Kinetics of Some Electron-Transfer Reactions of Iron(III)-2,2′-Bipyridyl Complex. Micellar Effect of Sodium Dodecyl Sulphate

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ABSTRACT: Iron(III)-2,2′-bipyridyl complex obtained, in situ, by direct mixing of iron(III) and 2,2′-bipyridyl, oxidizes aniline, thiourea, and ascorbic acid. 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 Berezin's approach. The binding constants of 2,2′-bipyridyl, aniline, thiourea, and ascorbic acid have been determined. © 1997 John Wiley & Sons, Inc. Int J Chem Kinet **29:** 171–179, 1997.

INTRODUCTION

Study of micellar effects on electron-transfer reactions is attracting the attention of a large number of workers. However, in most cases investigated so far, the reactions are of outer-sphere electron-transfer type proceeding through mechanisms involving simple bimolecular rate-limiting steps. On the other hand, many reactions involve one or more equilibria prior to the rate-limiting step and it is necessary to standardize the methodology in the kinetic analysis of such reactions. An effort has been made in this direction choosing the reactions of iron(III)-2,2′-bipyridyl complex, produced, in situ, by mixing iron(III) and 2,2′-bipyridyl. This complex is labile [1–4] and is different from *tris*(2,2′-bipyridyl) iron(III) which is substitution-inert and can not be obtained by direct mixing but only by the oxidation of the corresponding *tris*(2,2′-bipyridyl) 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 2,2′-bipyridyl and inverse square dependence on [H$^+$]. This has been shown to be due to preequilibria in which the iron(III)-bipyridyl complex is formed which subsequently oxidizes the substrate in the rate-limiting step. We have found that sodium dodecyl sulphate (SDS) has accelerating effect on these reactions. The kinetic analysis has been carried out combining the equilibrium technique and Berezin's partition model. To arrive at unambiguous conclusions about this model, the kinetic study has been carried out choosing reductants of diverse nature. The results are presented in this article.

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EXPERIMENTAL

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

The products of oxidation of aniline, thiourea, and ascorbic acid have been found to be azobenzene [7], formamidine disulphide [8], and dehydroascorbic acid [9], respectively, along with *tris*(2,2′-bipyridyl)-iron(II), the latter having a molar extinction coefficient of 8750 cm^{-1} mol^{-1} dm^3 ($\lambda = 510$ nm). In the presence of SDS, the molar extinction coefficient of $Fe(2,2'\text{-bipyridyl})_3^{2+}$ decreases to 8250 cm^{-1} mol^{-1} dm^3 at the cmc and remains constant with further increase in [SDS]. This shows that at [SDS] $\geq$ cmc, the product is completely bound by the micelle. The reaction mixture, in each case, has been found to initiate the polymerization of acrylo nitrile showing that the reaction involves the formation of free radical intermediates.

The course of reaction is followed by measuring the absorbance of *tris*(bipyridyl)-iron(II) formed at various times at 510 nm using Milton Roy (Spectronic 1201) spectrophotometer with kinetic attachment. The rate of oxidation of ascorbic acid is considerably higher and hence the course of the reaction is followed using stopped flow spectrophotometer (SFS-Biologic) at the same wavelength as in the case of oxidation of aniline or thiourea. At this wavelength, all the other mateials 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 mol dm^{-3} with sodium perchlorate. The concentration of 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 performed in each case and the rate constants were found to be reproducible within ± 5%.

RESULTS AND DISCUSSION

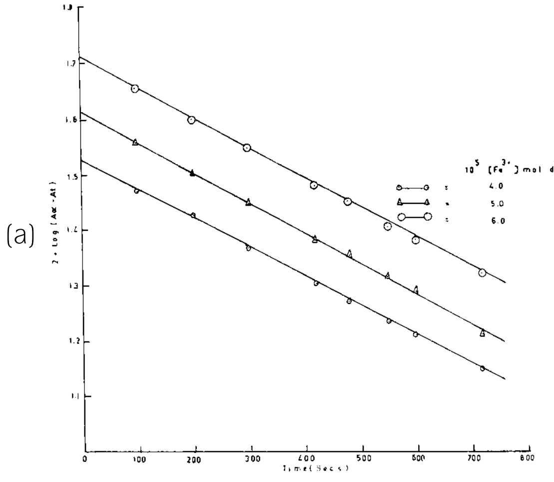
Determination of Binding Constants

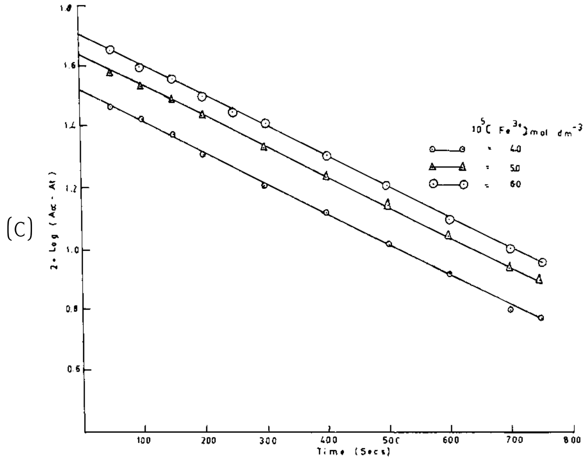
For determining binding constants of 2,2′-bipyridyl, aniline, thiourea, and ascorbic acid with SDS micelles at $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3} and $\mu = 0.1$ mol dm^{-3} adjusted with $NaClO_4$, spectra of these substances have been scanned at different SDS concentrations above cmc and under the conditions, [SDS] >> [substrate] or [bipyridyl]. A suitable wavelength is chosen ($\lambda = 255$ nm for aniline, 250 nm for thiourea, 220 nm for ascorbic acid, and 240 nm for 2,2′-bipyridyl). A_M and A_W^O, the absorbances in the presence of micelle and its absence, respectively, have been determined for various SDS concentrations. The binding constants have been determined using the equation [15].

$$1/(A_M - A_W^O) = 1/(A_M^O - A_W^O)\,(1 + 1/K_s C)$$

A_M^O is limiting absorbance in the presence of micelle. $1/(A_M - A_W^O)$ is plotted against C (i.e., stoichiometric concentration of SDS-cmc) and from slopes and intercepts of these plots, the binding constants of 2,2′-bipyridyl, aniline, thiourea, and ascorbic acid have been found to be 20.0 ± 2.0, 70.0 ± 3.0, 7.0 ± 2.0, and 28.0 ± 2.0 dm^3 mol^{-1}, respectively, at 30°C.

