Protonation on the Core Sites of $[Fe_4X_4(Y-n-C_{12}H_{25})_4]^{2-}$ (X, Y = S and Se) in Aqueous Micellar Solutions

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The pK_a values of $[Fe_4S_4(Y-n-C_{12}H_{25})_4]^{2-}$ and $[Fe_4Se_4(Y-n-C_{12}H_{25})_4]^{2-}$ (Y = S and Se) in non-ionic micellar solutions have been determined as 8.9—9.1 and 7.7, respectively, suggesting that the protonation of the clusters takes place on the sulphur or selenium atoms of the Fe_4X_4 core (X = S and Se) rather than on the terminal alkyl-thiolate and -selenolate ligands.

Iron–sulphur proteins function as electron transfer catalysts in various biological redox reactions,[1] although 4-Fe ferredoxins with hydrophobic environments are known to have stable hydrogen bonds. These are between the amide hydrogen of the peptide chain and a sulphur atom either of Fe_4S_4 core or of the terminal cysteine residue ligated on the iron atoms.[2] Recently, we have demonstrated that synthetic Fe_4S_4 clusters surrounded by hydrophobic substituents undergo protonation reactions in aqueous micellar solutions, and the protonated and deprotonated clusters exist as an equilibrium mixture below pH 10.[3] However the protonation site of the Fe_4S_4 cluster has not been proved. In connection with the hydrogen bonding involved in 4-Fe ferredoxins, this communication

reports the site of protonation for the series $[Fe_4X_4(Y-n-C_{12}H_{25})_4]^{2-}$ (X, Y = S, S; S, Se; Se, S; Se, Se) in non-ionic micellar solutions.

The tetrabutylammonium salts of $[Fe_4X_4(S-n-C_{12}H_{25})_4]^{2-}$ (X = S and Se) were synthesized in a manner similar to $[Fe_4X_4(SPh)_4]^{2-}$ (X = S and Se).[4,5] The same salts of the dodecylselenolate ligated cluster, $[Fe_4X_4(Se-n-C_{12}H_{25})_4]^{2-}$ (X = S and Se), were prepared by the ligand substitution reaction[6] of the corresponding $[Fe_4X_4(S-t-C_4H_9)_4]^{2-}$ (X = S and Se) with $n-C_{12}H_{25}SeH$.† The analytical values obtained

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† $n-C_{12}H_{25}SeH$ was prepared by the reaction of $n-C_{12}H_{25}Br$ with $(NH_2)_2C=Se$, being similar to the synthesis of $n-C_{12}H_{25}SH$.
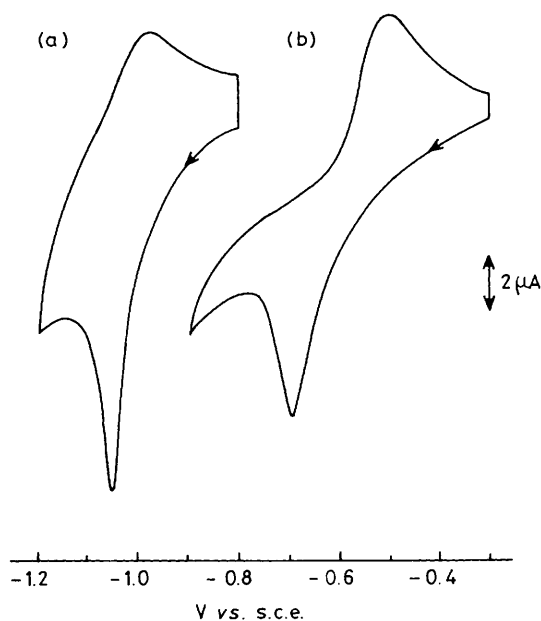
Figure 1. Cyclic voltammograms of $[Fe_4S_4(S\text{-}n\text{-}C_{12}H_{25})_4]^{2-}$ in DMF (a) and in an aqueous Triton X-100 solution (b); scan rate 0.2 V s^{-1}.

Figure 2. Plots of the $E_{1/2}$ values of the $[Fe_4X_4(YR)_4]^{2-/3-}$ redox couples in aqueous Triton X-100 micellar solutions vs. pH at 20 °C; X, Y = S, S (O); S, Se (●); Se, S (△); Se, Se (□); R = n-C$_{12}$H$_{25}$.

for all the clusters are in good agreement with the calculated values. An aqueous micellar solution of $[Fe_4X_4(Y\text{-}n\text{-}C_{12}H_{25})_4]^{2-}$ (X, Y = S and Se) was prepared by the addition of a dimethylformamide (DMF) solution (1 cm^3) of the cluster (10 μmol) to H$_3$PO$_4$–NaOH buffer solutions (25 cm^3, pH 5—11) containing Triton X-100 [(3.0—5.0) × 10^{-2} cm^3].

