

# Kinetics of oxidation of vanadium(IV) by iron(III)–1,10-phenanthroline complex: Micellar effect of sodium dodecyl sulphate

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## Abstract

Iron(III)–1,10-phenanthroline complex obtained, in situ, by direct mixing of iron(III) and 1,10-phenanthroline, oxidizes V(IV). The reaction is markedly accelerated by sodium dodecyl sulphate. The rate–[surfactant] profile exhibits a maximum. The kinetic analysis of the micellar effect has been carried out using Bereazin's approach. The binding constants of 1,10'-phenanthroline and V(IV) have been determined. © 1997 Elsevier Science B.V.

*Keywords:* Vanadium; Iron–1,10-phenanthroline; Sodium dodecyl sulphate

## 1. Introduction

Micellar effects on electron-transfer reactions of metal ion complexes attracted the attention of a large number of workers due to their importance in biological processes. However, the reactions mostly investigated were of simple bimolecular type without the involvement of preequilibria. But most of the electron-transfer reactions involve equilibria prior to the rate-determining step and it is necessary to standardise the methodology in the kinetic analysis of such reactions. An effort has been made in this direction, choosing the reactions of iron(III)–1,10-phenanthroline complex, produced, in situ, by mixing iron(III) and 1,10-phenanthroline. This complex has the composition  $\{\text{Fe}(\text{phen})_2(\text{H}_2\text{O})_2^{3+}\}$  [1–4] in the presence of  $\text{H}^+$ . This complex is labile [1–4] and is different from tris(1,10-phenanthroline) iron(III) which can not be obtained by the direct mixing of iron(III) and phenanthroline but by the oxidation of the corresponding tris iron(II) complex. Subba Rao and co-workers investigated the reactions of the former complex [5–9] and showed that the reaction obeys first order kinetics in iron(III) and reductant and the rate has square dependence on the concentration of 1,10'-phenanthroline and inverse square dependence on  $[\text{H}^+]$ . This has been shown to be due to

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pre-equilibria in which the iron(III)–phenanthroline complex is formed which subsequently oxidises the substrate in the rate-limiting step. We have found that sodium dodecyl sulphate (SDS) has an accelerating effect on these reactions. The kinetic analysis has been carried out combining the equilibrium technique and Berezin's partition model and the results are presented in this paper.

## 2. Experimental

A known concentration of  $0.1 \text{ mol dm}^{-3}$  iron(III) in aqueous perchloric acid medium was prepared and standardised according to the methods described elsewhere [10,11]. A Fluka sample of sodium dodecyl sulphate (SDS) has been used in the preparation of  $0.1 \text{ mol dm}^{-3}$  solution. The purity of the sample was tested by determining the cmc ( $8.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) [12] conductometrically. The cmc of SDS corresponding to the present experimental conditions ( $\mu = 0.1 \text{ mol dm}^{-3}$ ) has been reported to be  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  [13,14].  $0.05 \text{ mol dm}^{-3}$  solutions of cobaltous nitrate, perchloric acid and 1,10-phenanthroline were prepared and estimated by standard methods.

The products of oxidation of vanadium(IV) have been found to be vanadium(V) [6], along with tris(1,10-phenanthroline) iron(III) which has a molar extinction coefficient of  $1.1 \times 10^4 \text{ cm}^{-1} \text{ mol}^{-1} \text{ dm}^3$  ( $\lambda = 510 \text{ nm}$ ) [15].

The course of the reaction is followed by measuring the absorbance of tris(1,10-phenanthroline) iron(II) formed at various times at 510 nm using a Milton Roy (spectronic 1201) spectrophotometer with kinetic attachment. At this wavelength, all the other materials concerned have negligible absorbance. All the kinetic runs were carried out keeping [SDS] in large excess such that the micellar surface covered by the binding of products is negligible. In the kinetic runs, the ionic strength was maintained constant at  $0.1 \text{ mol dm}^{-3}$  with sodium perchlorate. The concentration of  $\text{H}^+$  is at least 100 times more than iron(III) and no change in pH has been observed during the course of the reaction. Duplicate kinetic runs were always performed and the rate constants were found to be reproducible within  $\pm 5\%$ .

