An Electron Transfer Reaction catalysed by a Synthetic Iron–Sulphur Cluster in Cetyltrimethylammonium Bromide (CTAB) Micelles

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The synthetic iron–sulphur cluster (1) in the cetyltrimethylammonium bromide (CTAB) micelles catalysed the electron transfer reaction between dithionite and acridine derivatives.

Since Holm and co-workers prepared the first synthetic iron–sulphur cluster, $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$, in 1972,[1] several other varieties have been prepared in an attempt to model active sites of iron–sulphur proteins. However, attempts to utilize these synthetic clusters in electron transfer catalysis reactions in aqueous solutions have been unsuccessful,[2] mainly because of their instability under hydrolytic reaction conditions.[3] Various methods have been used in attempts to stabilize the synthetic cluster in aqueous solution, such as dissolving the compound in aqueous solution containing the high concentration of mercaptans,[3] and incorporation into micelles[4] or bilayer membranes.[5] Of these attempts, the use of micelles seems to provide the most promising systems, because it is well established that they provide hydrophobic environments similar to those of enzymes[6] and the reduction potential of the synthetic iron–sulphur cluster in micelles is shown to be similar to that of native ferredoxin [−0.24 to −0.49 V vs. normal hydrogen electrode (n.h.e.) in H_2O].[7] Recently we reported that both of the oxidizing and reducing forms of the synthetic iron–sulphur cluster (1) show fairly good stability in cetyltrimethylammonium bromide (CTAB) micelles and that electron transfer from aqueous dithionite to the dianion of (1) was reasonably fast.[8] In this communication, we report electron transfer reactions *catalysed* by (1) in CTAB micelles, which afford further insight into the redox activity of the synthetic iron–sulphur cluster.

Anthraquinone and acridine derivatives were investigated as the final electron acceptor in the CTAB micelles (Scheme 1). All solutions used were prepared in a carefully deoxygenated dry box and the kinetic measurements were carried out under anaerobic conditions. In a typical experiment, the reaction was initiated by addition of 0.4 ml of dithionite (12 mM) to 2 ml of a mixture of (1) $(3.6 \times 10^{-5}$ M), (4) $(7.2 \times 10^{-5}$ M), and CTAB (24 mM), through the 'syringe stopped flow' apparatus[9] under argon atmosphere. The reactions were followed by monitoring the increase of the characteristic absorptions of (2) and (3), and the decrease of the fluorescence observed for (4)—(6). The apparent first-order rate constants observed are shown in Table 1, together with reduction potentials of substrates in the aqueous micellar solution obtained by cyclic voltammetry. In all cases, reactions

in the CTAB micelles proceeded quantitatively without any appreciable side reactions being detected by the electronic spectra of recovered substrates [*e.g.* (4), λ_{max} 360 nm, ε 9.2 × 10^3] and of (1) (λ_{max} 400 nm, ε 1.7 × 10^4) in the reaction mixture after the oxidation with sodium anthraquinone-1,5-disulphonate [over 98 and 83% recovery of substrates and (1), respectively].

The overall electron transfer reactions from $S_2O_4^{2-}$ to the acridine derivatives, (4) and (5), were markedly accelerated in the presence of (1) ($k_{obs}/k_0 = 13$—18). In contrast with this, no

(1)

$R = CH_2CHNHCOC_{17}H_{35}-n-L$
      $|$
      CO_2Na
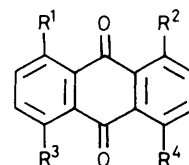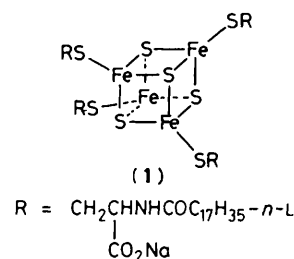
(2) $R^1 = R^2 = R^3 = R^4 = NHCOC_6H_{11}$-cyclo
(3) $R^1 = R^2 = R^3 = H, R^4 = NHC_{12}H_{25}$-$n$
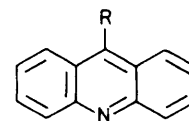

