Electrochemical and Spectral Characterization of Stable Iron(IV) Tetrakis-5,10,15,20-(*N*-methyl-4-pyridyl)porphyrin in Aqueous Solution at Room Temperature

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Stable iron(IV) tetrakis-5,10,15,20-(*N*-methyl-4-pyridyl)porphyrin has been generated electrochemically and characterized in aqueous solution at room temperature for the first time using the optically transparent thin-layer electrochemical method.

The characterization of oxoiron(IV) porphyrins[1] and oxo-iron(IV) porphyrin radical cations[2] is of interest in view of their proposed intermediacy in HRP II and I respectively. For the generation of oxoiron(IV) porphyrins, an electrochemical method in non-aqueous solution[3] and a chemical method in aqueous solution[4] have been reported. The electrochemical generation of iron(IV) porphyrins in water, however, has not been successful[5] owing to the destruction of the porphyrin ring.[6]

The cyclic voltammogram for the oxidation of iron(III) tetrakis-5,10,15,20-(*N*-methyl-4-pyridyl)porphyrin (Fe$^{\text{III}}$-TMPyP) in alkaline aqueous solution exhibits broad irreversible waves which indicate kinetically slow heterogeneous electron transfer.[7] Using the optically transparent thin-layer
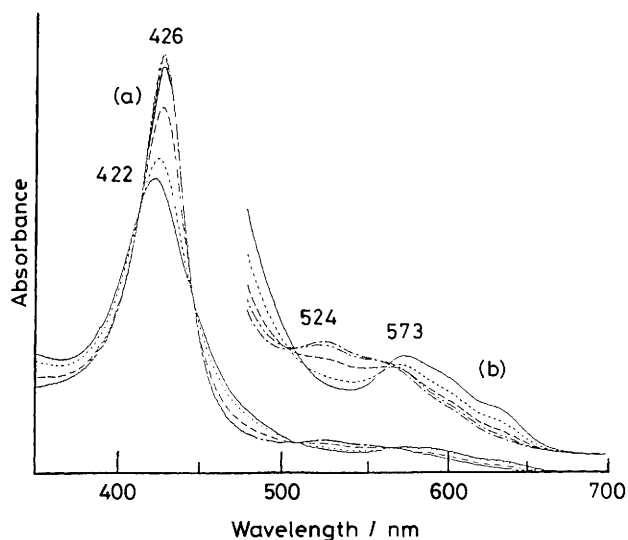
Figure 1. Thin-layer spectra of (a) 7.5×10^{-5} M and (b) 1.9×10^{-4} M Fe^{III}TMPyP at different electrode potentials in pH 9.0 aqueous solution. Reference electrode: Ag/AgCl (sat'd KCl). $E_{appl.}$ = 0.70, 0.80 (— · —); 0.65 (—··—); 0.60 (– – –); 0.55 (· · ·); 0.45 (——) V vs. Ag/AgCl.
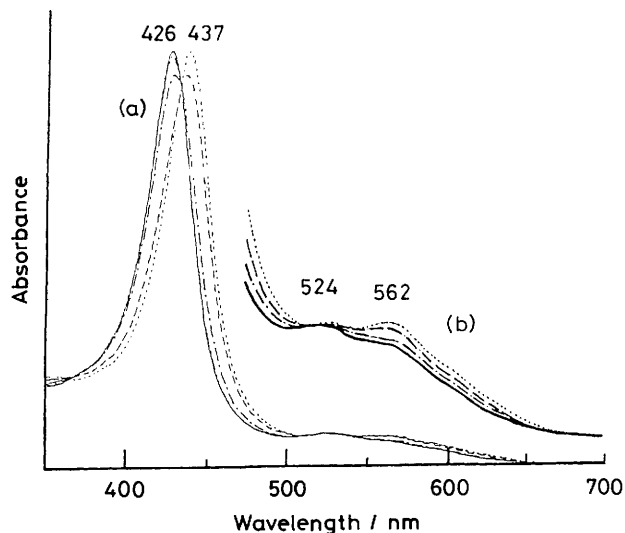

Figure 2. Spectral change of (a) 7.5×10^{-5} M and (b) 1.9×10^{-4} M O=Fe^{IV}TMPyP in different pH solutions. pH = 12.0 (· · ·); 11.0 (– – –); 10.0 (— · —); 8.0, 9.0 (——).

electrochemical (Ottle) method,[8] the thermodynamic potential as well as the number of electrons transferred in the oxidation reaction[9] can be obtained.

Figure 1 shows the spectral change of FeTMPyP at different potentials in pH 9.0 aqueous solution. Fe^{III}TMPyP exhibits absorption peaks at 422, 573, and 590 nm, while the oxidized form absorbs at 426, 524, and 547 nm. There are clean isosbestic points at 413, 446, 508, and 568 nm. The formal potential is +0.58 V (vs. Ag/AgCl) at pH 9.0 according to the literature.[9] The iron porphyrin is stable to repetitive potential steps at +0.40 and +0.80 V.