## 3. Results and discussion

### 3.1. Determination of binding constants

For determining the binding constant of 1,10-phenanthroline with SDS micelles at  $[\text{H}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$  and  $\mu = 0.1 \text{ mol dm}^{-3}$  adjusted with  $\text{NaClO}_4$ , spectra of this compound have been scanned at different SDS concentrations above cmc and under the condition  $[\text{SDS}] \gg [1,10\text{-phenanthroline}]$ . A suitable wavelength is chosen ( $\lambda = 330 \text{ nm}$ , where 1,10-phenanthroline obeys Beer's law).  $A_M$  and  $A_W^0$ , the absorbance in the presence of micelle and its absence, respectively, have been determined for various SDS concentrations. The binding constant has been determined using the equation [16]

$$1/(A_M - A_W^0) = 1/(A_M^0 - A_W^0)(1 + 1/K_s C) \quad (1)$$

$A_M^0$  is the limiting absorbance in the presence of micelles.  $1/(A_M - A_W^0)$  is plotted against  $C$  (i.e. stoichiometric concentration of SDS – cmc) and from slopes and intercepts of these plots, the binding constant of 1,10-phenanthroline has been found to be  $100.0 \pm 5.0 \text{ dm}^3 \text{ mol}^{-1}$  at  $30^\circ\text{C}$ .

The reaction obeys first order kinetics in iron(III) as shown by the linear plots of  $\log(A_\alpha - A_t)$

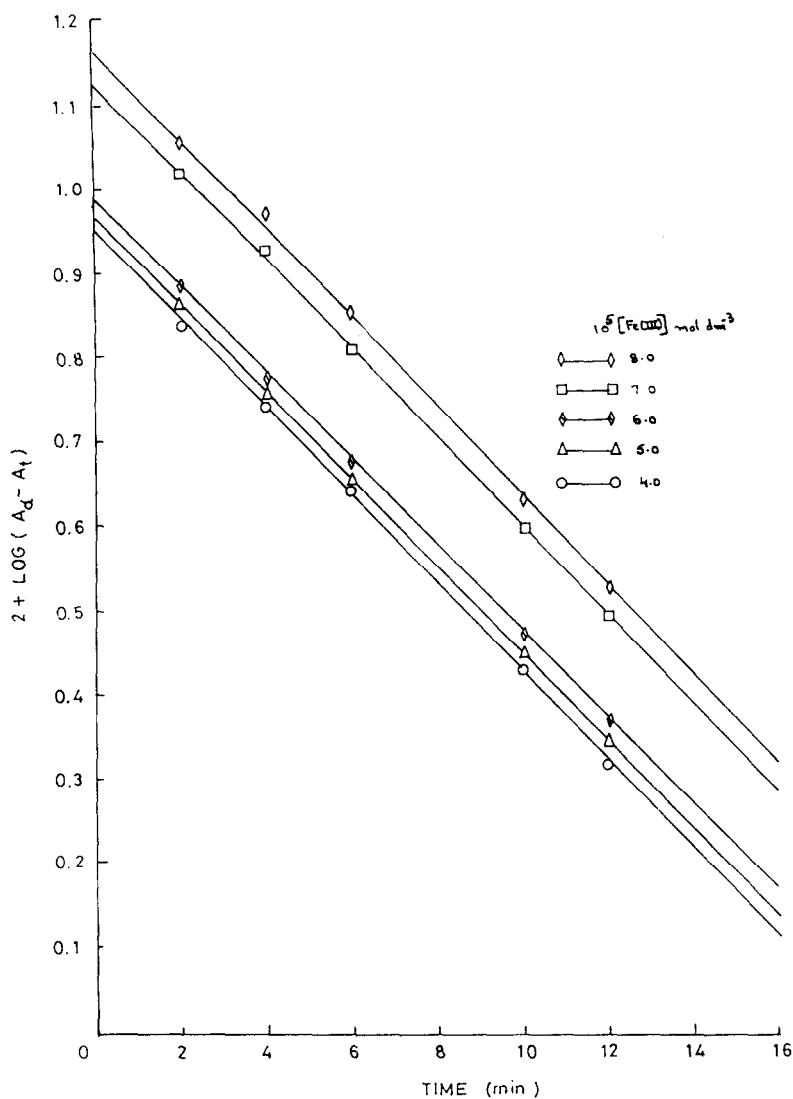


Fig. 1. Plots of  $\log(A_\infty - A_t)$  versus time ( $[V(IV)] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[Phen] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[H^+] = 0.1 \text{ mol dm}^{-3}$ ;  $[SDS] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $\mu = 0.1 \text{ mol dm}^{-3}$ ;  $T = 30.0 \pm 0.1^\circ\text{C}$ ).