Interestingly with each of the substrates, the same kinetic pattern has been observed: the reaction obeys first-order kinetics in iron(III) (Fig. 1) and substrate (Table I) but the rate is directly proportional to $[\text{bipyridyl}]^2$ over a ten-fold variation of bipyridyl concentration. Plot of k_ψ vs. $[\text{bipy}]^2$ (Fig. 2) is a straight line passing through origin. The nonobtainment of intercept shows that the contribution to the overall rate by path involving Fe_{aq}^{3+} can be neglected. Further, the direct proportionality between k_ψ vs. $[\text{bipy}]^2$ rules out the involvement of the 1 : 1 complex, $Fe(bipy)^{3+}$, as the active oxidizing species. The rate is proportional to $1/[H^+]^2$ over a ten-fold variation of H^+ ion (Fig. 3). The reaction is markedly accelerated by SDS (Table II). The acceleration in the presence of the micelle may be due to [16]: (i) the binding of the reactants in a small volume of Stern layer of the micelle thus leading to considerable concentration effect and (ii) due to the possibility that the transition state is stabilized more than the initial state in the micellar pseudo-phase leading to the lowering of the activation energy. Though SDS catalysis has been observed in each case, the acceleration was maximum with aniline as substrate (thirty times in the presence of SDS concentration of 5.0×10^{-3} mol dm^{-3}) whereas the extent of acceleration in the oxidation of ascorbic





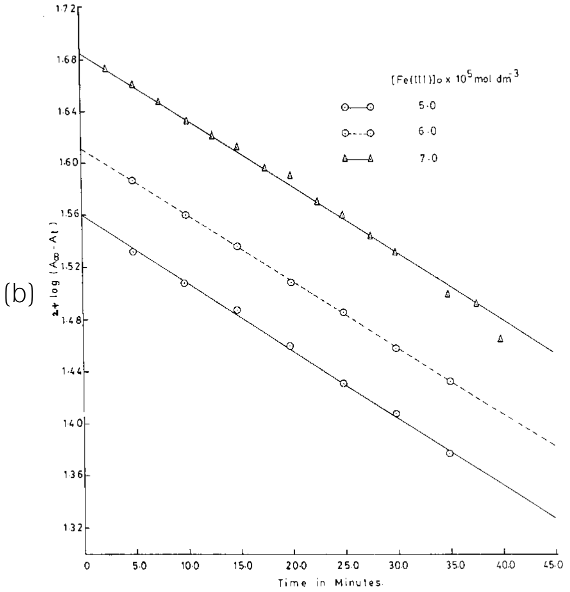


Figure 1 (a) Plots of Log ($A_\alpha - A_t$) vs. time. [Aniline] = 1.0×10^{-3} mol dm^{-3}; [Bipy] = 4.0×10^{-4} mol dm^{-3}; [H^+] = 4.0×10^{-3} mol dm^{-3}; [SDS] = 15.0×10^{-3} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; and Temp. = 30.0 ± 0.1°C. (b) Plots of Log ($A_\alpha - A_t$) vs. time. [Thiourea] = 2.0×10^{-3} mol dm^{-3}; [Bipy] = 4.0×10^{-4} mol dm^{-3}; [H^+] = 5.0×10^{-3} mol dm^{-3}; [SDS] = 10.0×10^{-3} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; and Temp. = 30.0 ± 0.1°C. (c) Plots of Log ($A_\alpha - A_t$) vs. time. [Ascorbic Acid] = 4.0×10^{-4} mol dm^{-3}; [Bipy] = 1.0×10^{-3} mol dm^{-3}; [SDS] = 1.0×10^{-2} mol dm^{-2}; [H^+] = 2.0×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; and Temp. = 30.0 ± 0.1°C.

acid and thiourea is much less, i.e., nearly six times. The greater acceleration of the oxidation of aniline may be due to greater concentration of aniline on the micellar surface. Further, aniline exists in the form of anilinium ion in the range of [H^+] ($1.0 \times 10^{-3} - 10.0 \times 10^{-3}$ mol dm^{-3}) whereas the ascorbic acid and thiourea exist as neutral species being bound less strongly by SDS micelles than the positively charged anilinium ion. There may also be greater stabilization of more positively charged transition state relative to the initial state in the case of anilinium ion.

The rate-[surfactant] profile has been found to have a maximum which is typical of bimolecular micellar-catalyzed processes [16]. According to Romsted [17] the maximum in the rate-[surfactant] profiles is produced by two opposing effects. Binding of the reactants in the Stern layers of the micelles begins at the cmc and they are transferred into small volume of the micellar pseudo-phase. There is thus concentration effect which is responsible for acceleration. This concentration effect is opposed by the continuous dilution of the reactants within the micellar pseudo-phase with increasing surfactant concentration. The former effect is predominant at lower surfactant concentration whereas the latter 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 bipyridyl can be considered to be in the protonated form, $HBipy^+$ (p*Ka* = 4.35 [18,19]). Aniline exists as anilinium ion (p*Ka* = 4.54 [20]) whereas thiourea and ascorbic acid are present in the unionized form under these conditions. (p*Ka* of ascorbic acid = 4.25 [21] and p*Ka* of protonated thiourea lies between −1 and −1.26 [22]).

