Redox Potential of Fe_4S_4 Cluster in Hydrophobic and Hydrophilic Spheres

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The redox behavior of the $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-/3-}$ couple was examined not only in a CH_2Cl_2 solution of a CH_2Cl_2/H_2O two phase system but also in the absence and presence of Triton X-100 in H_2O to elucidate the solvent effect of water on the redox potential of the cluster. Protonation of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{3-}$ takes place in those media, and protonated and unprotonated clusters exist as an equilibrium mixture. Although the redox potential of the cluster is hardly affected by the pK_a value, it is largely influenced by a thickness of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ adsorbed on a surface of an electrode in water. The $E_{1/2}$ value of the cluster in a near monomolecular layer on the electrode exhibits a pronounced anodic shift compared with that in CH_2Cl_2 and falls in the range of that of 4Fe- and 8Fe-ferredoxins. On the other hand, the cluster in the multimolecular layer does not show such an anodic shift of the $E_{1/2}$ value in water.

A variety of Fe_4S_4 clusters have been prepared[1] as a model of the active center of iron-sulfur proteins, which play key roles as electron-transfer catalysts in various biological redox reactions such as photosynthesis,[2] N_2-fixation,[3] NO_3^- reduction.[4] The redox potentials of synthetic Fe_4S_4 clusters in organic solvents obey the Hammet σ_p and Taft σ^* values of terminal thiolate ligands.[5] Water, however, gives a serious effect on the redox potentials of the clusters, since water soluble Fe_4S_4 clusters in the presence of excess of free thiolate ligands (due to an instability of water soluble Fe_4S_4 clusters in water) show a positive potential shift of the redox potentials by 250—400 mV in water compared with those in organic solvents.[6] A positive potential shift of $E_{1/2}$ (60—120 mV) of *Clostridium pasteurianum* ferredoxin in H_2O containing of 0—40 vol% Me_2SO_4, where the protein adopts its normal tertiary structure, compared with a synthetic Fe_4S_4 cluster ligated with cysteine in the same medium, therefore, has been ascribed to the tertiary structure of proteins.[6] We have reported that synthetic Fe_4S_4 clusters are protected from hydrolysis in aqueous lecithin vesicle[7] and micellar solutions,[8] and the redox potentials of the clusters in those media are essentially consistent with those of 4Fe- and 8Fe-ferredoxins. The redox potentials of synthetic Fe_4S_4 clusters as well as ferredoxins, therefore, are considered to be largely influenced by hydrophobic spheres in water. To elucidate the effect of hydrophobic spheres on the redox potential of a Fe_4S_4 cluster in water, the redox behavior of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ was examined not only in a CH_2Cl_2 solution of a CH_2Cl_2/H_2O two phase system but also in the absence and presence of Triton X-100 micellar solution using a glassy carbon and an Hg electrode.

Experimental

General Procedure and Materials. All manipulations were carried out under N_2 atmosphere. Commercially available guaranteed reagent grade of *p*- *t*-butylbenezenethiol was used without further purification. $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ was prepared according to the literature.[9]

Cyclic Voltammetry of the Cluster in a CH_2Cl_2/H_2O Two Phase System. An aqueous H_3PO_4-NaOH buffer (0.1 mol dm^{-3}, 20 cm^3) solution containing Bu_4NBr (1.8 mmol) was poured in a CH_2Cl_2 solution (20 cm^3) containing $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ (20 mg, 12 μmol) and Bu_4NBr (0.6 g, 1.8 mmol), and the mixture was stirred by bubbling N_2 for several minutes. Then, the cell was allowed to stand until the CH_2Cl_2 and H_2O phases were completely separated. The pH of the H_2O phase was adjusted by addition of a small amount of either aqueous NaOH or H_3PO_4 solution (0.1 mol dm^{-3}) to the H_2O phase, followed by stirring the mixture by the same method, and measured with a Toa Electronics pH meter HM-7B. The cyclic voltammograms of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ dissolved in the CH_2Cl_2 phase and adsorbed on a surface of Hg were obtained by using a Yanaco glassy carbon disk electrode GC-2p and Metrohm hanging mercury drop electrode, respectively. When the HMDE was used as a working electrode, voltage scan was started after the surface of a mercury drop (0.0187 cm^2) had been exposed to the aqueous phase. The working electrode, a Pt auxiliary electrode, and a luggin capillary of a reference electrode were immersed into the same phase either a CH_2Cl_2 or H_2O phase.