versus time under the conditions  $[Fe(III)] \ll [V(IV)]$  (Fig. 1) and first order with respect to V(IV) (Table 1), but the second order rate constant,  $k_2$  (obtained from the slopes of the linear plots of  $1/(A_\infty - A_t)$  versus time and multiplying the slopes with the molar extinction coefficient of  $Fe(phen)_3^{2+}$  under the conditions  $[V(IV)] = [Fe(III)]$ ), is directly proportional to  $[phen]^2$  (Fig. 2). Further,  $k_\psi$  is proportional to  $1/[H^+]^2$  (Fig. 3). The reaction is markedly accelerated by SDS up to a certain limit (Table 2). In the presence of  $[SDS] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$  the rate increases by 140 times. The acceleration in the presence of the micelle may be due to [17] (i) the binding of the reactants in a small volume of stern layer of the micelle, thus leading to a considerable concentration effect, and (ii) to the possibility that the transition state is stabilized more than the initial state in the micellar pseudophase, leading to the lowering of the activation energy.

The rate–[surfactant] profile has been found to have a maximum which is typical of bimolecular

Table 1

Effect of [V(IV)] on the rate ( $[\text{Fe(III)}] = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[\text{Phen}] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$ ;  $[\text{SDS}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $\mu = 0.1 \text{ mol dm}^{-3}$ ;  $T = 30.0 \pm 0.1^\circ\text{C}$ )

$10^4[\text{vandium}] (\text{mol dm}^{-3})$	$10^3 k_p (\text{s}^{-1})$
2.0	0.97
4.0	1.95
6.0	3.01
8.0	3.86
10.0	4.90
12.0	5.94

micellar-catalyzed processes [17]. According to Romsted [18], the maximum in the rate–[surfactant] profile is produced by two opposing effects. Binding of the reactants in the stern layers begins at the cmc and they are transferred into a small volume of the micellar pseudophase. There is thus a concentration effect which is responsible for acceleration. This concentration effect is opposed by the continuous dilution of the reactants within the micellar pseudophase with increasing surfactant concentration. The former effect is predominant at lower surfactant concentrations whereas the latter

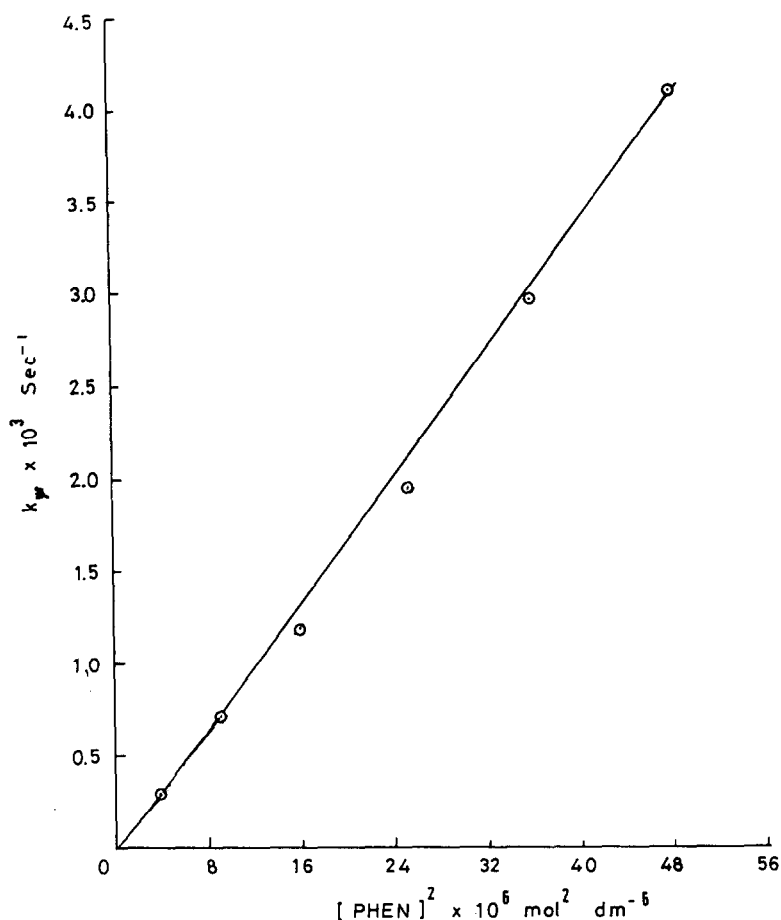


Fig. 2. Plot of  $k_p$  versus  $[\text{Phen}]^2$  ( $[\text{V(IV)}] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{Fe(III)}] = 8.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$ ;  $[\text{SDS}] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $\mu = 0.1 \text{ mol dm}^{-3}$ ;  $T = 30.0 \pm 0.1^\circ\text{C}$ ).