(4) $R = NHCOC_4H_9$-t
(5) $R = NHCOC_6H_{11}$-cyclo
(6) $R = NHC_{12}H_{25}$-n

Table 1. Apparent first-order rate constants (s^{-1}) of electron transfer reactions catalysed by (1).[a]

Substrate	λ/nm[b]	$E^{1/2}$/V vs. n.h.e.[c] in the aq. micelles	k_0[d]	k_{obs}[e]	k_{obs}/k_0
(2)	460 (E)	−0.35	$(1.4 \pm 0.1) \times 10^{-1}$	$(1.6 \pm 0.01) \times 10^{-1}$	1.14
(3)	410 (E)	−0.45	9.1 ± 0.1	9.2 ± 0.3	1.01
(4)	450 (F)	−0.51	$(6.5 \pm 0.4) \times 10^{-3}$	$(8.5 \pm 0.1) \times 10^{-2}$	13.1
(5)	450 (F)	−0.51	$(6.0 \pm 0.6) \times 10^{-3}$	$(1.1 \pm 0.1) \times 10^{-1}$	18.3
(6)	450 (F)	−0.91	$<1 \times 10^{-3}$	$<1 \times 10^{-3}$	−

[a] 25 ± 0.1 °C, pH 8.5, Tris-Cl (100 mM). [b] Wavelength used in the kinetic measurement; (E) electronic spectrum of the substrate in the reduced form; (F) fluorescence spectrum of the substrate in the oxidized form (excitation 360 nm). [c] [CTAB] 2 × 10^{-2} M, [Tris-Cl] 1 × 10^{-1} M, pH 8.5 ($E^{1/2}$ vs. n.h.e. = $E^{1/2}$ vs. Ag/AgCl + 0.20 V; working electrode Hg, counter electrode Pt, reference electrode Ag/AgCl). [d] [Substrate] 6 × 10^{-5} M, $[Na_2S_2O_4]$ 2 × 10^{-3} M, [CTAB] 2 × 10^{-2} M. [e] Concentrations as in note d, and (1) 3 × 10^{-5} M.
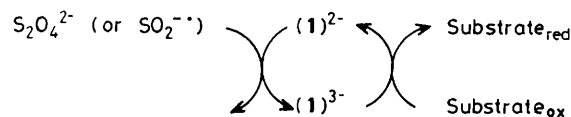
Scheme 1

appreciable acceleration was observed for the anthraquinone derivatives, though their absolute electron transfer rates are much larger than those of the acridine derivatives. Since the reduction potential of (**1**) in micelles (pH 8.5) was found to be -0.55 V vs. n.h.e. (very similar to that of native ferredoxin), these observations suggest that compounds having slightly higher reduction potentials than that of (**1**), such as (**4**) and (**5**), are very suitable as final electron acceptors in the successive electron transfer reactions catalysed by (**1**). Otherwise the direct electron transfer from $S_2O_4{}^{2-}$ proceeds too quickly and dominates the overall electron transfer reaction, as observed in the cases of (**2**) and (**3**) which have too high reduction potentials, or no practical electron transfer occurs, as in the case of (**6**) with too low a reduction potential. Furthermore, it should be noted that (**1**) really acts as an electron transfer catalyst for the reduction of (**4**) and (**5**), where turnover numbers for (**1**) are 1.8 and 1.9, respectively.†

Thus, the results described here demonstrate that the synthetic iron–sulphur cluster can catalyse the electron transfer reaction in aqueous media, if the cluster is stabilized and the reduction potentials of the electron donor and acceptor are suitably adjusted.

† Preliminary results show that a larger turnover number is possible in the present system, *e.g.* a turnover number of 7.5 was observed when concentrations of (**1**) 3×10^{-5} M, (**4**) 2.5×10^{-4} M, CTAB 5×10^{-3} M, and $S_2O_4{}^{2-}$ 8×10^{-3} M, were used.

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