Solubilization of the Cluster in an Aqueous Triton X-100 Micellar Solution. A DMF (1.0 cm^3) solution of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ (12 μmol) was added to a stirred aqueous solution (25 cm^3, pH 6—10) containing NaOH-H_3PO_4 (0.1 mol dm^{-3}) and Triton X-100 (0.05 mol dm^{-3}).

Preparation of a Cluster Modified Glassy Carbon and Hg Amalgamated Au Plate Electrode. A given amount of a CH_3CN solution of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ (1.0 mmol dm^{-3}) was dropped to the surface of a glassy carbon[10] or an Hg amalgamated Au plate (1.0 cm^3) by syringe techniques, and then dried under N_2 atmosphere.

Results and Discussion

Redox Behavior of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ in CH_2Cl_2/H_2O Two Phase System. The cyclic voltammogram (CV) of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ using a glassy carbon disk electrode (GC) shows a cathodic

and an anodic wave of the (2−/3−) redox couple at E_{pc}=−1.03 and E_{pa}=−0.90 V vs. SCE at a sweep rate 10 mV s^{-1} in dry CH_2Cl_2. Those redox waves are also observed at E_{pc}=−0.97 and E_{pa}=−0.89 V in a CH_2Cl_2 solution of a CH_2Cl_2/H_2O (pH=10.06) two phase system (Fig. 1a). Thus, H_2O in the CH_2Cl_2 phase causes a slight potential shift of the $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-/3-}$ redox couple. The peak currents of those redox waves in the wet CH_2Cl_2 phase were proportional to one-half order with respect to the sweep rate in the range of 10—300 mV s^{-1}. In addition, the electronic absorption spectrum of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ in wet CH_2Cl_2 did not show an appreciable change for 4 h. These results indicate that $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ stably exists in wet CH_2Cl_2 and undergoes a redox reaction in that medium. The redox potentials of Fe_4S_4 clusters solubilized in aqueous micellar solutions have been shown to be largely controlled by proton concentrations in bulk water.[8] The proton concentration in the CH_2Cl_2 phase of the CH_2Cl_2/H_2O system may also be equilibriated with that in the H_2O phase, as similar to the equilibrium between hydrophobic spheres of micelles and bulk water. Figure 2 shows the $E_{1/2}$ value ($E_{1/2}=(E_{pa}+E_{pc})/2$) of the $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-/3-}$ couple in the CH_2Cl_2 solution of the CH_2Cl_2/H_2O system at a sweep rate 10 mV s^{-1} at various pH of the H_2O phase. The $E_{1/2}$ value of the cluster in the CH_2Cl_2 solution is independent on pH of the H_2O phase in the pH range higher than 7.0, while shifted by −60 mV pH^{-1} in the pH lower than 7.0. This result clearly indicates that one proton participates in the $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-/3-}$ redox reaction[7,8] in the CH_2Cl_2 solution when pH of the H_2O phase is lower than 7.0, and protonated and unprotonated $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{3-}$ exist as an equilibrium mixture. The break point at pH 7.0 in the plot of $E_{1/2}$ vs. pH (○ in Fig. 2), therefore, may be associated with an apparent proton dissociation constant (pK_a') of protonated $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{3-}$. Despite a significant difference in the proton concentrations between the CH_2Cl_2 and H_2O phases of the CH_2Cl_2/H_2O system, the present pK_a'=7.0 still falls in the pK_a range of iron-sulfur proteins reported so far (pK_a=6.8—8.9).[11]

An Hg electrode has been used for the measurement of the redox potential of iron-sulfur proteins by taking advantage of a strong affinity of sulfur for Hg.[12] Otherwise, a direct electron transfer between the Fe_4S_4 cores and an electrode is strongly inhibited by an adsorption of polypeptide chains on the electrode. The CV of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ in the CH_2Cl_2 solution of the CH_2Cl_2/H_2O system using a hanging mercury drop electrode (HMDE) exhibited a very strong cathodic current of the $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-/3-}$ redox couple maybe due to a strong adsorption of the cluster on the surface of the HMDE, and the anodic and cathodic peak potentials of the redox couple were not determined correctly. To decrease the amount of the cluster adsorbed on the Hg surface, the HMDE was drawn up to the H_2O phase from the CH_2Cl_2 solution of $(Bu_4N)_2[Fe_4S_4$-