Iron(III) can be expected to be mainly present in the form, Fe_{aq}^{3+}. The dimeric form is present in negligible concentration at the low iron(III) concentrations employed (10^{-5} mol dm^{-3}). The first stage hydrolysis constant, K_{11}, for the hydrolysis of iron(III) has a value of 1.07×10^{-3} mol dm^{-3} [23]. In the presence of SDS micelles which bind Fe^{3+} more strongly than $FeOH^{2+}$, the hydrolysis constant, K'_{11} can be expected to decrease. K_{11} is related to K'_{11} by

Table I Effect of [Substrate] on Rate

A. Oxidation of Aniline: [Fe(III)] = 5.0×10^{-5} mol dm^{-3}; [Bipy] = 4.0×10^{-4} mol dm^{-3}; [H$^+$] = 6.0×10^{-3} mol dm^{-3}; [SDS] = 1.5×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

10^3[Aniline] mol dm^{-3}	$10^4 k_\psi$ s^{-1}
0.5	2.70
1.0	5.23
1.5	8.35
2.0	10.58
2.5	13.43
3.0	15.50
4.0	21.10
5.0	27.05

B. Oxidation of Thiourea: [Fe(III)] = 5.0×10^{-5} mol dm^{-3}; [Bipy] = 4.0×10^{-4} mol dm^{-3}; [H$^+$] = 5.0×10^{-3} mol dm^{-3}; [SDS] = 1.5×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

10^3[Thiourea] mol dm^{-3}	$10^4 k_\psi$ s^{-1}
0.5	0.45
1.0	0.88
1.5	1.30
2.0	1.75
2.5	2.25
3.0	2.65
4.0	3.50
5.0	4.50

C. Oxidation of Ascorbic Acid: [Fe(III)] = 2.0×10^{-5} mol dm^{-3}; [Bipy] = 1.0×10^{-3} mol dm^{-3}; [H$^+$] = 6.0×10^{-3} mol dm^{-3}; [SDS] = 1.0×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

10^3[Ascorbic acid] mol dm^{-3}	$10^2 k_\psi$ s^{-1}
1.0	0.64
2.0	1.28
4.0	2.54
5.0	3.13
6.0	3.76
8.0	5.08
10.0	6.27

the equation: $K'_{11} = K_{11}\,(1 + K'_A C)/(1 + K_A C)$ [16]. K'_A and K_A are the binding constants of FeOH^{2+} and Fe^{3+} respectively. Assuming that the binding is electrostatic in nature, K'_A and K_A can be calculated using the equation, $K = P\overline{V}$ where $\overline{V}$ is the standard molar volume of SDS (0.246 dm^3 mol^{-1} [24]). The partition coefficient, P, of charged species between micellar and aqueous phase is given by the equation P = $e^{Z\psi/25.7}$ [25] at 25°C where ψ is the surface potential of the micelle ranging between 85–110 mv [24] and z is the charge of the ion bound at the micelle. Assuming that ψ has a value of 85 mv, K'_A, the binding constant of Fe^{3+}, is 5.0×10^3 dm^3 mol^{-1} and K'_A has a value of 1.8×10^2 dm^3 mol^{-1}. The value of K'_{11} has then a value of 9.3×10^{-5} mol dm^{-3}. Thus in the presence of SDS, the concentration of FeOH^{2+} ($= (K'_{11}\,[\text{Fe(III)}]_{\text{total}})/(K'_{11} + [\text{H}^+])$) can be considered to be present 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.

$$\begin{array}{ccc} \text{Fe}^{3+}_{\text{w}} & \text{HBipy}^+_{\text{w}} & \text{S}_{\text{w}}\ \text{(Substrate)} \\ \Big\Updownarrow {\scriptstyle K_A} & \Big\Updownarrow {\scriptstyle K_B} & \Big\Updownarrow {\scriptstyle K_S} \\ \text{Fe}^{3+}_{\text{m}} & \text{HBipy}^+_{\text{m}} & \text{S}_{\text{m}} \end{array} \quad (1)$$

$$\text{Fe}^{3+}_{\text{m}} + \text{HBipy}^+_{\text{m}} \overset{K_{1,m}}{\rightleftharpoons} [\text{Fe(Bipy)}]^{3+}_{\text{m}} + \text{H}^+_{\text{m}} \quad (2)$$

$$[\text{Fe(Bipy)}]^{3+}_{\text{m}} + \text{HBipy}^+_{\text{m}} \overset{K_{2,m}}{\rightleftharpoons} [\text{Fe(Bipy)}_2]^{3+}_{\text{m}} + \text{H}^+_{\text{m}} \quad (3)$$

$$\text{Fe}^{3+}_{\text{w}} + \text{HBipy}^+_{\text{w}} \overset{K_{1,w}}{\rightleftharpoons} [\text{Fe(Bipy)}]^{3+}_{\text{w}} + \text{H}^+_{\text{w}} \quad (4)$$

$$[\text{Fe(Bipy)}]^{3+}_{\text{m}} + \text{HBipy}^+_{\text{w}} \overset{K_{2,w}}{\rightleftharpoons} [\text{Fe(Bipy)}_2]^{3+}_{\text{w}} + \text{H}^+_{\text{w}} \quad (5)$$

$$[\text{Fe(Bipy)}_2]^{3+}_{\text{m}} + \text{S}_{\text{m}} \xrightarrow{K_m} [\text{Fe(Bipy)}_2]^{2+}_{\text{m}} + \text{Product}_{\text{m}} \quad \text{(rate determining)} \quad (6)$$

$$[\text{Fe(Bipy)}_2]^{3+}_{\text{w}} + \text{S}_{\text{w}} \xrightarrow{K_w} [\text{Fe(Bipy)}_2]^{2+}_{\text{w}} + \text{Product}_{\text{w}} \quad \text{(rate determining)} \quad (7)$$

