)-PPDM and Ni(II)-PPDM in DMF, 0.1 M TEAP at 25 °C.

Concentration: about 4×10^{-4} M (but Cu-complex, about 2×10^{-4} M). Dotted lines indicate the base currents.

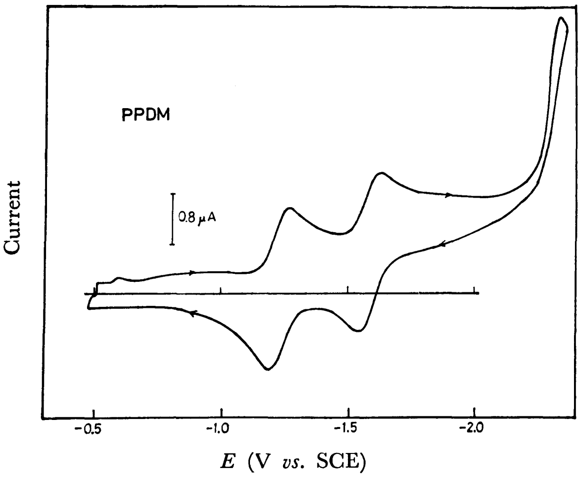

Fig. 2. Cyclic voltammogram of PPDM in DMF, 0.1 M TEAP at 25 °C.

Concentration: about 4×10^{-4} M. Scan rate: 0.2 V/s.

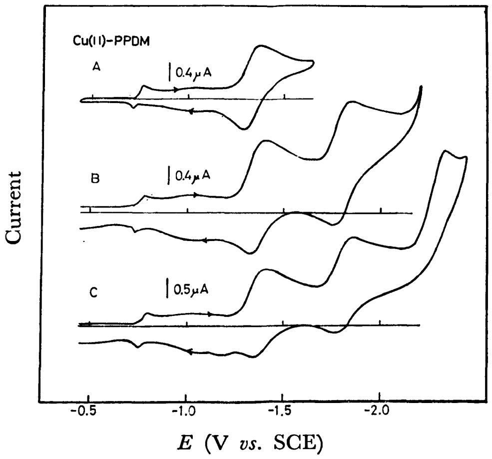

Fig. 3. Cyclic voltammogram of Cu(II)-PPDM in DMF, 0.1 M TEAP at 25 °C.

Concentration: about 2×10^{-4} M. Scan rate: A, 0.26 V/s; B, 0.5 V/s; C, 0.5 V/s.

The DC polarographic results were confirmed by cyclic voltammetry. A typical cyclic voltammogram of PPDM is shown in Fig. 2. The first two steps showed cathodic and anodic peak separation of about 60 mV indicative of a reversible one-electron step. Peak currents of the first two steps were proportional to the concentration of depolarizer (less than 4×10^{-4} M) and square root of the scan rate(0.1 to 1 V/s). The cathodic and anodic peak potentials for the first two steps were found to be independent of the concentration and of the scan rate over the range studies. These results again indicate that the first two steps are reversible one-electron processes. The third step appeared irreversible, showing no corresponding anodic peak. In the case of Cu(II)-PPDM and Ni(II)-PPDM, however, an additional anodic peak was observed at the potential about 0.1 V more positive than that of the first anodic peak, as shown in Fig. 3. In the case of Zn(II)-PPDM, one more anodic peak was observed between the first and second anodic peaks. These anodic peaks were not observed until the cathodic scan limit was extended to the third step. It is clear that these additional peaks are associated with the oxidation of the products produced at the third reduction step.

In AC polarography, these compounds gave four peaks. Fig. 4 shows a typical AC polarogram of PPDM. A small peak observed at the most positive

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[15] M. Senda and I. Tachi, *Rev. Polarogr.* (Kuoto), **10**, 79 (1962).

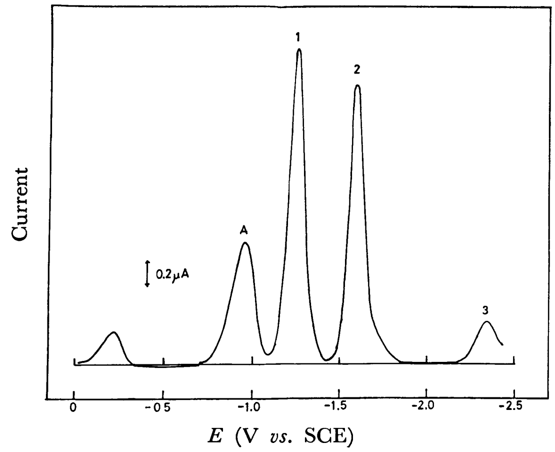

Fig. 4. AC polarogram of PPDM in DMF, 0.1 M TEAP at 25 °C.