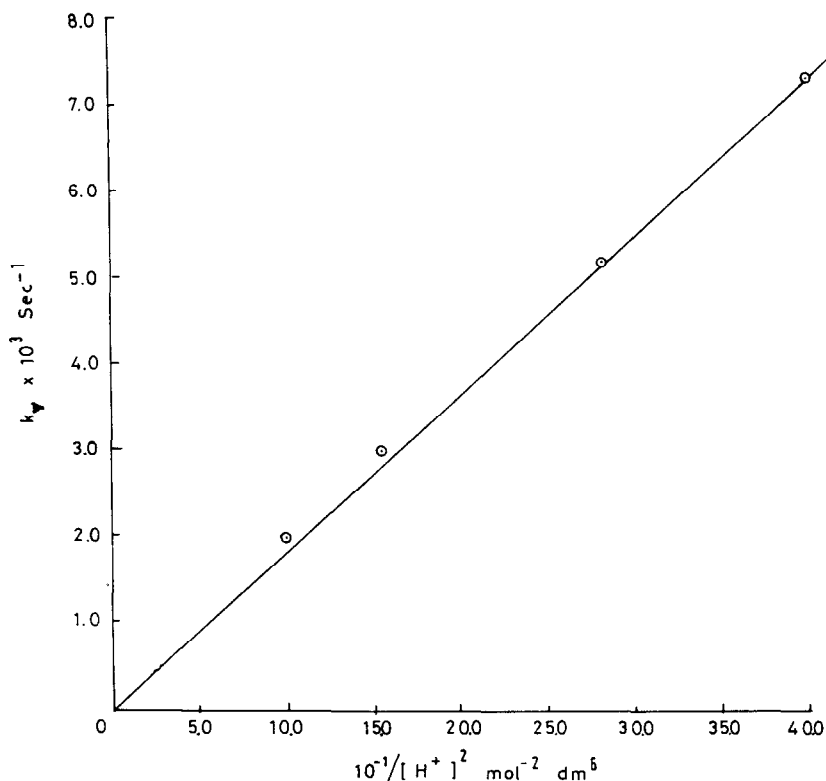


Fig. 3. Plot of  $k_p$  versus  $1/[H^+]^2$  ( $[V(IV)] = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $[Fe(III)] = 8.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[Phen] = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[SDS] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $\mu = 0.1 \text{ mol dm}^{-3}$ ;  $T = 30.0 \pm 0.1^\circ\text{C}$ ).

becomes important at higher concentrations of surfactant, resulting in maximum in the rate–[surfactant] profile.

In the range of  $H^+$  ion concentration employed in the present study, all phenanthroline can be considered to be in the protonated form,  $Hphen^+$  (The  $pK_a$  of  $Hphen^+$  is 4.86 [19]). Vanadium(IV) is known to be in the form  $VO^{2+}$  in mineral acid solution. In the presence of 1,10-phenanthroline it is

Table 2

Effect of [SDS] on the rate ( $[Fe(III)] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[Phen] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$   $[H^+] = 0.1 \text{ mol dm}^{-3}$ ;  $[vanadium] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $\mu = 0.1 \text{ mol dm}^{-3}$ ;  $T = 30.0 \pm 0.1^\circ\text{C}$ )

$10^3[SDS] \text{ (mol dm}^{-3}\text{)}$	$k_2 \text{ (mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\text{)}$
0.0	0.068
1.0	12.69
2.0	15.02
4.0	16.68
5.0	11.69
6.0	9.44
8.0	6.72
12.0	4.17
16.0	2.74
20.0	1.64
24.0	1.31
28.0	0.92

known to form 1:1 ( $\log K_1 = 5.47$ ) and 1:2 ( $\log K_2 = 4.22$ ) [20] complexes. The concentrations of these 1:1 and 1:2 complexes are given by the equations

$$[\text{V(IV)(Phen)}] = \frac{K_1 K_a [\text{V(IV)}][\text{Hphen}^+][\text{H}^+]}{[\text{H}^+]^2 + K_1 K_a [\text{Hphen}^+][\text{H}^+] + K_1 K_2 K_a^2 [\text{Hphen}^+]^2} \quad (2a)$$