According to the scheme the reaction in micellar as well as aqueous phase involves a prior interaction between Fe^{3+} and 2,2′-bipyridyl, (the latter mainly existing in the form of HBipy$^+$) leading to the formation of 1:2 complex, Fe(Bipy)$_2$$^{3+}$, in successive equilibria, which is the active oxidizing species. The complex formed between FeOH^{2+} and bipyridyl, (Bipy)$_2$FeOH^{2+} with smaller positive charge does not appear to be effective oxidizing species. It is known that FeOH^{2+} is a poorer oxidant compared to Fe^{3+} [26]. In all these cases, free radical intermediates of the reductants are formed in the rate-determining step [6–7]. In the case of oxidation of aniline C_6H_5NH is formed which is further oxidized to C_6H_5N in a fast step. C_6H_5N dimerizes to produce the final azo product. In the case of thiourea, thiourea radicals are formed in the rate-limiting step which dimerize in the fast step producing the disulphide product. In the case

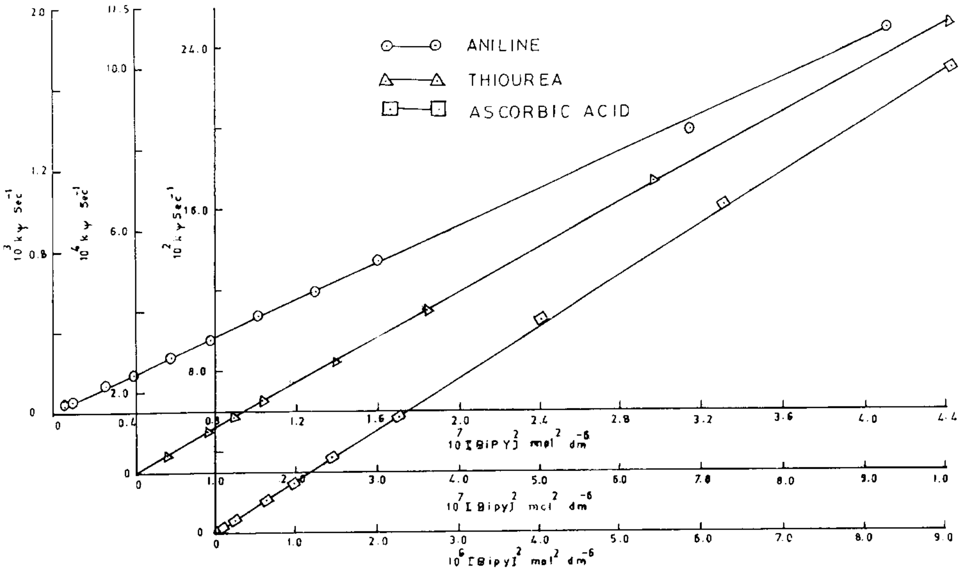


Figure 2 Plots of k_ψ vs. [Bipyridyl]^2. (a) Aniline: [Fe(III)] = 5.0×10^{-5} mol dm^{-3}; [H$^+$] = 5.0×10^{-3} mol dm^{-3}; [SDS] = 1.5×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; Temp. = 30.0 ± 0.1°C; and [Aniline] = 1.0×10^{-3} mol dm^{-3}. (b) Thiourea: [Fe(III)] = 5.0×10^{-5} mol dm^{-3}; [H$^+$] = 5.0×10^{-3} mol dm^{-3}; [SDS] = 1.5×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; Temp. = 30.0 ± 0.1°C; and [Thiourea] = 2.0×10^{-3} mol dm^{-3}. (c) Ascorbic Acid: [Fe(III)] = 2.0×10^{-5} mol dm^{-3}; [H$^+$] = 6.0×10^{-3} mol dm^{-3}; [SDS] = 1.0×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; Temp. = 30.0 ± 0.1°C; and [Ascorbic acid] = 4.0×10^{-4} mol dm^{-3}.