Concentration: about 4×10^{-4} M. A.C. frequency: 100 Hz; AC voltage: 10 mV (p-p).

potential is considered to be due to a trace of iodide anion remaining in supporting electrolyte because it was observed also with the base solution. Three AC peaks observed at -1.24, -1.61 and -2.4 V will be denoted by Peaks 1, 2 and 3, respectively. These three peaks correspond respectively to the three reduction steps in DC polarography. The summit potentials of Peaks 1 and 2, being independent of concentration, agreed with the corresponding DC half-wave potentials within experimental error. The half-width of these peaks were about 90 mV. The summit currents were proportional to the concentration over the range studied(see Fig. 5). The apparent lower height of Peak 2 in comparison with Peak 1 is in large part due to the decreasing of drop time. The lower height of Peak 3 is due to its irreversibility. These AC results are in good agreement with the results in DC polarography and cyclic voltammetry.

The AC peak observed at around -0.95 V, being denoted by Peak A, had no counter part in DC polarography. Figure 5 shows the dependence of the summit potentials and summit current of the AC peaks 1, 2, and A on the concentration of PPDM. The behavior of 1 and 2 is that of the reversible process. In contrast, with increasing concentration of the depolrizer the summite current of Peak A increased nonlinearly and approached a limiting value and the summit potential shifted to more negative potential. With a rise in temperature the summit current decreased and the summit potential was shifted to more positive potential, as shown in Fig. 6. Further, the rising potential of Peak A approximately agreed with the potential where the depression of the DC residual current was restored. These results indicate that Peak A is a tensammetric desorption wave.[15,16] This assignment was clonfirmed also by electrocapillary measurements. Fig. 7 shows the electrocapillary curves(drop time–potential curves). The addition of depolarizer to the base solution caused a significant depression of drop time at the potential

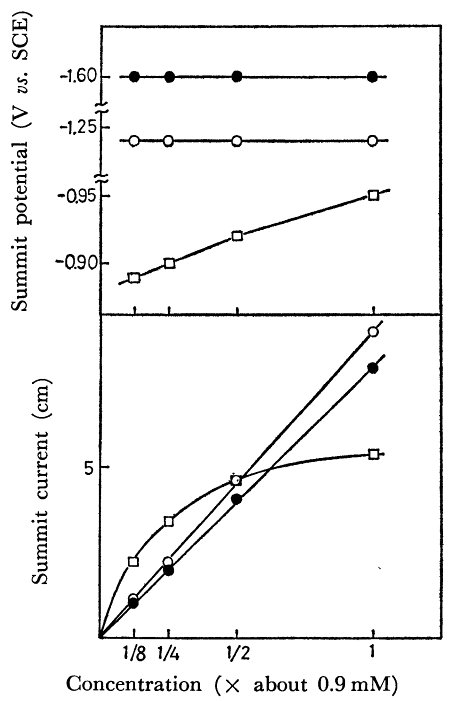

Fig. 5. Dependence of the summit potentials and summit currents on the concentration of PPDM in DMF, 0.1 M TEAP at 25 °C.

□: Peak A; ○: Peak 1; ●: Peak 2.

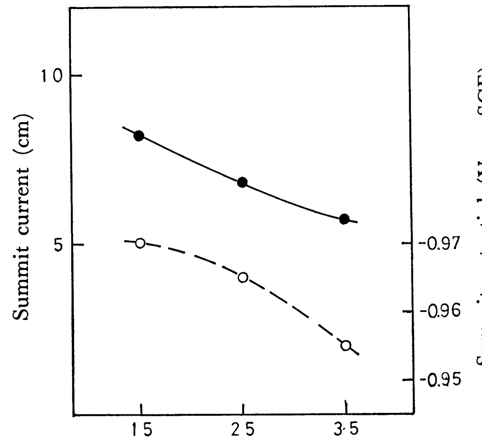

Fig. 6. Effect of temperature on the summit potential and summit current of Peak A of PPDM in DMF, 0.1 M TEAP.

Concentration: about 4×10^{-4} M. ●: summit current; ○: summit potential.

more positive than about -1.0 V, and the magnitude of the depression increased with increasing concentration of depolarizer. However, at the potential more negative than -1.1 V the depression was no more observed. These observations are consistent with the AC and DC polarographic results described above and indicate that the adsorption effects on the electrode process are practically negligible at the potential more negative than -1.1 V.