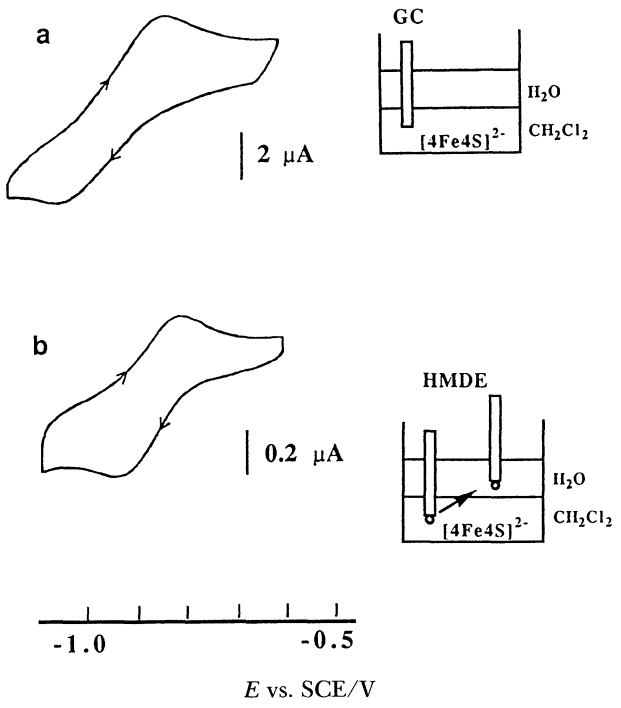

Fig. 1. Cyclic voltammograms of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ using a glassy carbon electrode in a CH_2Cl_2 solution (a) and an HMDE in an H_2O phase (b) of the CH_2Cl_2/H_2O (pH 10.06) system; sweep rate 10 mV s^{-1}.

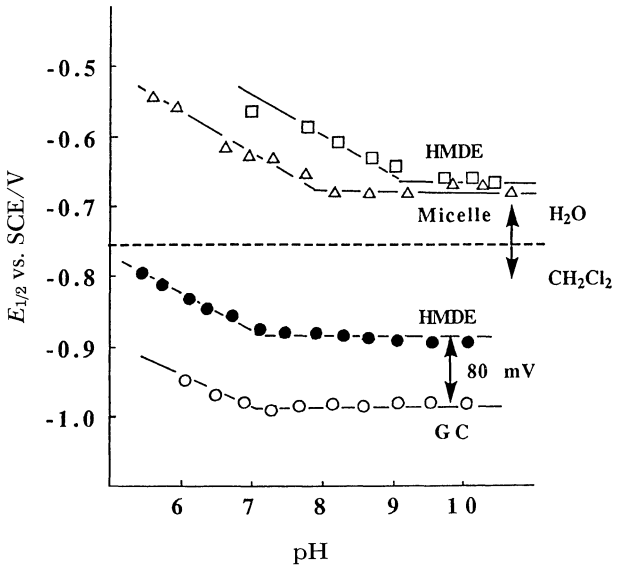

Fig. 2. $E_{1/2}$ values of the $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-/3-}$ redox couple in the CH_2Cl_2 solution of the CH_2Cl_2/H_2O system using GC (○) and HMDE (●), and in the absence (□) and presence of Triton X-100 (△) using HMDE.

