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The Redox Potential of a Synthetic Fe_4S_4 Cluster. Protonation/Deprotonation Equilibria of the Oxidized and Reduced Species

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The redox potential of $[Fe_4S_4(S\text{-}\underline{p}\text{-}C_6H_4C_8H_{17}\text{-}\underline{n})_4]^{2-}$ in an aqueous poly-α-dimethylamino-ε-capramide solution is shifted by -55 mV/pH in the pH range 6.0 to 8.5 at 4 °C, suggesting that not only the oxidized but also reduced forms of the cluster undergo protonation/deprotonation equilibria. The spread of the redox potential of the cluster in the present study covers most of the redox potentials of 4-Fe ferredoxins reported so far.

Iron-sulfur proteins are known to function as an electron transfer catalyst in various biological redox reactions such as nitrate reduction, CO_2- and N_2-fixation, H_2-evolution, and so on.1) Of various Fe-S proteins, low potential 4-Fe ferredoxins exhibit the redox potentials in a relatively limited range (-0.52 - -0.73 V <u>vs</u>. SCE) around pH 7.0.2) Proton concentrations, however, give complicated effects on the redox potentials of those proteins; some of which display a shift -60 mV/pH at ambient temperature,3) while others exhibit slight dependence of the redox potentials on pH (0 - -24 mV/pH).4) This letter reports the pH dependence of the redox potential of a synthetic Fe_4S_4 cluster, $[Fe_4S_4(S\text{-}\underline{p}\text{-}C_6H_4C_8H_{17}\text{-}\underline{n})_4]^{2-}$ ($[4\text{-}Fe]^{2-}$), which may be interpreted in terms of protonation/deprotonation equilibria not only of the oxidized but also of the reduced clusters solubilized in an aqueous poly-α-dimethylamino-ε-capramide (PDACA) solution.

The tetrabutylammonium salt of $[4\text{-}Fe]^{2-}$ was prepared according to the literature.[5)] PDACA supplied by Toray Co. Ltd. was purified by dialysis. An aqueous PDACA solution of $[4\text{-Fe}]^{2-}$ was prepared by adding a DMF (0.7 cm^3) solution of $(Bu^n{}_4N)_2[4\text{-Fe}]$ (17 mg, 10 μmol) to an H_3PO_4-NaOH buffer solution (0.1 mol/dm^3, 30 cm^3) containing PDACA (0.1 g). The cyclic voltammograms were obtained by the use of a hanging mercury drop electrode (HMDE) (Metrohm E-410) in water (pH 4.5 - 10.5) at 4 °C after a fresh mercury drop had been maintained at -0.30 V vs. SCE for 2 min.

The cyclic voltammogram of $[4\text{-Fe}]^{2-}$ solubilized in an aqueous PDACA solution at pH 6.3 shows a pair of cathodic and anodic waves of the $[4\text{-Fe}]^{2-/3-}$ couple at -0.56 and -0.52 V vs. SCE, respectively, as shown in Fig. 1. A large cathodic peak current compared with an anodic one may result from a stronger adsorption of $[4\text{-Fe}]^{2-}$ to the surface of an HMDE than the adsorption of $[4\text{-Fe}]^{3-}$ associated with the anodic peak current,[6)] as reported previously.[5)] The peak potentials of the cathodic and anodic waves are both shifted negatively with increasing the pH value in the range 6.0 to 8.5. The E_{av} values calculated from the average of the cathodic and anodic peak potentials of the redox couple[7)] at various pH are depicted in Fig. 2, which shows a slope -55 mV/pH in the pH range 6.0 to 8.5, whereas E_{av} is almost