Reduction of Ni(II)-PPDM. A polarogram of this compound is shown in Fig. 1. The DC and AC

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[16] B. Breyer and H. H. Bauer, "Alternating Current Polarography and Tensammetry," Interscience Publishers, New York, (1963).

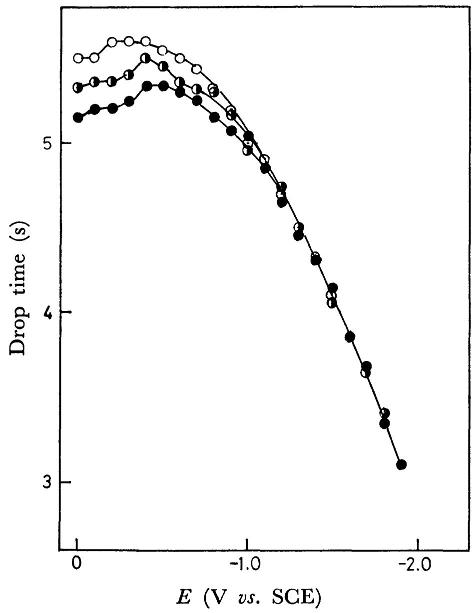

Fig. 7. Electrocapillary curves of a DMF solution containing 0.1 M TEAP(○), and in the presence of 1/8 (◑) and 1/1(●)× *ca.* 4×10^{-4} M MPDM in the base solution at 25 °C.

polarographic properties of the first two steps were essentially the same as those of the other metalloporphyrins described above. The first step in DC polarography was a one-electron reversible step, but the height of the second step was slightly larger than that of the first one. This slight increase of the current would be attributed to electroreduction of products that were produced in chemical reactions, including protonation, following the second electrochemical step. The third and fourth DC steps were poorly defined, irreversible waves.

Reduction of Co(II)-PPDM. Co(II)-PPDM in DMF gave two well-defined polarographic waves at −0.96 and −2.06 V, and an ill-defined wave at −2.35 V, as shown in Fig. 8. A small maximum was also observed at about −1.1 V on the first step. The limiting currents of the first two steps were proportional to square root of the mercury column height, indicating that these were controlled by diffusion. When corrected for drop time, the two wave heights were in the ratio of 1 : 0.9. The wave slopes for the first and second steps were 70 and 60 mV, respectively.

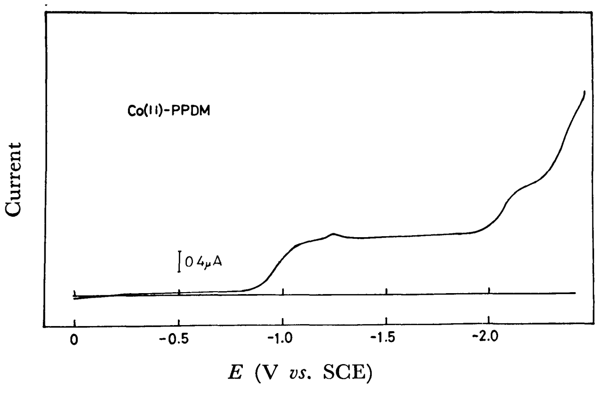

Fig. 8. DC polarogram of Co(II)-PPDM in DMF, 0.1 M TEAP at 25 °C.
Concentration: about 4×10^{-4} M.

A cyclic voltammogram of Co(II)-PPDM is shown in Fig. 9. The first wave, corresponding to the first DC step, has a complicated shape, which may be ascribed to the adsorption of metalloporphyrin molecules on the electrode surface. In contrast, the second peak, appearing at the potential of the second DC step, has the normal shape with a corresponding anodic peak, indicating that the second step is a simple one-electron reversible reduction.