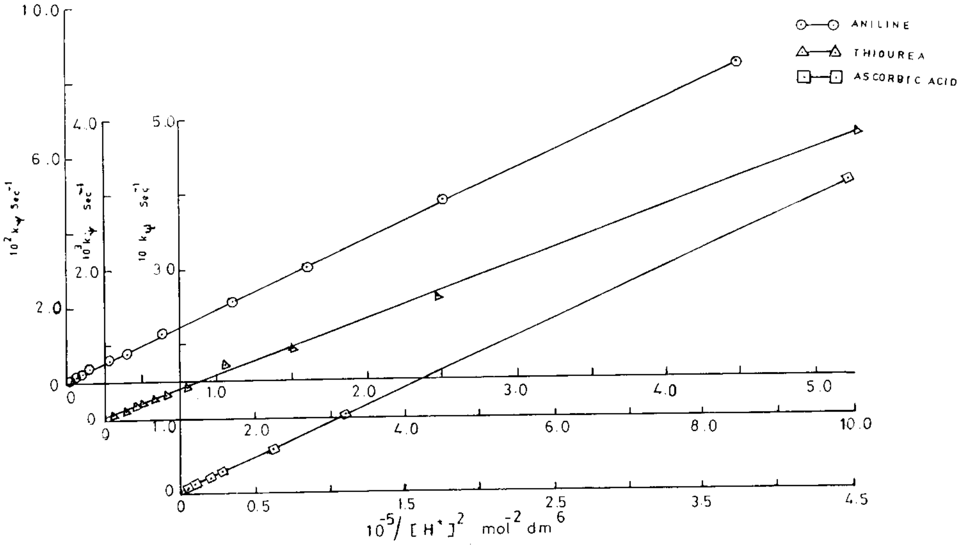


Figure 3 Plots of 1/[H$^+$]^2 vs. k_ψ. (a) Aniline: [Fe(III)] = 5.0×10^{-5} mol dm^{-3}; [Bipy] = 4.0×10^{-4} mol dm^{-3}; [SDS] = 1.5×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; Temp. = 30.0 ± 0.1°C; and [Aniline] = 1.0×10^{-3} mol dm^{-3}. (b) Thiourea: [Fe(III)] = 5.0×10^{-5} mol dm^{-3}; [Bipy] = 4.0×10^{-4} mol dm^{-3}; [SDS] = 1.5×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; Temp. = 30.0 ± 0.1°C; and [Thiourea] = 2.0×10^{-3} mol dm^{-3}. (c) Ascorbic Acid: [Fe(III)] = 2.0×10^{-5} mol dm^{-3}; [Bipy] = 1.0×10^{-3} mol dm^{-3}; [SDS] = 1.0×10^{-2} mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; Temp. = 30.0 ± 0.1°C; and [Ascorbic Acid] = 4.0×10^{-4} mol dm^{-3}.

Table II Effect of [SDS] on the Rate

A. Oxidation of Aniline: [Fe(III)] = 5.0 × 10^{-5} mol dm^{-3}; [Bipy] = 4.0 × 10^{-4} mol dm^{-3}; [H^{+}] = 4.0 × 10^{-3} mol dm^{-3}; [Aniline] = 2.0 × 10^{-3} mol dm^{-3}; μ = 0.1 mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

10^3[SDS] mol dm^{-3}	$10^4 k_\psi$ s^{-1}
0.0	1.72
5.0	51.80
8.0	43.00
10.0	36.80
15.0	24.80
20.0	17.16
25.0	13.63
30.0	10.54
35.0	8.33
40.0	6.72
45.0	5.56

B. Oxidation of Thiourea: [Fe(III)] = 5.0 × 10^{-5} mol dm^{-3}; [Bipy] = 4.0 × 10^{-4} mol dm^{-3}; [H^{+}] = 5.0 × 10^{-3} mol dm^{-3}; [Thiourea] = 2.0 × 10^{-3} mol dm^{-3}; μ = 0.1 mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

10^3[SDS] mol dm^{-3}	$10^4 k_\psi$ s^{-1}
0.0	1.05
2.0	6.54
5.0	3.45
8.0	2.30
10.0	2.11
15.0	1.75
20.0	1.45
25.0	1.23
30.0	1.05
35.0	0.91

C. Oxidation of Ascorbic Acid: [Fe(III)] = 2.0 × 10^{-5} mol dm^{-3}; [Bipy] = 1.0 × 10^{-3} mol dm^{-3}; [H^{+}] = 6.0 × 10^{-3} mol dm^{-3}; [Ascorbic acid] = 4.0 × 10^{-4} mol dm^{-3}; μ = 0.1 mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

10^3[SDS] mol dm^{-3}	$10^2 k_\psi$ s^{-1}
0.0	3.35
1.0	8.65
2.0	16.20
3.0	8.40
4.0	5.70
6.0	3.17
8.0	2.80
10.0	2.53
12.0	2.20
16.0	1.80
18.0	1.60
20.0	1.38

of oxidation of ascorbic acid, the free radical intermediate formed in the rate-limiting step is rapidly oxidized to dehydroascorbic acid. The reduction product of $\mathrm{Fe(Bipy)_2}^{3+}$ is $\mathrm{Fe(Bipy)_2}^{2+}$ which interacting with HBipy^{+} forms the *tris* bipyridyl iron(II).

$$\mathrm{Fe(Bipy)_2^{3+}} + \mathrm{HBipy^+} \xrightarrow{\text{fast}} \mathrm{Fe(Bipy)_3^{2+}} + \mathrm{H^+} \quad (8)$$

This step should not be rate-determining, the only rate determining steps being steps 6 and 7 as required by the concentration dependence of rate on the reactants and bipyridyl. If the formation of tris(bipyridyl)iron(II) (step 8) is also rate-determining, plot of log ($A_\alpha - A_t$) 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

$$= \frac{\begin{array}{c} k_{\mathrm{m}}K_{1,\mathrm{m}}K_{2,\mathrm{m}}\mathrm{p_A p_B}^2\,\mathrm{p_S}[\mathrm{Fe(III)}]_t/(1 + K_{\mathrm{A}}C) \\ [\mathrm{HBipy}^+]_t^2/(1 + K_{\mathrm{B}}C)^2\,[\mathrm{S}]_t/(1 + K_{\mathrm{S}}C)\,\overline{\mathrm{V}}C \end{array}}{\begin{array}{c} [\mathrm{H}^+]_{\mathrm{m}}^2 + \mathrm{p_B}K_{1,\mathrm{m}}[\mathrm{HBipy}^+]_t/(1 + K_{\mathrm{B}}C)\,[\mathrm{H}^+]_{\mathrm{m}} \\ + \mathrm{p_B}^2K_{1,\mathrm{m}}K_{2,\mathrm{m}}[\mathrm{HBipy}^+]_t^2/(1 + K_{\mathrm{B}}C)^2 \end{array}}$$

$$+ \frac{\begin{array}{c} k_{\mathrm{w}}K_{1,\mathrm{w}}K_{2,\mathrm{w}}[\mathrm{Fe(III)}]_t/(1 + K_{\mathrm{A}}C)\,[\mathrm{HBipy}^+]_t^2/ \\ (1 + K_{\mathrm{B}}C)^2\,[\mathrm{S}]_t/(1 + K_{\mathrm{S}}C)\,(1 - \overline{\mathrm{V}}C) \end{array}}{\begin{array}{c} [\mathrm{H}^+]_{\mathrm{w}}^2 + K_{1,\mathrm{w}}[\mathrm{HBipy}^+]_t/(1 + K_{\mathrm{B}}C)\,[\mathrm{H}^+]_{\mathrm{w}} \\ + K_{1\mathrm{w}}K_{2\mathrm{w}}[\mathrm{HBipy}^+]_t^2/(1 + K_{\mathrm{B}}C)^2 \end{array}} \quad (9)$$