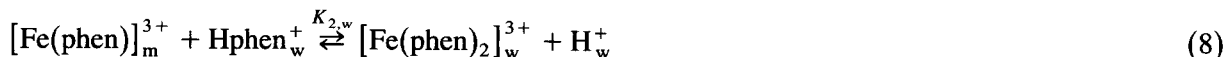
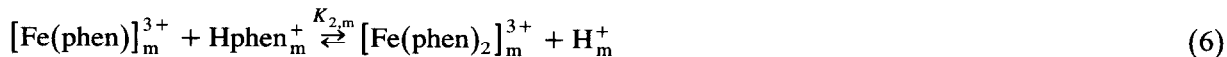
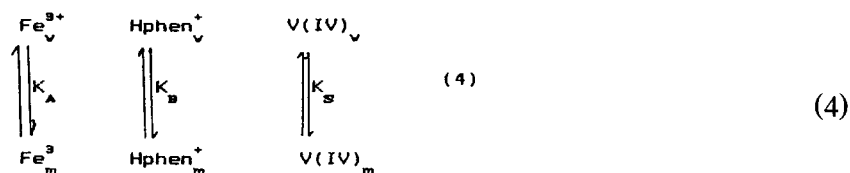
$$[\text{V(IV)(Phen)}_2] = \frac{K_1 K_2 K_a [\text{V(IV)}][\text{Hphen}^+]^2}{[\text{H}^+]^2 + K_1 K_a [\text{Hphen}^+][\text{H}^+] + K_1 K_2 K_a^2 [\text{Hphen}^+]^2} \quad (2b)$$

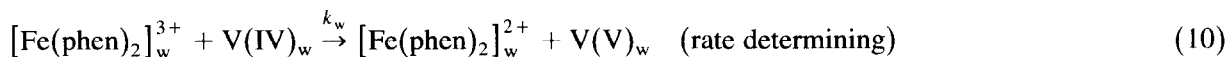
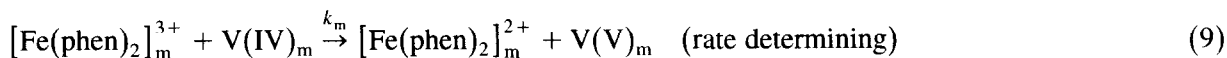
where  $K_a$  is the dissociation constant of  $\text{Hphen}^+$ . Using these equations, the authors found that the concentrations of these phenanthroline complexes of  $\text{V(IV)}$  are negligibly small at the  $\text{H}^+$  ion concentration employed ( $0.1 \text{ mol dm}^{-3}$ ) and can be neglected. Hence almost all  $\text{V(IV)}$  can be expected to be present in the uncomplexed form  $\text{VO}^{2+}$ . Iron(III) can be expected to be mainly present in the form of  $\text{Fe}_{\text{aq}}^{3+}$ . The dimeric form is present in negligible concentration at the low iron(III) concentrations employed ( $10^{-5} \text{ mol dm}^{-3}$ ). The first stage hydrolysis constant,  $K_{11}$ , for the hydrolysis of iron(III) has a value of  $1.07 \times 10^{-3} \text{ mol dm}^{-3}$  [21]. In the presence of SDS micelles, which bind  $\text{Fe}^{3+}$  more strongly than  $\text{FeOH}^{2+}$ , the hydrolysis constant,  $K'_{11}$  can be expected to decrease.  $K_{11}$  is related to  $K'_{11}$  by the equation [17]