In AC polarography, this compound gave four peaks, as shown in Fig. 10. Three AC peaks observed at −0.96, −1.14 and −2.05 V will be denoted by Peaks 1, A and 2, respectively. The summit potential of Peaks 1 and 2 agreed with the half-wave potentials of the first and second steps, respectively. Figure 11 shows the dependence of the summit current and summit potentials on the bulk concentration of depolarizer. The summit current of Peak 2 was proportional to the concentration and its summit potential was nearly independent of the concentration. Moreover, the waveform of Peak 2 was practically symmetrical with respect to the summit potential with a half-width of about 100 mV. On the other hand, with increasing concentration of the depolarizer the summit current

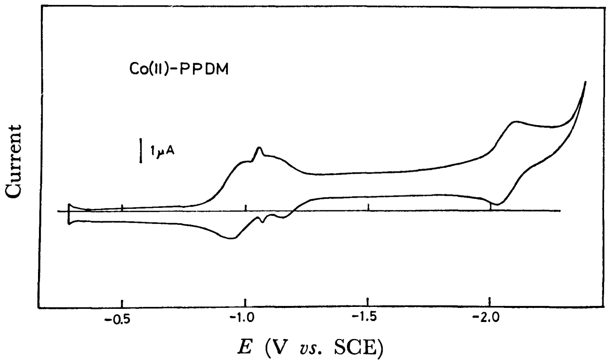

Fig. 9. Cyclic voltammogram of Co(II)-PPDM in DMF, 0.1 M TEAP at 25 °C.
Concentration: about 4×10^{-4} M. Scan rate: 0.42 V/s.

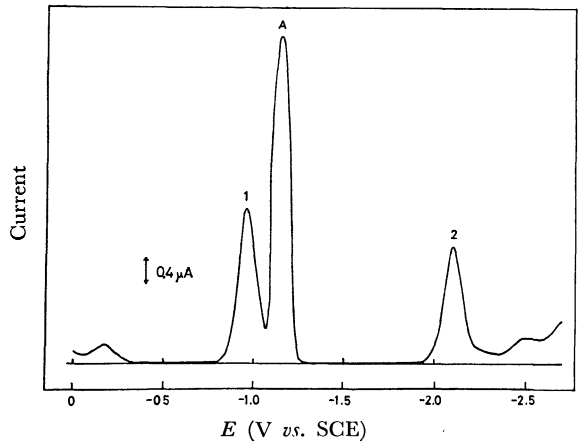

Fig. 10. AC polarogram of Co(II)-PPDM in DMF, 0.1 M TEAP at 25 °C.
Concentration: about 4×10^{-4} M. AC frequency: 100 Hz; AC voltage: 10 mV.

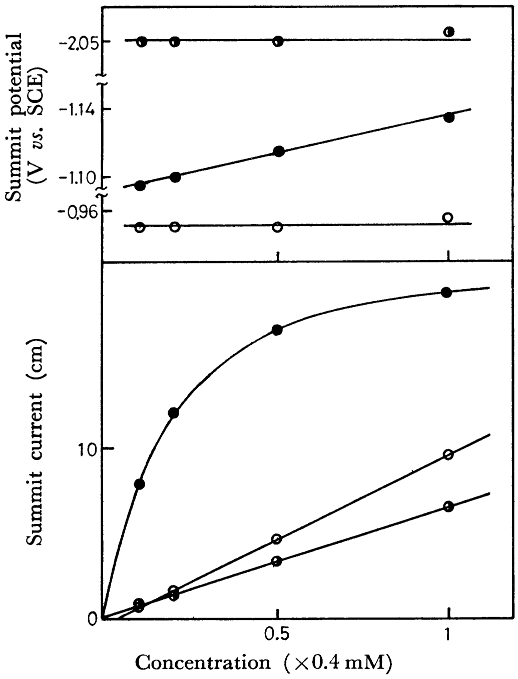

Fig. 11. Dependence of the summit potentials and summit currents on the concentration of Co(II)-PPDM in DMF, 0.1 M TEAP at 25 °C. ●: Peak A; ○: Peak 1; ◑: Peak 2.

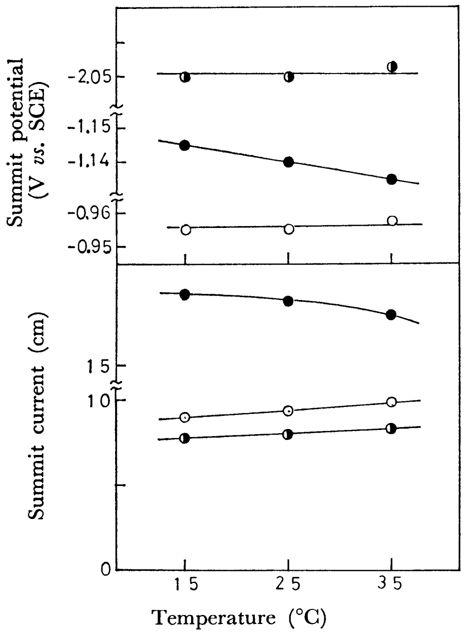

Fig. 12. Effect of temperature on the summit potentials and summit currents of Co(II)-PPDM in DMF, 0.1 M TEAP.
Concentration: about 4×10^{-4} M. ●: Peak A; ○: Peak 1; ◑: Peak 2.

