Solvation as the Determining Factor for the Redox Potential of $Fe_4S_4[S-(CH_2)_nCO_2]^{6-}$ Cluster Ions

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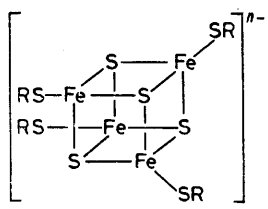
Summary The redox potentials of $Fe_4S_4(SR)_4^{2-}$ ions are not greatly affected by the close proximity of negative charges in the –SR ligands but become more positive when the hydrogen bonding ability of the solvent is increased, thereby suggesting the role of hydrogen bonds in determining the potentials of protein bound clusters.

THE iron–sulphur cluster ion (**1**) has been synthesized and its structure verified by *X*-ray crystallography.[1] Owing to the solubility of (**1**) in aqueous solution it has been a useful model for the $Fe_4S_4(Cyst)_4^{2-}$ clusters of ferredoxin iron–sulphur proteins in kinetic studies of water–lyate species solvolysis, ligand exchange, and cluster acid–base properties.[2] The $1e^-$ reduction potential of (**1**) in aqueous solution was found [−0·58 V *vs.* standard hydrogen electrode (s.h.e.)] to be similar to that for the ferredoxins (*ca.* −0·4 V *vs.* s.h.e.).[3] This similarity in redox potential may be due to the electrostatic interaction of the four uninegative charges (*i.e.* $-CO_2^-$) at *ca.* 4·5 Å from the binegative Fe_4S_4 core or, alternatively, simply to water playing a major role in determination of redox potential.[4]



(1) R = $-[CH_2]_2CO_2^-Na^+$ $n = 6$

(2) R = $-[CH_2]_3CO_2^-Na^+$ $n = 6$

(3) R = $-CH_2CHMe_2$ $n = 2$

The polarographic half-wave potential of (**1**), (**2**), and (**3**) are presented in the Table. Comparison of potentials of compounds (**1**) and (**2**) in aqueous solution shows that an extension of chain length by one methylene group does not change the ease of electron transfer as measured by half-wave redox potentials. Reduction potentials of the Fe_4S_4 cores of $Fe_4S_4(SR)_4^{n-}$ clusters are therefore not detectably influenced by the presence of charged groups in close

TABLE. Polarographic data for the 6−/7− redox couple of (**1**) and (**2**) and the 2−/3− redox couple of (**3**), at 25 °C.

Compound	$E_{\frac{1}{2}}$/V[a]
(**1**) in H_2O	−0·82[b]
(**2**) in H_2O	−0·81[c]
(**1**) in MeOH	−1·13[d]
	−1·10[e]
(**2**) in MeOH	−1·18[d]
(**3**) in MeOH	−1·18[d]

[a] Versus standard calomel electrode; ± 10—20 mV, all determinations performed anaerobically, using a dropping mercury electrode. [b] 0·1 M $HS[CH_2]_2CO_2^-$, 0·1 M $LiClO_4$, pH = 9·50. [c] 0·1 M $HS[CH_2]_3CO_2^-$, 0·1 M $LiClO_4$, pH = 9·50. [d] 0·1 M $(Bu^n_4N)Br$. [e] No supporting electrolyte.

proximity. Transfer from water to a solvent (MeOH) of much lower dielectric constant does not bring about any change in electrostatic effect on the reduction potential. This may be seen by comparison of the potentials of (**1**), (**2**), and (**3**) in MeOH. In fact, the comparison of (**1**) and (**3**) in MeOH shows that even complete removal of charged groups does not appreciably affect the measured potential. Comparison of (**1**), (**2**), and (**3**) in MeOH shows that, in polar organic solvents, clusters possessing alkanethiolate ligands have essentially identical redox potentials. There also appears to be little or no interference by the supporting electrolyte upon the possible redox effects of intramolecular charges, since essentially the same voltages were measured for (**1**) in both the absence and presence of supporting electrolyte. Transfer of (**1**) and (**2**) from aqueous to methanol solvents resulted in the 2−/3− redox couples for both compounds becoming more negative.

Since the reduction potentials for 2−/3− couples of the ferredoxins (*ca.* −0·67 V *vs.* standard calomel electrode)[4] are similar to potentials of synthetic clusters obtained in aqueous solutions, one may conclude that the local environment of the clusters in ferredoxins provides a property shared by water. The sites at which Fe_4S_4 clusters are bound to ferredoxins are not readily accessible to water solvent.[5] It is reasonable to suppose that the common features of water solvent and the binding sites are the known hydrogen bonds which occur between the sulphurs of both cluster core and ligands and the protein backbone amide hydrogens.[6] This view is supported by the observation that disruption of the tertiary structure (with concomitant hydrogen bond breakage) of ferredoxins upon transfer from H_2O to Me_2SO–H_2O (80 : 20 v/v) results in their redox potentials becoming more negative.[4]

The less negative reduction potentials of both protein bound and water soluble synthetic $Fe_4S_4(SR)_4^{n-}$ clusters, relative to the water insoluble analogues, therefore appear to be due primarily to the presence of hydrogen bonding, and the close proximity of charges to a cluster is of no importance.

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