$$K'_{11} = K_{11}(1 + K'_A C)/(1 + K_A C) \quad (3)$$

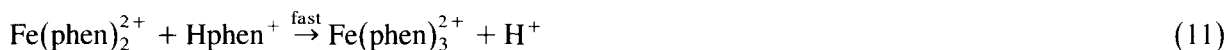
$K'_A$  and  $K_A$  are the binding constants of  $\text{FeOH}^{2+}$  and  $\text{Fe}^{3+}$ , respectively. Assuming that the binding is electrostatic in nature,  $K'_A$  and  $K_A$  can be calculated using the equation  $K = P\bar{V}$  where  $\bar{V}$  is the standard molar volume of SDS ( $0.246 \text{ dm}^3 \text{ mol}^{-1}$ ) [22]. The partition coefficient,  $P$ , of charged species between the micellar and aqueous phase is given by the equation  $P = e^{Z\psi/25.7}$  [23] at  $25^\circ\text{C}$  where  $\psi$  is the surface potential of the micelle ranging between 85–110 mV [22] and  $Z$  is the charge of the ion bound at the micelle. Assuming that  $\psi$  has a value of 85 mV,  $K_A$ , the binding constant of  $\text{Fe}^{3+}$ , is  $5.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  and  $K'_A$  has a value of  $1.8 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ . The value of  $K'_{11}$  has then a value of  $9.3 \times 10^{-5} \text{ mol dm}^{-3}$ . Thus in the presence of SDS, the concentration of  $\text{FeOH}^{2+}$  ( $= (K'_{11}[\text{Fe(III)}]_{\text{total}})/(K'_{11} + [\text{H}^+])$ ) can be considered to be presented in insignificant amounts. Further, if the hydrolysis of iron(III) is to an appreciable extent, a more complex acid dependence of rate would have been observed.

The authors propose the following scheme to explain all the kinetic features:





According to the scheme, the reaction in the micellar as well as the aqueous phase involves a prior interaction between  $\text{Fe}^{3+}$  and 1,10-phenanthroline (the latter mainly existing in the form of  $\text{Hphen}^+$ ), leading to the formation of 1:2 complex,  $\text{Fe}(\text{phen})_2^{3+}$ , in successive equilibria, which is the active oxidising species. The complex formed between  $\text{FeOH}^{2+}$  and phenanthroline,  $(\text{phen})_2\text{FeOH}^{2+}$  with smaller positive charge, does not appear to be as effective. It is known that  $\text{FeOH}^{2+}$  is a poorer oxidant compared to  $\text{Fe}^{3+}$  [24]. The reduction product of  $\text{Fe}(\text{phen})_2^{3+}$  is  $\text{Fe}(\text{phen})_2^{2+}$  which, interacting with  $\text{Hphen}^+$ , produces the tris(phenanthroline)iron(II):



This step should not be rate-determining, the only rate determining steps being the steps of Eqs. (9) and (10), as required by the concentration dependence of the rate on the reactants and phenanthroline. If the formation of tris(1,10-phenanthroline) iron(II) (Eq. (11)) is also rate-determining, the plot of  $\log(A_{\infty} - A_t)$  should have been biphasic which is, however, not observed.

Combining equilibrium treatment and Berezin's approach it can be shown that the rate-law is given by the equation

Rate

$$= \frac{k_{\text{m}} K_{1\text{m}} K_{2\text{m}} \{P_{\text{A}}[\text{Fe}^{3+}]_{\text{t}} / (1 + K_{\text{A}}C)\} \{P_{\text{B}}^2[\text{Hphen}^+]_{\text{t}}^2 / (1 + K_{\text{B}}C)^2\} \{P_{\text{S}}[\text{V}(\text{IV})]_{\text{t}} / (1 + K_{\text{S}}C)\} \bar{V}C}{[\text{H}^+]_{\text{m}}^2 + K_{1\text{m}} P_{\text{B}}[\text{Hphen}^+]_{\text{t}} [\text{H}^+]_{\text{m}} / (1 + K_{\text{B}}C) + K_{1\text{m}} K_{2\text{m}} P_{\text{B}}^2[\text{Hphen}^+]_{\text{t}}^2 / (1 + K_{\text{B}}C)^2} + \frac{K_{\text{w}} K_{1\text{w}} K_{2\text{w}} \{[\text{Fe}^{3+}]_{\text{t}} / (1 + K_{\text{A}}C)\} \{[\text{Hphen}^+]_{\text{t}}^2 / (1 + K_{\text{B}}C)^2\} \{[\text{V}(\text{IV})]_{\text{t}} / (1 + K_{\text{S}}C)\} (1 - \bar{V}C)}{[\text{H}^+]_{\text{w}}^2 + K_{1\text{w}} [\text{Hphen}^+]_{\text{t}} [\text{H}^+]_{\text{t}} [\text{H}^+]_{\text{w}} / (1 + K_{\text{B}}C) + K_{1\text{w}} K_{2\text{w}} [\text{Hphen}^+]_{\text{t}}^2 / (1 + K_{\text{B}}C)^2} \quad (12)$$