In this equation, $\mathrm{p_A}$, $\mathrm{p_B}$, and $\mathrm{p_S}$ represent the partition coefficients of Fe^{3+}, HBipy^{+}, and substrate between micellar and aqueous pseudo-phases, K_{A}, K_{B}, K_{S} are the corresponding binding constants; ^{2}m and ^{2}w signify micellar and aqueous phases. $\overline{\mathrm{V}}$ is molar volume, and 'C' is ([SDS]-cmc). The equation though looking formidable, undergoes considerable simplification. The binding constant of iron(III) (K_{A}) has a value around 5.0 × 10^3 dm^3 mol^{-1} and hence $(1 + K_{\mathrm{A}}C) \cong K_{\mathrm{A}}C$ at [SDS] >> cmc. Thus iron(III) is mostly present in the micellar phase and hence the extent of reaction in aqueous phase (i.e., the second term in eq. (9)) can be neglected. Further, the rate is directly proportional to 1/[H^{+}]^2 and [Bipy]^2. Hence, the terms

$$\frac{K_{1\mathrm{m}}\mathrm{p_B}\,[\mathrm{H}^+]_{\mathrm{m}}[\mathrm{HBipy}^+]_t}{(1 + K_{\mathrm{B}}C)} \text{ and }$$

$$\frac{K_{1\mathrm{m}}K_{2\mathrm{m}}\mathrm{p_B}^2\,[\mathrm{HBipy}^+]_t^2}{(1 + K_{\mathrm{B}}C)^2}$$

in eq. (9) can be considered to be negligible in comparison with $[\mathrm{H}^+]_{\mathrm{m}}^2$. Hence under these conditions, the equation reduces to

Rate

$$= \frac{k_m K_{1m} K_{2m}\, P_B{}^2\, P_B\, [Fe^{3+}]_t\, [H\ bipy^+]_t{}^2\, [S]_t}{([H^+])_m{}^2\, (1 + K_B C)^2\, (1 + K_S C)} \qquad (10)$$

In eq. (9), $[H^+]_m$ is the concentration of H^+ ion in moles per litre of micellar phase ($m_{H+}{}^s/\overline{V}$ in Romsted's formulation) given by the equation [27]

$$[H^+]_m = \frac{0.82\, [H^+]_t}{\{[H^+]_t + [Na^+]_t\}\, \overline{V}} \qquad (11)$$

The equation approximates to [27]

$$[H^+]_m = \frac{0.82\, [H^+]_t}{[Na^+]_t\, \overline{V}} \qquad (12)$$

under the experimental conditions employed, $[Na^+]_t >> [H^+]_t$. Hence, $[H^+]_m$ is directly proportional to $[H^+]_t$. The rate constant, k_ψ (= Rate/$[Fe^{3+}]_t$),

$$k_\psi = \frac{k'_m K_{1m} K_{2m} p_B{}^2 p_S\, [HBipy]_t{}^2 [S]_t}{([H^+]_t{}^2 (1 + K_B C)\, {}^2 (1 + K_S C))} \qquad (13)$$

where

$$k'_m = \frac{k_m}{(0.82[H^+]/[Na^+]_t\, \overline{V})^2}$$

or

$$\frac{1}{k_\psi (1 + K_B C)^2} = \frac{[H^+]_t{}^2}{k'_m K_{1m} K_{2m} p_B{}^2 p_S\, [HBipy^+]_t{}^2\, [S]_t} + \frac{K_S C [H^+]_t{}^2}{k'_m K_{1m} K_{2m} p_B{}^2 p_S\, [HBipy^+]_t{}^2\, [S]_t} \qquad (14)$$

The validity of rate-law has been tested by calculating $1/(k_\psi (1 + K_B C)^2)$ and plotting vs. 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 constants of substrates ($C_6H_5NH_3{}^+$, H_2A, and Thiourea) calculated from the values of slopes and intercepts of the above plot are presented in Table III and compared with the values determined. The value of $k'_m K_{1m} K_{2m} P_B{}^2 P_S$ has been calculated from the intercepts of these plots. The results show that the value of the binding constant obtained from these kinetic data are in reasonable agreement with the values obtained by nonkinetic method supporting the validity of rate-law and