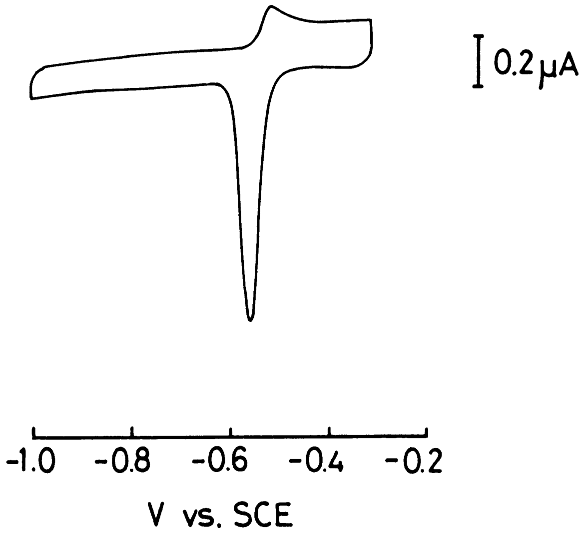


Fig. 1. Cyclic voltammogram of $[4\text{-Fe}]^{2-}$ (0.32 $mmol/dm^3$) in an aqueous PDACA solution at pH 6.3; HMDE (0.018 cm^2) at 200 mV/s.

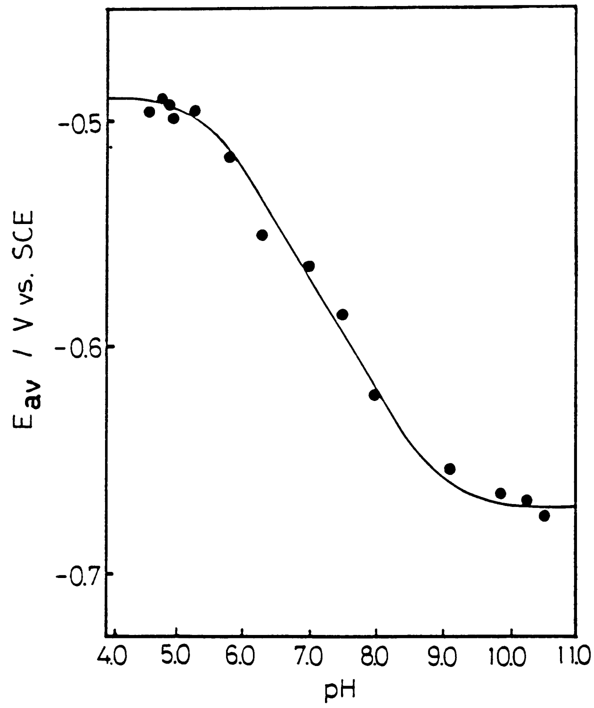
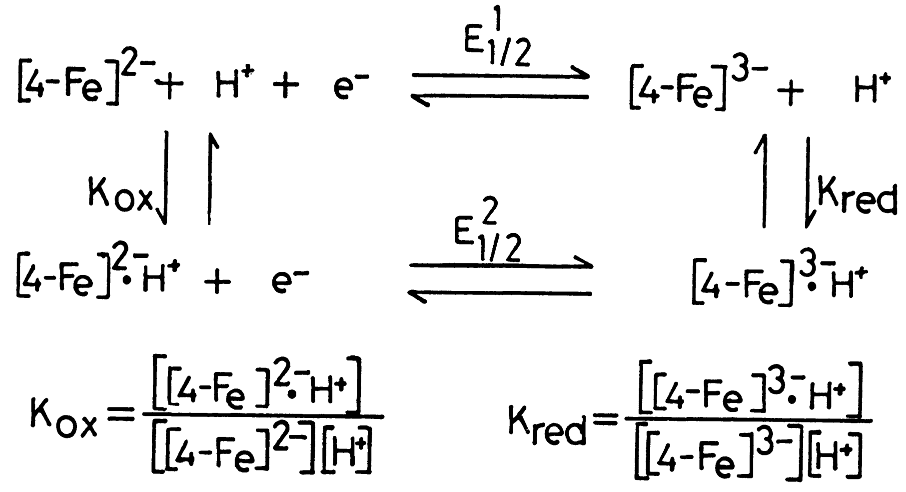


Fig. 2. The E_{av} value of the $[4\text{-Fe}]^{2-/3-}$ redox couple at various pH and a simulation curve under the assumption that $K_{ox} = 4.0 \times 10^5$ and $K_{red} = 7.9 \times 10^8$.