of Peak A increased nonlinearly and approached a limiting value and its summit potential shifted to more negative potential. The summit current of Peak 1 increased linearly with the concentration, but the linear regression line intersected with the current axis at a negative value. The summit potential of Peak 1 was practically independent of the concentration. Effect of temperature on the summit currents and summit potentials is shown in Fg. 12. The sumit currents of Peaks 1 and 2 inclined to increase with a rise in temperature and the apparent shift of their summit potentials are negligibly small. The temperature coefficients of these summit currents were in the order of that of AC reversible peak.[17] On the contrary, the summit current of Peak A decreased and its summit potential shifted to more positive potential with a rise in temperature. Namely, the behavior of Peak A was characteristic of the tensammetric desorption wave.

In conclusion it may be stated that the first DC wave is a reversible one-electron reduction wave overlapped with an adsorption post wave,[18] though the latter is poorly separated from the main wave. The AC polarographic behavior of peaks 1 and A reasonably supports this interpretation.[19] The adsorption effect is negligible at the potential more negative than −1.2 V. The second DC wave is a simple reversible one-electron reduction wave.

Reduction of Mn(III)Cl·H_2O-PPDM and Fe(III)Cl-PP. In DC polarography, the Mn(III)-complex gave four reduction steps and an oxidation double wave, as shown in Fig. 13. Polarographic reduction of Mn(II)-porphyrin derivatives in aprotic media has been studied by Boucher and Garber.[4] The results in the present study were, for the most part, in good agreement with those reported by them. The oxidation double wave was identified as an oxidation wave due to chloride anion. This suggests that an axial ligand such as chloride anion is displaced by a solvent molecule in such a strongly coordinating solvent as DMF, which is consistent with spectral observation by Boucher.[12] In AC polarography, was observed a peak of asymmetric shape at the potential of the first redox waves as well as four AC peaks corresponding to the tensammetric desorption (Peak A) and the second, third and fourth reduction steps (Peaks 1, 2 and 3, see Fig. 4).

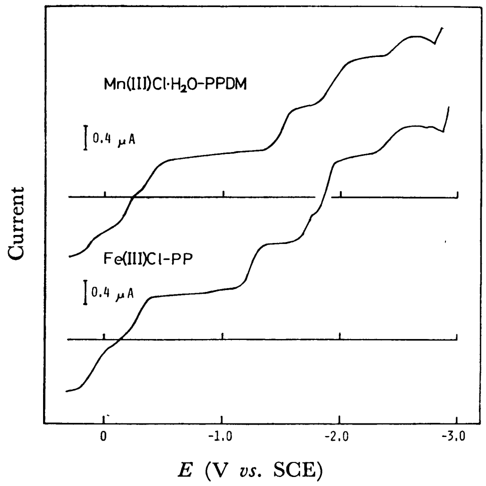

Fig. 13. DC polarograms of Mn(III)Cl·H_2O·PPDM and Fe(III)Cl·PP in DMF, 0.1 M TEAP at 25 °C.
Concentration: about 4×10^{-4} M.

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TABLE 1. POLAROGRAPHIC RESULTS ON PORPHYRINS AND METALLOPORPHYRINS IN DMF CONTAINING 0.1 M TEAP AT 25 °C

Compound	$-E_{1/2}(1)$a)	$\Delta E(1)$b)	$-E_{1/2}(2)$a)	$\Delta E(2)$b)	$-E_{1/2}(3)$a)
PPDM	1.24	0.06	1.61	0.06	2.34
MPDM	1.34	0.06	1.74	0.06	2.58
Ni(II)PPDM	1.34	0.06	1.89	0.06	2.11c)
Cu(II)PPDM	1.37	0.06	1.82	0.06	2.26
Zn(II)PPDM	1.49	0.06	1.84	0.06	2.30
Co(II)PPDM	0.96	0.07	2.06	0.06	2.35
Fe(III)Cl-PP	0.28	0.07	1.20	0.06	1.64d)
Mn(III)Cl·H_2O-PPDM	0.37	0.08	1.49	0.06	1.97e)

a) Volts *vs.* aq. SCE. b) $\Delta E = E_{1/4} - {}_{3/4}$ (in V). c) One more wave at −2.7 V. d) Two more waves at −1.84 and −2.4 V. e) One more wave at −2.4 V.