Figure 1 shows the cyclic voltammograms of $[Fe_4S_4(S\text{-}n\text{-}C_{12}H_{25})_4]^{2-}$ in DMF and in an aqueous micellar solution (pH 7.0) containing (n-C$_4$H$_9$)$_4$NClO$_4$ and H$_3$PO$_4$–NaOH as supporting electrolytes, respectively, using an Hg working electrode at 20 °C. The $E_{1/2}$ values approximated by an average of the cathodic and anodic peak potentials of the $[Fe_4S_4(S\text{-}n\text{-}C_{12}H_{25})_4]^{2-/3-}$ redox couple were −1.02 V in DMF and −0.59 V [vs. saturated calomel electrode (s.c.e.)] in an aqueous micellar solution, the latter of which is compared with the redox potentials of 4-Fe (−0.52 to −0.67 V vs. s.c.e.) and 8-Fe (−0.65 to −0.73 V vs. s.c.e.)[7] ferredoxins in water. Similarly, the $E_{1/2}$ values of the analogous $[Fe_4X_4(Y\text{-}n\text{-}C_{12}H_{25})_4]^{2-}$ (X, Y = S, Se; Se, S; Se, Se) in aqueous micellar solutions at pH 7.0 are shifted cathodically by ca. 300 mV in DMF.‡

The proton concentration of the solution has a great influence on the $E_{1/2}$ values of the present clusters, as shown in Figure 2, which confirms that the $E_{1/2}$ values of $[Fe_4S_4(Y\text{-}n\text{-}C_{12}H_{25})_4]^{2-}$ and $[Fe_4Se_4(Y\text{-}n\text{-}C_{12}H_{25})_4]^{2-}$ (Y = S and Se) are shifted by −55 mV/pH, while they remain constant for pH greater than ca. 9.0 for the Fe$_4$S$_4$ clusters and 7.7 for the Fe$_4$Se$_4$ clusters. The pH dependence of $E_{1/2}$ values with the slope −55 mV/pH for all the clusters, $[Fe_4X_4(Y\text{-}n\text{-}C_{12}H_{25})_4]^{2-}$ (X, Y = S and Se), may be explained in terms of participation of a single proton in the redox reactions of those clusters, as discussed in the redox reaction of $[Fe_4S_4(SC_6H_4\text{-}p\text{-}n\text{-}C_8H_{17})_4]^{2-/3-}$ in an aqueous micellar solution.[3] Thus, the

protonated and deprotonated species exist as an equilibrium mixture in aqueous micellar solutions below pH ca. 9.0 and 7.7 for the Fe$_4$S$_4$ and Fe$_4$Se$_4$ clusters, respectively.§ The difference in pK_a values (8.9—9.1 and 7.7 for the clusters with the Fe$_4$S$_4$ and Fe$_4$Se$_4$ cores, respectively) appears mainly to come from the difference between the sulphur and selenium atoms of the Fe$_4$X$_4$ core (X = S and Se), whereas the fact that S or Se is present in the terminal ligands hardly influences the pK_a values. This result reveals that the protonation of the present synthetic clusters takes place at the sulphur or selenium atoms of the Fe$_4$X$_4$ core (X = S and Se).

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‡ The $E_{1/2}$ values of $[Fe_4X_4(Y\text{-}n\text{-}C_{12}H_{25})_4]^{2-/3-}$ (X, Y = S and Se) redox couples in micellar solutions are −0.89 V for X, Y = S, Se; −0.85 V for X, Y = Se, S; and −0.91 V (vs. s.c.e.) for X, Y = Se, Se, whereas those in DMF are −1.23 V for X, Y = S, Se; −1.08 V for X, Y = Se, S; and −1.15 V (vs. s.c.e.) for X, Y = Se, Se.
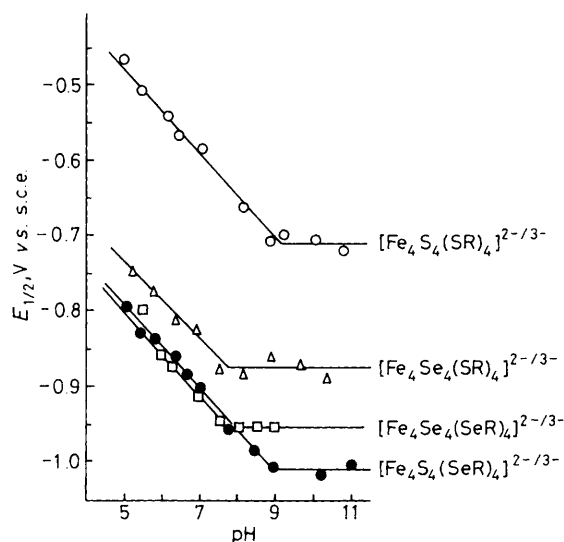
§ Although Fe$_4$S$_4$ clusters with alkylthiolate ligands such as $[Fe_4S_4(SC_4H_9)_4]^{2-}$ and $[Fe_4S_4(SCH_2CH_2CO_2^-)_4]^{6-}$ are reported to undergo hydrolysis reactions in N-methylpyrrolidinone–H$_2$O mixture,[8,9] the present clusters, $[Fe_4X_4(Y\text{-}n\text{-}C_{12}H_{25})_4]^{2-}$ (X, Y = S and Se), solubilized in aqueous micellar solutions, are stable under a N$_2$ atmosphere for at least 4 h, as confirmed by monitoring the visible spectra.