and  $k_{\psi} = \text{Rate} / [\text{Fe}^{3+}]_{\text{t}}$

In this equation,  $P_{\text{A}}$ ,  $P_{\text{B}}$ ,  $P_{\text{S}}$  represent the partition coefficients of  $\text{Fe}^{3+}$ ,  $\text{Hphen}^+$  and substrate between the micellar and aqueous pseudo phases,  $K_{\text{A}}$ ,  $K_{\text{B}}$ ,  $K_{\text{S}}$  are the corresponding binding constants and m and w signify micellar and aqueous phases.  $\bar{V}$  is molar volume and 'C' is  $([\text{SDS}] - \text{cmc})$ . The equation, though looking formidable, undergoes considerable simplification. The binding constant of iron(III) ( $K_{\text{A}}$ ) has a value around  $5.0 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$  and hence  $(1 + K_{\text{A}}C) \cong K_{\text{A}}C$  at  $[\text{SDS}] \gg \text{cmc}$ . Thus iron(III) is mostly present in the micellar phase and hence the extent of reaction in the aqueous phase (i.e. the second term in Eq. (12)) can be neglected. Further, the rate is directly proportional to  $1/[\text{H}^+]^2$  and  $[\text{phen}]^2$ . Hence the terms

$$\frac{K_{1\text{m}} P_{\text{B}} [\text{H}^+]_{\text{m}} [\text{Hphen}^+]_{\text{t}}}{(1 + K_{\text{B}}C)} \quad \text{and} \quad \frac{K_{1\text{m}} K_{2\text{m}} P_{\text{B}}^2 [\text{Hphen}^+]_{\text{t}}^2}{(1 + K_{\text{B}}C)^2}$$

in Eq. (12) can be considered to be negligible in comparison with  $[\text{H}^+]_{\text{m}}^2$ . Hence, under these conditions, the equation reduces to

$$\text{Rate} = \frac{k_{\text{m}} K_{1\text{m}} K_{2\text{m}} P_{\text{B}}^2 P_{\text{S}} [\text{Fe}^{3+}]_{\text{t}} [\text{Hphen}^+]_{\text{t}}^2 [\text{V}(\text{IV})]_{\text{t}}}{[\text{H}^+]_{\text{m}}^2 (1 + K_{\text{B}}C)^2 (1 + K_{\text{S}}C)} \quad \text{and} \quad P_{\text{A}} \bar{V} = K_{\text{A}} \quad (13)$$

In Eq. (12),  $[H^+]_m$  is the concentration of  $H^+$  ions in moles per litre of micellar phase ( $= m_{H^+}^s/\bar{V}$  in Romsted's formulation) given by [25]:

$$[H^+]_m = \frac{0.82[H^+]_t}{\{[H^+]_t + [Na^+]_t\}\bar{V}} \quad (14)$$

In all the kinetic runs, the value of  $[H^+]_t + [Na^+]_t$  is kept constant at  $0.1 \text{ mol dm}^{-3}$ . Hence  $[H^+]_m$  is equal to  $8.2 [H^+]_t/\bar{V}$ . The rate constant

$$k_2 (= \text{Rate}/[Fe^{3+}]_t[V(IV)]_t) = \frac{k'_m K_{1m} K_{2m} P_B^2 P_s [Hphen^+]_t^2}{([H^+]_t^2 (1 + K_B C)^2 (1 + K_s C))} \quad (15)$$

where

$$k'_m = \frac{k_m}{(8.2 \bar{V})^2}$$

On rearrangement Eq. (15) changes to

$$\frac{1}{k_2(1 + K_B C)^2} = \frac{[H^+]_t^2}{k'_m K_{1m} K_{2m} P_B^2 P_s [Hphen^+]_t^2} + \frac{K_s C [H^+]_t^2}{k'_m K_{1m} K_{2m} P_B^2 P_s [Hphen^+]_t^2} \quad (16)$$

The validity of the rate-law has been tested by calculating  $1/(k_2(1 + K_B C)^2)$  and plotting versus  $C$  using the values of  $K_B$  determined from UV spectral data. A straight line has been obtained with a positive intercept (Fig. 4) and  $K_s$ , the binding constant of V(IV) has been calculated to be  $(33.0 \pm 0.5) \text{ dm}^3 \text{ mol}^{-1}$  from the values of slope and intercept of the above plot. The value of  $K_s$  is