$(SC_6H_4Bu^t(p\text{-}))_4]$ after dipping the top end of the electrode in the CH_2Cl_2 phase for less than one minute. Even after this procedure, the surface of the HMDE placed in the H_2O phase was covered with a drop of the CH_2Cl_2 solution of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$. The CV of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ in the CH_2Cl_2 drop in H_2O (pH=10.06) is depicted in Fig. 1b, which shows the (2−/3−) redox couple at E_{pc}=−0.93 and E_{pa}=−0.82 V at a sweep rate 10 mV s^{-1} (Fig. 1b). The $E_{1/2}$ value of the cluster in the CH_2Cl_2 drop on the HMDE against pH are also plotted in Fig. 2 (●). The $E_{1/2}$ value of the cluster in the CH_2Cl_2 drop on the HMDE in the H_2O phase is shifted to a positive potential by 80 mV compared with that determined by a GC electrode in the CH_2Cl_2 phase (○ and ● in Fig. 2). The 80 mV difference in two lines may result from an adsorption of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ on an Hg electrode, since an $E_{1/2}$ value of a synthetic Fe_4S_4 cluster undergoes a positive potential shift by 80 mV due to an adsorption on a surface of an Hg electrode.[7] Taking account of the adsorption energy of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ on Hg, the redox potential of the cluster in the CH_2Cl_2 drop in the H_2O phase may be essentially unchanged that in wet CH_2Cl_2. Furthermore, an agreement of the break points (pK_a') of the plots of pH vs. $E_{1/2}$ in the CH_2Cl_2 drop on the HMDE with that in the CH_2Cl_2 phase (○ and ● in Fig. 2) indicates that the proton concentration in the bulk CH_2Cl_2 phase is maintained in the CH_2Cl_2 drop on the HMDE in the H_2O phase.

Redox Reaction in Aqueous Phases. As described above, one proton participates in the $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-/3-}$ redox reaction in the CH_2Cl_2 solution of the CH_2Cl_2/H_2O system, and protonated and unprotonated $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{3-}$ exists as an equilibrium mixture. Comparison of the pK_a value of the protonated $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{3-}$ in wet CH_2Cl_2 with that in an aqueous micellar solution may afford an information about the solvent effect of water on the redox potential of the cluster. As an adsorption of the surfactant on a GC electrode[13] inhibited the electron transfer to $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ in an aqueous Triton X-100 micellar solution, the CV of the aqueous micellar solution of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ was obtained by using HMDE, as depicted in Fig. 3a. Two cathodic waves (E_{pc}=−0.84 and −0.69 V) and one anodic wave (E_{pa}=−0.64 V) were observed at pH 10.20 in the initial scan. The strong cathodic waves compared with the anodic one are indicative of the stronger adsorption of the (2−) state of the cluster on a surface of an Hg electrode than the (3−) one.[7,8] In the following sweep, the −0.84 V cathodic wave almost disappears, while the −0.69 V cathodic wave remains at the same potential with decreasing the peak current. In the micellar solution, the coulombs consumed in the cathodic wave are proportional to the number of the clusters adsorbed on the Hg electrode, since only the

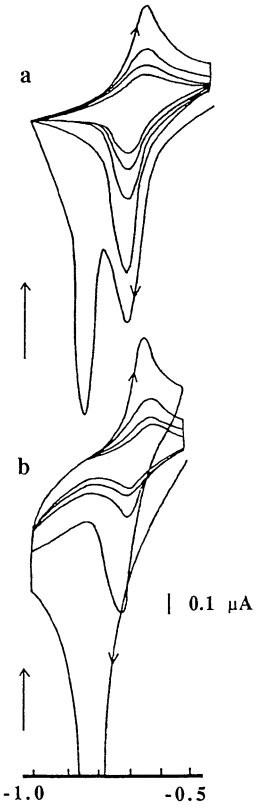

Fig. 3. Multi-sweep cyclic voltammograms of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ in an aqueous Triton X-100 micellar solution at pH 10.20 (a), and of [4Fe4S]/HMDE in H_2O at pH 10.00 (b); sweep rate 10 mV s^{-1}.

cluster adsorbed on the Hg electrode undergoes the one-electron redox reaction. Although the exact area of the −0.83 V cathodic wave in the initial scan could not be determined due to overlap with the −0.69 V cathodic wave, the surface concentration of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ on the HMDE in the second potential sweep could be evaluated from the area of the −0.69 V cathodic wave. On the basis of the surface area of the HMDE (0.0187 cm^2), the surface concentration of the cluster calculated from the wave was 2.9×10^{-10} mol cm^{-2}. This value is somewhat larger than the surface concentration of the monomolecular layer of $[Fe_4S_4(SC_6H_4C_8H_{17}{}^n(p\text{-}))_4]^{2-}$ adsorbed on an Hg electrode (1.6×10^{-10} mol cm^{-2}).[7] The strong −0.83 V cathodic wave observed only in the initial scan, therefore, may be assigned to the redox couple resulting from a multimolecular adsorption of the cluster on the HMDE. The disappearance of the −0.83 V cathodic wave in the second sweep, therefore, may be caused by desorption of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{3-}$ due to not only a stronger coulomb repulsion of the neighboring (3−) state of the clusters but also a migration of the counter ion into the multimolecular layer of the cluster formed on a fluid Hg surface to