DC polarogram of Fe(III)Cl-PP is shown in Fig. 13. The first and second reduction steps were one-electron diffusion-controlled steps. Three more reduction waves were observed. An oxidation wave was also observed. In AC polarography, five peaks were observed, but a peak corresponding to the DC third step was not observed.

Discussion

The half-wave potentials of the porphyrins and metalloporphyrins measured in this study are summarized in Table 1. Polarographic reduction of tetraphenylporphin (TPP) and its metal complexes in dimethylsulfoxide has been studed by Felton and Linschitz.2) On comparing the half-wave potentials of PPDM complexes with those of TPP complexes, we may find that the difference between the corresponding steps was nearly constant; for the first step, 0.19 V (TPP–PPDM), 0.16 V (Ni-TPP—Ni-PPDM), 0.17 V (Cu-TPP—Cu-PPDM), 0.18 V (Zn-TPP—Zn-PPDM), 0.14 V (Co-TPP—Co-PPDM), and for the second step, 0.14 V (TPP–PPDM), 0.14 V (Ni-PPT—Ni-PPDM), 0.14 V (Cu-TPP—Cu-PPDM), 0.12 V (Zn-TPP—Zn-PPDM), 0.19 V (Co-TPP—Co-PPDM). This result suggests that the polarographic reduction of these metal-PPDM complexes proceeds in a similar manner as that of metal-TPP complexes. Accordingly, the first two reduction steps of Ni(II)-PPDM, Cu(II)-PPDM and Zn(II)-PPDM will be assigned to successive addition of one electron to orbitals belonging mainly to the porphyrin ring, and the first step of Co(II)–PPDM to addition of one electron to a metal-centered orbital.2)

The first DC waves of Fe(III)Cl-PP and Mn(III)-Cl·H_2O-PPDM should reasonably be assigned to the reduction of a trivalent metal complex to a divalent metal complex. The half-wave potential of the first step of Fe(III)-complex is 0.09 V more positive than that of Mn(III)-complex. Correspondingly, the difference in reduction potentials between hematoporphyrin complexes of Fe(III) and Mn(III) in aqueous solution is reported to be 0.05 to 0.08 V.2),21) The subsequent reduction steps of the trivalent metalloporphyrins should be assigned to the reduction of the divalent metalloporphyrins.

The observed order of increasing negative half-wave potential of the first step of the divalent metalloporphyrins or the second step of the trivalent metalloporphyrins is $\mathrm{Co} \ll \mathrm{Fe} < \mathrm{Ni} \lesssim \mathrm{Cu} \ll \mathrm{Zn} \simeq \mathrm{Mn}$. On the other hand, the calculated order22) of increasing negative charge on the porphyrin moiety is $\mathrm{Mn} \ll \mathrm{Fe} < \mathrm{Cu} \lesssim \mathrm{Ni} < \mathrm{Co} < \mathrm{Zn}$. The observed order $\mathrm{Fe} < \mathrm{Ni} \lesssim \mathrm{Cu} \ll \mathrm{Zn}$ should be considered as practically agreed with the calculated order of increasing negative charge in the porphyrin moiety. This is in harmony with the charge in the porphyrin moiety. This is in harmony with the stated conclusion that the addition of electron to these metalloporphyrins, except Fe(II)-complex, takes place in porphyrin moiety. For Fe(II)-complex the possibility of the electron addition to metal-centered orbital may not be excluded. It is also noted that the half-wave potential of Fe(II)-complex (second step of Fe(III)Cl-PP) is more positive than that of the free base, PPDM (Table 1). The half-wave potential of Mn(II)-PPDM is much more negative than predicted from the molecular orbital calculation, in which a planar configuration is assumed. This discrepancy may be interpreted by assuming that in Mn(II)-porphyrins the metal atom is out of the plane of the porphyrin, so that the porphyrin ring retains a high negative charge in this configuration because of the poor sigma donation of the porphyrin to the metal. The assumed structure is consistent with the ease of demetallation of Mn(II)-porphyrin derivatives20) and the lack of strong mixing of metal dπ orbitals with ring π orbitals, as suggested by the spectral data.4,23)

The half-wave potential of Co(II)-PPDM is remarkably more positive than predicted by the calculation. This result may be understood by the reason that in this complex the electron is added to the metal-centered orbital, exceptionally among the divalent metalloporphyrins studied.

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