Scheme 1.

independent of the pH values not only lower than 5.0 but also higher than 9.5. Such a characteristic pH dependence of the E_{av} value may be explained in terms of protonation/deprotonation equilibria of the oxidized and reduced clusters, $[4\text{-Fe}]^{2-}$ and $[4\text{-Fe}]^{3-}$, solubilized in aqueous PDACA solutions, as represented in Scheme 1, where K_{ox} and K_{red} are the equilibrium constants for the protonation reactions to $[4\text{-Fe}]^{2-}$ and $[4\text{-Fe}]^{3-}$, respectively, and $E^1{}_{1/2}$ and $E^2{}_{1/2}$ are the half-wave potentials of the redox reactions of completely deprotonated and protonated species, respectively. The half-wave potential $E_{1/2}$ for the overall electrode reaction, $[4\text{-Fe}]^{2-} \rightleftharpoons [4\text{-Fe}]^{3-}$, can be expressed by Eq. 1 or 2,[8]

$$E_{1/2} = E^1{}_{1/2} + \frac{RT}{F}\ln\frac{1 + K_{red}[H^+]}{1 + K_{ox}[H^+]} \qquad (1)$$

$$E_{1/2} = E^2{}_{1/2} - \frac{RT}{F}\ln\frac{K_{red}}{K_{ox}}\frac{1 + K_{ox}[H^+]}{1 + K_{red}[H^+]} \qquad (2)$$

where R, T, and F are the gas constant, temperature, the Fraday constant, respectively. In view of the result that E_{av} is shifted anodically with increasing the proton concentration (Fig. 2), K_{red} should be larger than K_{ox} in Eq. 1. Therefore, $E_{1/2}$ approaches to the $E^1{}_{1/2}$ value in Eq. 1 or the $E^2{}_{1/2}$ value in Eq. 2 under the proton concentrations being $K_{red}[H^+] << 1$ or $K_{ox}[H^+] >> 1$. Thus, the $E^1{}_{1/2}$ and $E^2{}_{1/2}$ values correspond to E_{av} of the $[4\text{-Fe}]^{2-/3-}$ couple at higher than 9.5 and lower pH than 5.0 (Fig. 2), respectively, where E_{av} is independent of pH. The $E_{1/2}$ values at various proton concentrations calculated from Eq. 1 or 2 under the assumption that K_{ox} and K_{red} are 4.0 x 10^5 and 7.9 x 10^8 mol^{-1} dm^3, respectively,[9)] gave an excellent fit to the E_{av} values of $[4\text{-Fe}]^{2-}$ at various pH, as shown in a solid line in Fig. 2, which clearly shows that the slope of the line continuously changes from 0 to -55 mV/pH in the pH range 4.5 to 10.5. Thus, the protonation/deprotonation equilibria of the oxidized and reduced forms of the cluster adsorbed on an HMDE in an aqueous PDACA solution may well explain the pH dependence of the redox potentials of 4-Fe ferredoxins as well. In addition, the variation of E_{av} with pH in the present study covers most of the redox potentials of 4-Fe ferredoxins reported so far.

References

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6) Neither cathodic nor anodic peak due to the $[4\text{-Fe}]^{2-/3-}$ redox couple was observed when a glassy carbon electrode was used in place of an HMDE.

7) The E_{av} values are essentially constant ($\pm$10 mV) irrespective of the sweep rate from 50 to 500 mV/s.

8) a) P. L. Dutton and D. F. Wilson, Biochim. Biophys. Acta, 346, 165 (1974); b) R. S. Magliozzo, B. A. McIntosh, and W. V. Sweeny, J. Biol. Chem., 257, 3506 (1982).

9) A similar treatment for the redox potential of clostridium pasteurianum ferredoxin has been reported, though neither pK_{red} nor $E^1{}_{1/2}$ has been determined experimentally.[8b)]

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