maintain the charge neutrality (vide infra). The $E_{1/2}$ value of the cluster adsorbed on the HMDE in aqueous Triton X-100 micellar solutions, therefore, was employed after both E_{pc} and E_{pa} values become constant in the multiscanning CV (usually the third or fourth sweep). The plot of $E_{1/2}$ of the cluster vs. pH of the aqueous micellar solution (△ in Fig. 2) also clearly shows the break point at pH 7.8 due to the pK_a of the protonated $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{3-}$. The shift of the p$K_a$ 7.8 in the micellar solution from 7.0 in wet CH_2Cl_2 suggests that protonation of the cluster in the former takes place more easily than in the latter. It is also worthy to note that the $E_{1/2}$ value in the aqueous micellar solution is shifted to positive potentials about by 200 mV compared with that in the CH_2Cl_2 solution, and falls in the range of the redox potentials of 4Fe- and 8Fe-ferredoxins (−0.52 to −0.73 V vs. SCE around pH 7.0).[6]

The redox behavior of the cluster on the HMDE was measured in the absence of Triton X-100 to elucidate the effects of hydrophobic spheres of micelles on the redox potential of the cluster in H_2O. The present cluster is not soluble in H_2O. A cluster modified HMDE ([4Fe4S]/HMDE), therefore, was prepared by dipping the HMDE in a dry CH_2Cl_2 solution of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ (0.40 mmol dm^{-3}) for less than one minute, followed by drying under N_2 stream. The [4Fe4S]/HMDE displays a very strong cathodic wave at E_{pc}=−0.83 V and an anodic wave at E_{pc}=−0.64 V in the initial scan in H_2O at pH 10.00 (Fig. 3b). As similar to the aqueous micellar solution, the −0.83 V cathodic wave disappears in the second scan, and a new cathodic wave is observed at −0.70 V with the surface concentration of 2.6×10^{-10} mol cm^{-2}. Thus, the very strong −0.83 V cathodic wave in the first scan is assigned to the multimolecular adsorption of the cluster on the Hg electrode. After the second potential sweep, the −0.70 V cathodic wave was slightly shifted to positive potentials with decreasing the peak current, and finally the constant value $E_{1/2}$=−0.65 V (E_{pc}=−0.66 V and E_{pa}=−0.63 V) was obtained. This result also indicates that the peak potential of the (2−/3−) redox couple is dependent on the thickness of the cluster adsorbed on the electrode (or the amount of the cluster adsorbed) and becomes a constant value when the thickness of the adsorbed cluster approaches to a monomolecular layer. The plot of the $E_{1/2}$ obtained after the constant value in H_2O against pH shows the pK_a 8.9, as depicted in Fig. 2 (□). Despite the difference in the pK_a of the cluster in the absence (8.9) and presence of the surfactant (7.8) in H_2O, the $E_{1/2}$ values at higher pH than their pK_a values are essentially consistent with each other (□ and △ in Fig. 2). This result indicates that hydrophobic spheres of micelles hardly affect the redox potential of the Fe_4S_4 cluster on an Hg electrode in H_2O.

Redox Reaction in Multi-Adsorption Layer in H_2O. We have reported that a $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ modified glassy carbon plate stably undergoes a redox reaction without desorption from the GG plate in water.[10] In accordance with this, the $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ (1×10^{-8}mol) modified GC plate ([4Fe4S]/GC, 1.0 cm^2) also shows a cathodic and anodic wave at E_{pc}=−1.14 and E_{pa}=−0.87 V in water at pH 10.04 (Fig. 4a). A strong cathodic current at potentials more negative than −1.2 V comes from H_2 evolution catalyzed by the reduced cluster,[10,14] and the pattern was unchanged in the multi-sweep CV for 30 min.[15] Although the peak separation between the cathodic and anodic waves of the [4Fe4S]/GC is fairly large compared with that of the [4Fe4S]/HMDE,[16] the $E_{1/2}$ value (−1.02 V vs. SCE) of the [4Fe4S]/GC at pH 10.04 is close to that in a dry CH_2Cl_2 solution obtained by a GC disk electrode rather than that of [4Fe4S]/HMDE in H_2O. Thus, the redox potential of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ aggregated on the GC plate[17] does not undergo a positive potential shift by water. This is quite contrast to the $E_{1/2}$ value of the monomolecular layer of the [4Fe4S]/HMDE in water at pH 10.0 (□ in Fig. 2). To compare the redox behavior of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ modified GC plate with an Hg electrode in H_2O, a cluster modified Hg amalgamated Au plate electrode ([4Fe4S]/HgAu) was prepared by addition of CH_3CN solution of $(Bu_4N)_2[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]$ on the surface of an Hg amalgamated Au plate (1×10^{-8} mol, 1.0 cm^2),[17] followed by drying under N_2 atmosphere. The [4Fe4S]/HgAu exhibits a cathodic and an anodic waves at

