

desferoxiamine B+ascorbate, 5-7% for catecoylamides+ascorbate and 2.7% for EDTA [2,3].

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PS5.32 — TU

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ELECTROCHEMICAL PROPERTIES OF $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_5)_4]^{-2}$, ANALOGUE OF THE ACTIVE SITE OF IRON-SULFUR PROTEINS, IN AQUEOUS MICELLAR SOLUTIONS

In order to elucidate the mechanism by which the protein region of iron-sulfur proteins modulates the redox potentials of otherwise identical 4Fe-4S clusters, we investigated the properties of the title cluster (t^{-2}) in water, the physiological solvent for proteins. The title cluster is water-insoluble, but becomes soluble in the presence of detergents [1], and by using detergents differing in structure and

in charge we attempted to simulate different protein-cluster interactions.

Synthesis of $[(\text{Et})_4\text{N}]_2[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_5)_4]$ was performed in aqueous solution as described by KURTZ *et al.* [2,3]. A stock solution of t^{-2} was anaerobically prepared in DMF, and t^{-2} concentration determined using $\epsilon_{457} = 17,700 \text{ M}^{-1} \text{ cm}^{-1}$. For electrochemical measurements the stock solution of t^{-2} in DMF was anaerobically diluted in 5% (v/v) detergent in 0.2 M Tris/sulfate buffer pH 9.00, to a final concentration of 1.34 mM t^{-2} and 5% (v/v) DMF. A three-electrodes configuration was used. All the potentials quoted here refer to saturated calomel electrode (SCE). Fig. 1 shows the cyclic voltammograms of t^{-2} dissolved in buffer/detergent mixtures of different composition and in the presence of excess thiophenol.

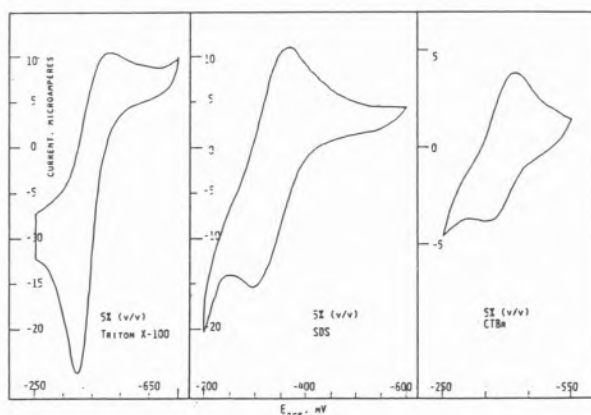


Fig. 1

Cyclic voltammograms of aqueous solutions of t^{-2} in the presence of different detergents. Cyclic voltammograms of 1.34 mM t^{-2} (in 0.2 M Tris/sulfate pH 9.0, 5% (v/v) DMF, 100 mM thiophenol containing also detergents as given in the figure) were recorded at a scan rate of 50 mV/sec

In the absence of this latter no oxidation (anodic) peak can be detected, likely because of the hydrolytic decomposition of the t^{-3} species generated in the reduction process. Excess thiophenol prevents the hydrolytic process, thus allowing the monoelectronic, quasi-reversible redox process involving the t^{-2}/t^{-3} couple to be observed. Both anodic and cathodic currents (i_a and i_c) were found to be directly proportional to the concentration of t^{-2} . In aqueous detergents, the measured values of E_0 are by far higher than those reported for the same compound dissolved in DMF

(-1.04 V vs. SCE [4]) or for water solutions of $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{CH}_2\text{OH})_4]^{-2}$ (-0.75 V vs. SCE [5,6]). Table I compares electrochemical figures

gents on E_o , and to test the reactivity of water-micellar solutions of t^{-2} towards physiological redox couples.

Table I

detergent	scan rate (ν) mV/sec	E_c mV	i_c μA	E_a mV	i_a μA	E mV	i_c/i_a	$i_c/\nu^{1/2}$
SDS	10	-364	4.3	-307	6.2	57	0.69	1.36
	20	-364	6.9	-300	9.9	64	0.70	1.54
	50	-364	11.5	-295	15.2	69	0.73	1.58
CTBr	10	-404	1.8	-336	2.7	68	0.68	0.59
	20	-413	2.9	-348	3.2	65	0.92	0.66
	50	-417	4.1	-338	4.3	79	0.97	0.59
Triton X-100	10	-510	5.4	-416	10.2	94	0.53	1.71
	20	-510	8.3	-406	17.9	104	0.46	1.86
	50	-516	10.9	-397	24.8	119	0.44	1.54
BRIJ 35	10	-497	4.3	-412	5.4	85	0.79	1.34
	20	-496	5.5	-409	8.7	87	0.63	1.23
	30	-495	7.5	-400	13.6	95	0.55	1.07