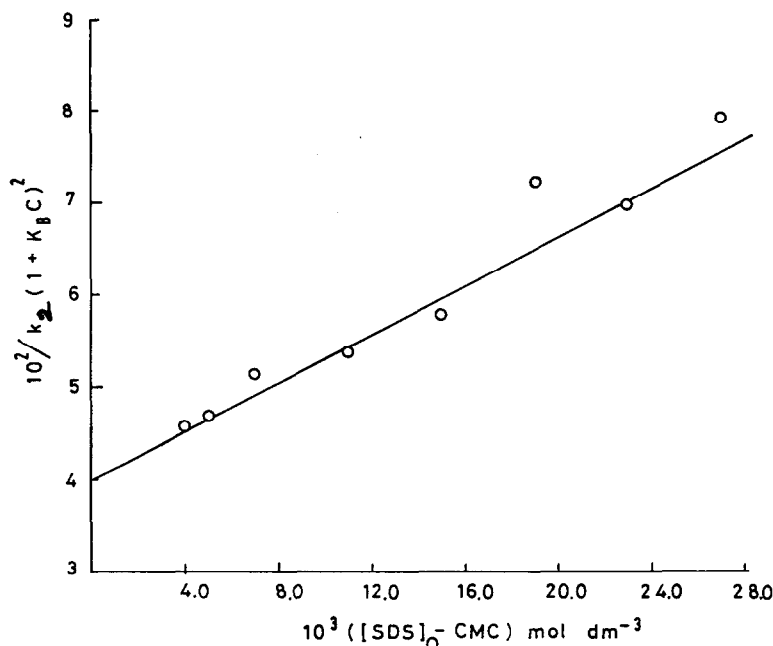


Fig. 4. Plot of  $1/(k_2(1 + K_B C)^2)$  versus  $([SDS] - \text{cmc})$  ( $[V(IV)] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[Fe(III)] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[Phen] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[H^+] = 0.1 \text{ mol dm}^{-3}$ ;  $\mu = 0.1 \text{ mol dm}^{-3}$ ;  $T = 30.0 \pm 0.1^\circ\text{C}$ ).



Table 3

[Fe(III)] =  $4.0 \times 10^{-5}$  mol dm<sup>-3</sup>; [vanadium] =  $4.0 \times 10^{-4}$  mol dm<sup>-3</sup>; [SDS] =  $3.0 \times 10^{-2}$  mol dm<sup>-3</sup>;  $K_s = 33.0$  mol<sup>-1</sup> dm<sup>3</sup>;  $K_B = 100.0$  mol<sup>-1</sup> dm<sup>3</sup>;  $k'_m K_{1m} K_{2m} P_B^2 P_s = 6.25 \times 10^4$ ;  $\mu = 0.1$  mol dm<sup>-3</sup>;  $T = 30.0 \pm 0.1^\circ\text{C}$

$10^2[\text{H}^+]$ (mol dm <sup>-3</sup> )	$10^3[\text{Phen}]$ (mol dm <sup>-3</sup> )	$10^3 k_{\psi_{\text{obs}}}$ (s <sup>-1</sup> )	$10^3 k_{\psi_{\text{cal}}}$ (s <sup>-1</sup> )
10.0	2.0	0.33	0.34
10.0	4.0	1.18	1.34
10.0	6.0	2.99	3.02
5.0	5.0	7.64	8.40
8.0	5.0	3.00	3.28
10.0	5.0	1.96	2.10

much smaller than that expected for a bipoisitive ion. However, a low value of 80 has been obtained for the binding constant of Fe<sup>2+</sup> with SDS micelles at an ionic strength of 0.12 mol dm<sup>-3</sup> where the surface potential is known to be much less [22]; the bigger VO<sup>2+</sup> ion with a much smaller charge/size ratio can be expected to have a still smaller value of the binding constant. The value of  $k'_m K_{1m} K_{2m} P_B^2 P_s$  has been calculated from the intercepts of these plots. The validity of the rate-law is further tested by calculating  $k_{\psi}$  from the knowledge of  $k'_m K_{1m} K_{2m} P_B^2 P_s$  ( $6.25 \times 10^4$ ) and  $K_A$ ,  $K_B$  and  $K_s$ . The experimental and calculated values of  $k_{\psi}$  are in reasonable agreement, (Table 3) further lending support to the rate-law. Thus the consistent results obtained for the oxidation of V(IV) by the iron(III)–phenanthroline complex in the presence of SDS micelles support the validity of the kinetic model employed by the authors for interpreting the micellar effect of SDS on the electron-transfer reactions of the iron(III)–phenanthroline complex.

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