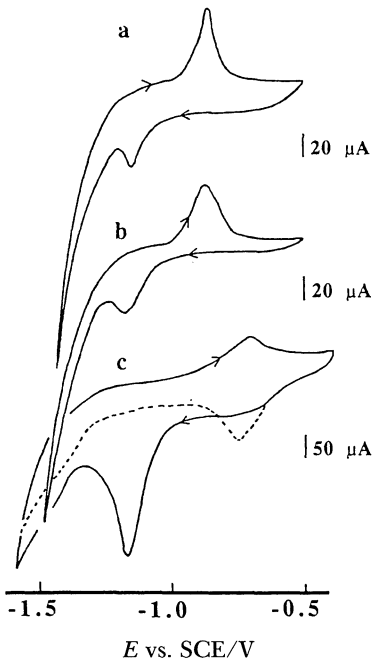

Fig. 4. Cyclic voltammograms of [4Fe4S]/GC at 10 mV s^{-1} (a) in H_2O (pH 10.04), and [4Fe4S]/HgAu at 10 mV s^{-1} (b) and 100 mV s^{-1} (c) in H_2O (pH 10.06); a dotted line is the second potential sweep.

E_{pc}=−1.16 and E_{pa}=−0.87 V at the sweep rate 10 mV s^{-1} in H_2O at pH 10.06 (Fig. 4b). The amounts of the cluster calculated from the areas of the −1.16 V cathodic and the −0.87 anodic waves were 2.9×10^{-9} and 5.6×10^{-9} mol, respectively. The decrease in the coulombs consumed in the cathodic wave compared with that in the anodic one may be due to subsequent H_2 evolution catalyzed by the reduced cluster. Despite the disagreement of the peak currents of those waves, the peak potentials are almost completely consistent with those of the [4Fe4S]/GC at the same pH. On the other hand, the CV of the [4Fe4S]/HgAu affords a quite different pattern, when the sweep rate is increased to 100 mV s^{-1}; a strong cathodic wave and an anodic one are observed at E_{pc}=−1.16 and E_{pa}=−0.70 V in the initial potential sweep (a solid line in Fig. 4c). In the following potential sweep, the −1.16 V cathodic wave completely disappears, and a new cathodic wave appears at −0.76 V (a dotted line in Fig. 4c). It should be noticed that the redox waves at E_{pc}=−0.76 V and the E_{pa}=−0.70 V, which are observed in the second sweep, are close to those of the monomolecular layer of [4Fe4S]/HMDE. The marked difference in the CV of the voltage scanning at 10 and 100 mV s^{-1} may be explained by desorption of the cluster from the multimolecular layer on the surface of HgAu plate; the charge neutrality of the multimolecular layer of the cluster on the HgAu plate is maintained by the transport of the counter ion into and out of the contacting aqueous phase, so that a rapid transport of counter ion into the multimolecular layer of the cluster accelerates the detachment of the cluster from the layer to form a near monomolecular layer on the HgAu electrode. In accordance with this assumption that the amounts of the cluster on the HgAu plate[18] were determined as 5.6×10^{-9} and 5.4×10^{-10} mol from the areas of the −0.87 anodic wave of Fig. 4b (10 mV s^{-1}) and the −0.70 V one of Fig. 4c (100 mV s^{-1}), respectively.