The pK_{a1} and pK_{a2} of Fe^{III}TMPyP are 5.5 and 11.8 respectively,[10] and the dimerization constant[11,12] K_D is 2×10^3
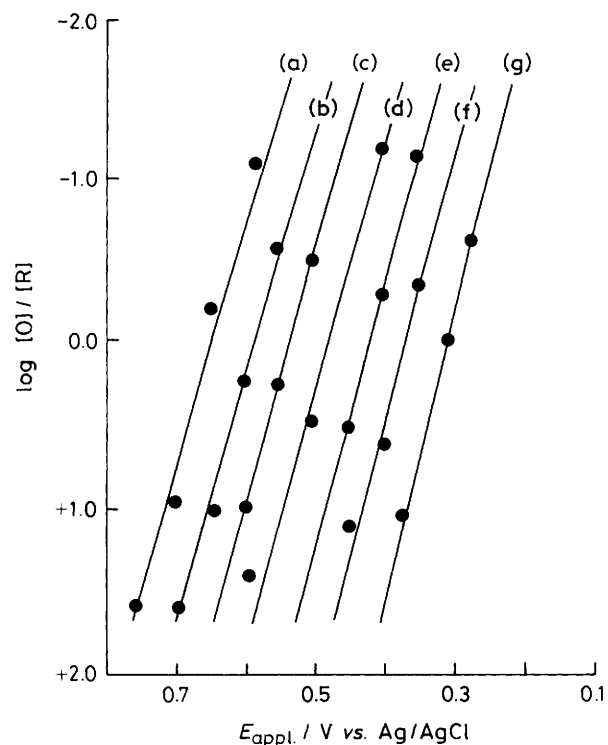
Figure 3. Plot of log [O]/[R] vs. $E_{appl.}$ in various pH solutions. [O] = [O=Fe^{IV}TMPyP]; [R] = [Fe^{III}TMPyP]. The calculation method used is shown in ref. 9. pH = (a) 8.0, (b) 9.0, (c) 10.0, (d) 11.0, (e) 11.5, (f) 12.0, (g) 13.0.

mol^{-1} dm^3, equation (1). For a pH 9.0 solution of 7.5×10^{-5} and 1.9×10^{-4} M Fe^{III}TMPyP, the dimer ratios are estimated to be 14 and 32%, respectively. The absorption spectrum of the μ-oxo-dimer appears not to interfere with the spectral change in the electro-oxidation process. This can be explained in several ways. Firstly, the small ratio of the μ-oxo-dimer and the slight difference of its absorption spectrum from that of the monomer probably cause negligible effects. Secondly, during bulk electrolysis at a certain potential, the consumption of (OH)Fe^{III}TMPyP will perturb the dynamic equilibrium between the monomer and dimer. The consequence would be dissociation of the dimer to give the monomer.

$$2 \, (OH)Fe^{III}TMPyP \xrightleftharpoons{K_D} TMPyPFe^{III}\text{-}O\text{-}Fe^{III}TMPyP + H_2O \tag{1}$$

Figure 2 shows the spectral change of Fe^{IV}TMPyP at different pH values. The absorbances at 426 and 524 nm in pH 8.0 solution decrease as pH increases, while those at 437 and 562 nm increase. There are isosbestic points at 432 and 523 nm. The spectral change from pH 8.0 to 12.0 indicates that the pK_a of the oxidized form is 10.5 by the spectrophotometric method.[5]

A plot of log [O]/[R] vs. $E_{appl.}$ at various pH values[9] is shown in Figure 3. According to the Nernst equation (2), the slope of approximately 60 mV/(log [O]/[R]) indicates that the number of electrons transferred, n, is 1.0. Hester et al.[13] reported the chemical oxidation of Fe^{III}TMPyP in pH 9 solution, the reaction being monitored by transient resonance Raman spectroscopy. A transient intermediate exhibits a new band at 812 cm^{-1}, indicating the existence of O=Fe^{IV}TMPyP. It is known that porphyrin ring oxidation would cause nucleophilic attack by hydroxide ion and then the destruction

of the porphyrin.[6] Thus, it is conceivable that the iron(III) centre is oxidized to iron(IV).

$$E_{appl.} = E^{o\prime} + (RT/nF)\log [O]/[R] \qquad (2)$$

The intercept (log $[O]/[R]$ = 0) corresponds to the $E^{o\prime}$. In pH <10.5 and pH > 11.8 regions, the $E^{o\prime}$ vs. pH plot exhibits a slope of 58 mV/pH, which indicates that one proton is transferred in the redox reaction. In the 10.5 < pH < 11.8 region, however, the slope is approximately 110 mV/pH, indicative of two proton transfer to achieve one electron transfer. The oxidative chemistry of $Mn^{III}TMPyP$ involving proton transfer has been reported[14] and the formation of $O=Mn^{IV}TMPyP$ has been identified by resonance Raman spectroscopy.[15] The results show that the oxidative chemistry of $Fe^{III}TMPyP$ is very similar to that of $Mn^{III}TMPyP$ in aqueous media. Thus, the oxidation of $Fe^{III}TMPyP$ involves several species depending on the pH value of the aqueous solution, equations (3)—(5).

The spectroelectrochemical results have established the presence of the stable iron(IV) porphyrin species in aqueous
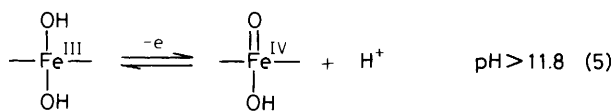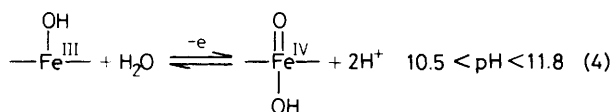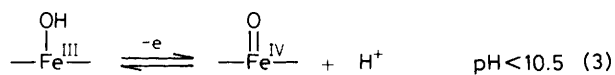
solution at room temperature. The acid-form/base-form equilibrium is also of interest in connection with heme-containing enzymes.

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