obtained with solutions of t^{-2} in the presence of different detergents, and shows that the electrochemical process is quasi-reversible and diffusion-controlled. A comparison among the values of $i_c/\nu^{1/2}$ in Table I provides also evidences about the actual inclusion of t^{-2} in the micelles. A comparison among the different micellar environments shows that the charge of the micelle plays a minor role in the modification of E_o of the enclosed t^{-2} , whereas exclusion of solvent water appears to have a major effect. With Triton X-100 and Brij 35 (having highly solvated poly-oxyethylenic hydrophilic chains) the lowest E_o values were measured.

E_o increases with CtBr (cetyltetrammonium bromide) likely as a consequence of either the positive charge carried by the micelles and/or their compactness. The influence of the micellar compactness (*i.e.* of their ability to screen the cluster from water) is further made evident when considering that the negatively-charged, highly-compact SDS (sodium dodecyl sulfate) micelles allow the highest value of E_o to be measured. Work is in progress to discriminate more properly among charge and hydrophobicity effects of the deter-

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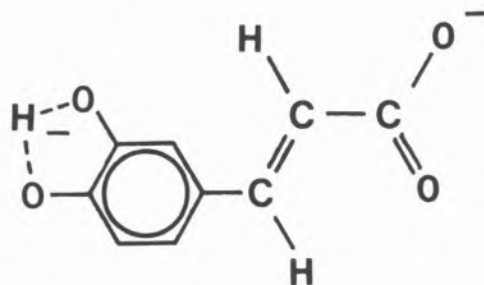
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COMPLEXATION OF COPPER(II) IONS BY CAFFEIC ACID

The bioavailability to plants of metal ions, either as micro-nutrients or as toxins, is strongly influenced by coordinating ligands which may be present in the soil or the artificial nutrient solution in which the plant grows [1]. In order to contribute to the understanding of the role of coordination equilibria in the transport of metal ions to plant roots, we are undertaking chemical speciation studies of soil and nutrient solutions by means of computer simulation [2,3]. Amongst the information needed for our computer models are formation constants for the manifold metal-ligand-proton complexes that can be found. Of special interest are various phenolic ligands which are known to be exuded by plant roots under certain conditions and which are believed to participate in the transport of iron from the surrounding soil or nutrient solution to the root membrane [4]. The root-exuded phenolic compound of major importance is caffeic acid. Indeed, it has been postulated that under the conditions prevailing in soils, caffeic acid tends to reduce iron (III) to iron (II), the necessary state of oxidation for iron ions to be absorbed by plant roots [4]. Since caffeic acid can potentially form complexes with all the types of metal ion which occur in soil and nutrient solutions, it is an essential component for inclusion in our speciation models. Moreover, since there is a paucity of formation constant data reported in the literature for caffeate-metal-proton complexes, we are undertaking an extensive programme of investigation into the solution equilibria of these systems. On our poster, we intend to present re-

sults obtained by glass electrode potentiometry and NMR for copper (II).

In its own right, caffeic acid is an interesting coordinating ligand purely from the inorganic chemical point of view. This arises from the two coordination sites, one at each end of the molecule. Taking the ligand species to be the dianion,



(denoted hereafter by L^{2-}) protonation constants have been determined, yielding the results in the Table. Note that whereas one of the catecholic oxygens is reasonably acidic, with a pK_a of 8.72, the second is very strongly basic (cf. catechol: $pK_{a1} = 13.0$, $pK_{a2} = 9.23$) [6]. This has been attributed to hydrogen bonding between the hydroxyl and phenoxide groups [7]. We have made no attempt to determine the first protonation constant of the trianion of caffeic acid.

Table
Logarithms of protonation constants (β_H) determined for L^{2-} at 25°C and $I = 0.100 \text{ mol dm}^{-3}$ (Na) [Cl]. d = the standard deviation in $\log \beta_H$. n = the number of experimental observations

Reaction	$\log \beta_H$	d	n
$L^{2-} + H^+ \rightleftharpoons LH^-$	8.72	.003	389
$L^{2-} + 2H^+ \rightleftharpoons LH_2$	13.13	.004	389

Preliminary results obtained for the complexation titrations have been used to construct the diagram in the Figure. The latter shows the distribution of caffeate-copper(II)-proton complexes detected in aqueous solutions with total concentrations of the components that are typical of the titrations in this study.

Although we can be reasonably certain of the stoichiometry of the species in the figure, the structures are not known at this stage and may be merely speculated upon. Thus the following are suggested