The $E_{1/2}$ value of the near monomolecular layer of [4Fe4S]/HMDE and [4Fe4S]/HgAu is shifted to positive potentials in water, while that of the multimolecular layer of [4Fe4S]/HgAu and [4Fe4S]/GC in water is very close to the value in CH_2Cl_2. Thus, the influence of water on the redox potential of the Fe_4S_4 cluster in the multi- and monomolecular layer is quite different from each other. As similar to the monomolecular layer in H_2O, the redox potential of the cluster contacting with the H_2O phase (near the surface of the multimolecular layer) would undergo a pronounced solvent effect by water. On the other hand, a hydrophobicity of the terminal ligand $SC_6H_4Bu^t(p\text{-})$ of the Fe_4S_4 cluster may depress penetration of bulk water into the multimolecular layer, so that the redox potential of the cluster contacting electrode (at the bottom of the multimolecular layer) may be isolated from bulk water. This assumption suggests that the redox potential of the cluster in the multimolecular layer is largely dependent on the distance from the aqueous phase. The redox reaction of the cluster in the multimolecular layer may be caused by an electron self-exchange between neighboring oxidized and reduced clusters. In addition, the electron transfer between the electrode and the cluster takes place only in the first layer of the adsorption layer (contacted with the electrode), and then the electron is transferred successively to the surface of the multimolecular layer (Fig. 5a). Accordingly, the electrode can detect only the redox potential of the cluster contacted with the electrode. In harmony with this, a multisweep CV of the cluster of the multimolecular adsorption on Hg electrodes displays a positive potential shift of the $E_{1/2}$ value with decreasing the peak current by gradual desorption of the cluster, and reaches a constant value at the near monomolecular layer (Fig. 5b). The fact that the $E_{1/2}$ value of the multimolecular layer of the [4Fe4S]/GC and [4Fe4S]/HgAu in H_2O is close to that in a CH_2Cl_2 solution suggests that the effect of the aggregate of the cluster on the redox potential is essentially same as that of an organic solvent. It is, therefore, concluded that hydrophobic spheres around the Fe_4S_4 core in water do not cause an anodic shift of the redox potential of the cluster.

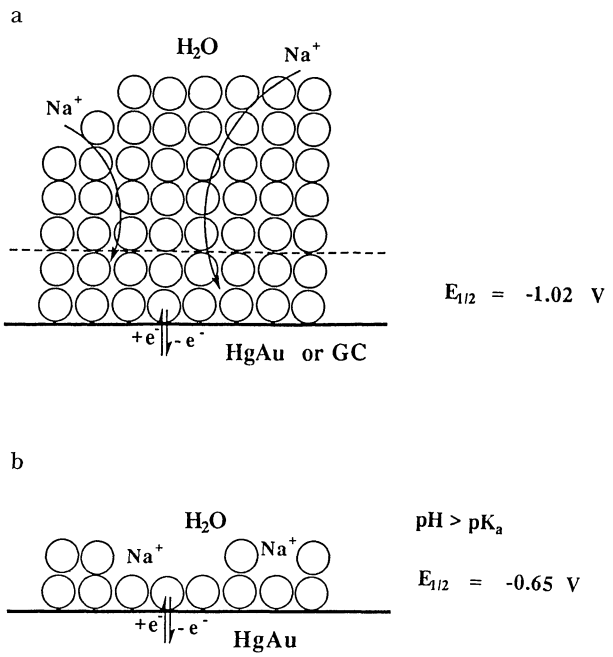

Fig. 5. Redox of Fe_4S_4 cluster in a multimolecular (a) and near monomolecular layer (b) on an HgAu electrode.

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15) The fast desorption of $[Fe_4S_4(SC_6H_4Bu^t(p\text{-}))_4]^{2-}$ from the multimolecular layer on the [4Fe4S]/HMDE compared with that from the [4Fe4S]/GC may be due to a fluidity of the surface of an Hg. On the other hand, a strong affinity of sulfur for Hg stabilizes the monomolecular layer on the Hg electrode.

16) Peak separation of an adsorbed species becomes an increase with decreasing the electron transfer of the electrode and the adsorbed species. The configurational change between oxidized and reduced cluster adsorbed on the GC plate may, therefore, be slower than that on an Hg electrode.

17) When the cluster in a CH_3CN solution was solidified on the GC and HgAu plate under N_2, the cluster is not homogeneously distributed over the surface of those electrode.

18) The surface of the HgAu plate is not as smooth as that of the HMDE. So, the surface area of the HgAu plate is considered to be fairly larger than 1.0 cm^2.