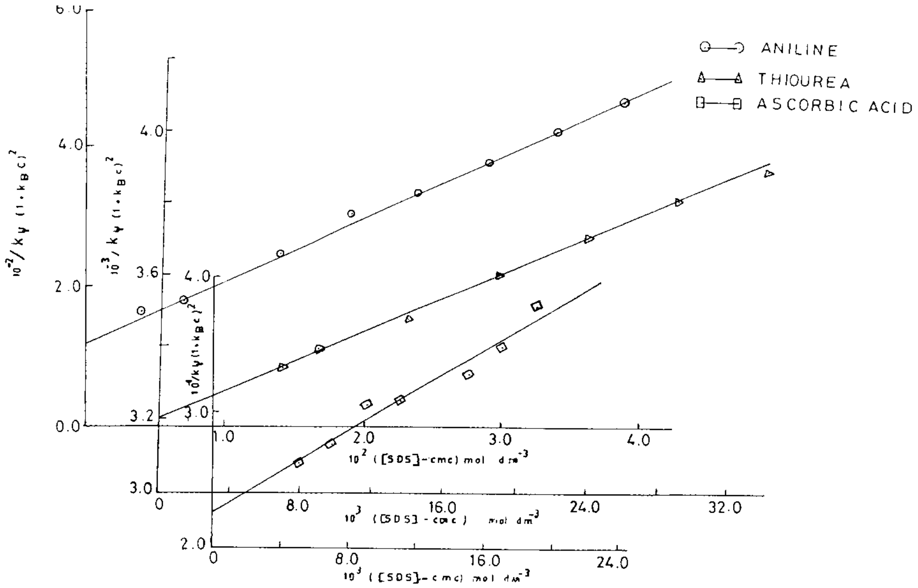


Figure 4 Plots of $1/k_\psi (1 + K_B C)^2$ vs. [SDS]-cmc. (a) Aniline: $[Fe(III)] = 5.0 \times 10^{-5}$ mol dm^{-3}; $[Bipy] = 4.0 \times 10^{-4}$ mol dm^{-3}; $[H^+] = 4.0 \times 10^{-3}$ mol dm^{-3}; $[Aniline] = 2.0 \times 10^{-3}$ mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; and Temp. = 30.0 ± 0.1°C. (b) Thiourea: $[Fe(III)] = 5.0 \times 10^{-5}$ mol dm^{-3}; $[Bipy] = 4.0 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 5.0 \times 10^{-3}$ mol dm^{-3}; $[Thiourea] = 2.0 \times 10^{-3}$ mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; and Temp. = 30.0 ± 0.1°C. (c) Ascorbic Acid: $[Fe(III)] = 2.0 \times 10^{-5}$ mol dm^{-3}; $[Bipy] = 1.0 \times 10^{-3}$ mol dm^{-3}; $[H^+] = 6.0 \times 10^{-3}$ mol dm^{-3}; $\mu = 0.1$ mol dm^{-3}; [Ascorbic acid] $= 4.0 \times 10^{-4}$ mol dm^{-3}; and Temp. = 30.0 ± 0.1°C.

Table III Binding Constants

S. No	Species	Binding Constants Obtained from Kinetic Data	Binding Constants Obtained from Spectral Data
1	Bipyridyl	–	20.0 ± 2.0
2	Aniline	73.0 ± 2.0	70.0 ± 3.0
3	Thiourea	9.0 ± 2.0	7.0 ± 0.6
4	Ascorbic acid	33.0 ± 2.0	28.0 ± 6.0

Table IV Effect of H$^+$ Ion and Bipyridl Concentrations on Rate

A. Oxidation of Aniline: $[\mathrm{Fe(III)}] = 4.0 \times 10^{-5}$ mol dm^{-3}; [Aniline] $= 1.0 \times 10^{-3}$ mol dm^{-3}; [SDS] $= 1.5 \times 10^{-2}$ mol dm^{-3}; $[K_S] = 73.0$ mol^{-1} dm^{-3}; $K_B = 20.0$ mol^{-1} dm^3; $k_m K_{1m} K_{2m} P_B{}^2 P_S = 4.0 \times 10^2$; $\mu = 0.1$ mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

$10^3[\mathrm{H}^+]$ mol dm^{-3}	10^4[Bipy] mol dm^{-3}	$10^3 k_{\psi\ \mathrm{obs}}$ s^{-1}	$10^3 k_{\psi\ \mathrm{cal}}$ s^{-1}
5.0	1.6	0.13	0.124
5.0	2.0	0.18	0.193
5.0	2.8	0.35	0.378
2.5	4.0	2.98	3.090
4.0	4.0	1.24	1.210
5.0	4.0	0.70	0.770

B. Oxidation of Thiourea: $[\mathrm{Fe(III)}] = 5.0 \times 10^{-5}$ mol dm^{-3}; [Thiourea] $= 2.0 \times 10^{-3}$ mol dm^{-3}; [SDS] $= 1.5 \times 10^{-2}$ mol dm^{-3}; $K_S = 9.0$ mol^{-1} dm^{-3}; $K_B = 20.0$ mol^{-1} dm^3; $k_m K_{1m} K_{2m} P_B{}^2 P_S = 24.3$; $\mu = 0.1$ mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

$10^3[\mathrm{H}^+]$ mol dm^{-3}	10^4[Bipy] mol dm^{-3}	$10^4 k_{\psi\ \mathrm{obs}}$ s^{-1}	$10^4 k_{\psi\ \mathrm{cal}}$ s^{-1}
5.0	2.0	0.44	0.42
5.0	3.0	1.00	0.95
5.0	4.0	1.75	1.68
2.5	4.0	7.15	6.74
3.0	4.0	4.05	4.68
4.0	4.0	2.30	2.63

C. Oxidation of Ascorbic Acid: $[\mathrm{Fe(III)}] = 2.0 \times 10^{-5}$ mol dm^{-3}; [Ascorbic acid] $= 4.0 \times 10^{-4}$ mol dm^{-3}; [SDS] $= 1.0 \times 10^{-2}$ mol dm^{-3}; $K_S = 33.0$ mol^{-1} dm^3; $K_B = 20.0$ mol^{-1} dm^3; $k_m K_{1m} K_{2m} P_B{}^2 P_S = 4.0 \times 10^3$; $\mu = 0.1$ mol dm^{-3}; and Temp = 30.0 ± 0.1°C.

$10^3[\mathrm{H}^+]$ mol dm^{-3}	10^3[Bipy] mol dm^{-3}	$10^2 k_{\psi\ \mathrm{obs}}$ s^{-1}	$10^2 k_{\psi\ \mathrm{cal}}$ s^{-1}
6.0	1.0	2.52	2.46
6.0	1.5	5.70	5.53
6.0	2.0	10.50	9.87
7.0	1.0	1.90	1.81
8.0	1.0	1.39	1.38
10.0	1.0	0.92	0.86

hence the mechanism. The validity of the rate-law is further tested by calculating k_ψ from the knowledge of $k'_m K_{1m} K_{2m} p_B{}^2 p_S$ and K_A, K_B and K_S and using eq. (13).

In each of the oxidations, the experimental and calculated value of k_ψ are in reasonable agreement (Table IV) further lending support to the rate-law. Thus the consistent results obtained for the oxidation of these reductants of diverse nature by the iron(III)-bipyridyl 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)-bipyridyl complex.

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APPENDIX

Since the reaction is investigated under the conditions, $[\mathrm{Fe(III)}]_O << [\mathrm{Bipy}]_O$, [SDS], the mass balance can be written in the form:

$$[\mathrm{Fe(III)}]_{m/w} = [\mathrm{Fe}^{3+}]_{m/w} + [\mathrm{Fe(Bipy)}]_{m/w}{}^{3+} + [\mathrm{Fe(Bipy)}_2]_{m/w}{}^{3+} \quad (1)$$

where $[\mathrm{Fe(III)}]_{m/w}$ is the total Fe(III) concentration in micellar or aqueous phase and $[\mathrm{Fe}^{3+}]_{m/w}$, $[\mathrm{Fe(Bipy)}]_{m/w}{}^{3+}$, and $[\mathrm{Fe(Bipy)}_2]_{m/w}{}^{3+}$ are the corresponding equilibrium concentration in micellar or aqueous phases. The concentration of the reactive oxidizing species $[\mathrm{Fe(Bipy)}_2]^{3+}$ in micellar or aqueous phases is given by:

$$[\mathrm{Fe(Bipy)}_2]_{m/w}{}^{3+} = \frac{K_{1m/w} K_{2m/w} [\mathrm{HBipy}]_{m/w}{}^2 [\mathrm{Fe(III)}]_{m/w}}{[\mathrm{H}^+]_{m/w}{}^2 + K_{1m/w} [\mathrm{HBipy}]_{m/w} [\mathrm{H}^+]_{m/w} + K_{1m/w} K_{2m/w} [\mathrm{HBipy}]_{m/w}{}^2}$$

According to Berezin for solute, x, distribution between micellar and aqueous phases, the concentration in micellar phase is given by the equation,

$$[\mathrm{x}]_{\mathrm{m}} = \frac{\mathrm{P}_X[\mathrm{x}]_t}{1 + K_{\mathrm{x}}[\mathrm{C}]} \qquad 3(\mathrm{A})$$

and

$$[\mathrm{x}]_{\mathrm{w}} = \frac{[\mathrm{x}]_t}{1 + K_{\mathrm{x}}[\mathrm{C}]} \qquad 3(\mathrm{B})$$

where $[\mathrm{x}]_t$ is the total concentration, P_{x} is partition coefficient between pseudo-phases and K_{x} is the binding constant of x.

The total rate of the reaction according to the mechanism is given by the equation:

$$\begin{aligned}\text{Rate} &= k_{\mathrm{m}}[\mathrm{Fe(Bipy)_2}^{3+}]_{\mathrm{m}}[\mathrm{Co(Bipy)_3}^{2+}]_{\mathrm{m}}\,\overline{\mathrm{V}}\mathrm{C} \\ &\quad + k_{\mathrm{w}}[\mathrm{Fe(Bipy)_3}^{2+}]_{\mathrm{w}}[\mathrm{Co(Bipy)_3}^{2+}]_{\mathrm{w}}(1 - \overline{\mathrm{V}}\mathrm{C}) \qquad (4)\end{aligned}$$

Using the eqs. (1)–(4) the rate law for the system is given as:

$$\text{Rate} = \frac{\begin{array}{c} k_{\mathrm{m}}K_{1\mathrm{m}}K_{2\mathrm{m}}\{\mathrm{P_A}[\mathrm{Fe}^{3+}]_t/(1 + K_{\mathrm{A}}\mathrm{C})\}\{\mathrm{P_B}^2[\mathrm{HBipy}^+]_t^2/ \\ (1 + K_{\mathrm{B}}\mathrm{C})^2\}\{\mathrm{P_S}[[\mathrm{Co(Bipy)_3}]^{2+}]_t/(1 + K_{\mathrm{S}}\mathrm{C})\,\overline{\mathrm{V}}\mathrm{C}\end{array}}{\begin{array}{c}([\mathrm{H}^+]_{\mathrm{m}}^2 + K_{1\mathrm{m}}\mathrm{P_B}[\mathrm{HBipy}^+]_t[\mathrm{H}^+]_{\mathrm{m}}/(1 + K_{\mathrm{B}}\mathrm{C}) \\ + K_{1\mathrm{m}}K_{2\mathrm{m}}\mathrm{P_B}^2\,[\mathrm{HBipy}^+]_t^2/(1 + K_{\mathrm{B}}\mathrm{C})^2\end{array}} + \frac{\begin{array}{c} k_{\mathrm{w}}K_{1\mathrm{w}}K_{2\mathrm{w}}\{[\mathrm{Fe}^{3+}]_t/1 + K_{\mathrm{A}}\mathrm{C})\} \\ \{[\mathrm{HBipy}^+]_t^2/)1 + K_{\mathrm{B}}\mathrm{C})^2\} \\ \{[\mathrm{Co(Bipy)_3}^{2+}]_t/(1 + K_{\mathrm{S}}\mathrm{C})\}\,(1 - \overline{\mathrm{V}}\mathrm{C})\end{array}}{\begin{array}{c}([\mathrm{H}^+]_{\mathrm{w}}^2 + K_{1\mathrm{w}}[\mathrm{HBipy}^+]_t[\mathrm{H}^+]_{\mathrm{w}}/(1 + K_{\mathrm{B}}\mathrm{C}) \\ + K_{1\mathrm{w}}K_{2\mathrm{w}}[\mathrm{HBipy}^+]_t^2/(1 + K_{\mathrm{B}}\mathrm{C})^2\end{array}} \qquad (5)$$

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