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Kinetic and mechanistic study of electron transfer from L-ascorbic acid and diols to Fe(III) chelates in aqueous H_2SO_4 acid and micellar media

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Abstract

A detailed kinetic study of oxidation of L-ascorbic acid and other related diols has been undertaken by two types of Fe(III) chelates viz., blue complexes and Blau's yellow complexes. Application of Marcus theory substantiated an inner sphere electron transfer from L-ascorbic acid (or diol) to Fe(III) chelates (Blau's yellow complexes), while an outer sphere mechanism was operative in the case of blue complexes. Reactions were found to be catalysed by both anionic and cationic micelles (SDS and CTAB respectively). Catalysis was explained due to the stabilisation of transition state due to electrostatic interactions operating between cationic form of Fe(III) chelates and anionic CTAB respectively. Mechanism of micellar path could be explained by binding model.

Keywords: Kinetics; Mechanism; Electron transfer; Ascorbic acid; Iron; Sulphuric acid; Micelles

1. Introduction

Oxidation of organic compounds does not proceed by Fe(III) in sulphuric acid medium even under reflux conditions. However, the reaction proceeds smoothly even at ordinary temperatures in the presence of ligands such as 1,10-phenanthroline (phen), α,α'-bipyridyl (bipy). Our preliminary investigations show that the oxidation is faster in low acidities and very slow or almost sluggish in higher concentrations of sulphuric acid even in the presence of heterocyclic (ligands) bases such as phenanthroline. A survey of the literature shows that yellow–brown complexes are obtained when bipyridyl, phenanthroline or substituted analogous ligands are directly added to Fe(III) [1–5]. These yellow–brown complexes are proved to be entirely different from blue complexes of Fe(III) which are obtained only by the oxidation of Fe(II)chelates of phen, bipy, (for example, ferroin). It was also further reported that yellow complexes of Fe(III) are substitution labile while the blue complexes are substitution inert. Following the kinetics of oxidation of various organic compounds [3–9] by Fe(III) in H_2SO_4 medium (catalysed by phen or bipy) an account is now given on the kinetic investigation of certain benzene diols (H_2A) viz., L-ascorbic acid, catechol, hydroquinone and resorcinol by the same oxidising species. It

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is also proposed to correlate the specific rate constants with electrode potentials using Marcus' theory of linear free energy relationship [10].

In order to support the findings of this study, the authors have also taken up this investigation by using blue complexes of Fe(III) as oxidants in addition to yellow complexes.

The effect of organised assemblies on the rates and equilibria of reactions has attracted the attention of several chemists and biochemists in recent past [11]. The interest is mainly based on the realization that many biochemical reactions proceed in micro heterogeneous systems which comprise an aqueous and a lipophilic moiety [12]. Among the biochemical functions, the redox systems are of primary importance because entire electron transport occurs in these systems [13]. The investigation of electron transfer processes in micellar media is, however, taken up by examining properly selected reactions [14–18]. Oxidation of ferrocene by Fe^{3+} (aquo ion) [15,16], metal chelates with hydrophobic ligands such as tris(1,10-phenanthroline)–cobalt(III) and analogous complexes [17]. On the basis of these studies, it was proposed that ferrocene and ferrocenium ion could be used as suitable probes for metalloprotein redox studies [18]. Such interesting features prompted the authors to extend the present investigation in organised micellar media in order to gain an insight into the mechanistic aspects.

2. Experimental details

2.1. Reagents

Fe(III) sulphate solution has been prepared and standardised according to literature procedures [1–5]. Benzene diols (H_2A) such as resorcinol, hydroquinone, catechol, L-ascorbic acid, 1,10-phenanthroline, α,α'-bipyridyl, nitrophenanthroline, sodium lauryl sulphate (SDS or SLS), cetyltrimethylammonium bromide (CTAB) and Triton X-100 (Tx) are either Fluka, Aldrich or Merck samples. All other chemicals are of BDH AnalaR Grade.

Methanol (Merck) has been refluxed over KOH and I_2 for about two hours, distilled twice and used for solvent effect studies. The dielectric constant data for different aquomethanol mixtures have been obtained from literature [10].

2.2. Kinetic measurements

The progress of the reaction has been followed by recording the absorbance values of ferroin or corresponding analogous Fe(II) chelates at 510 nm and regular intervals of time on Beckman DU-Model spectrophotometer equipped with thermostated quartz cells. Results are reproducible within $\pm 3\%$.

2.3. Potentiometric measurements

Dissociation constants for the step

$$H_2A \overset{K_d}{\rightleftharpoons} HA^- + H^+$$

have been determined by potentiometric techniques with a Systronics (India) pH meter equipped with a combination of glass and calomel electrode assembly. Formal potentials for Fe(III)/Fe(II) in the presence of ligand and H_2A/A couples in sulphuric acid medium have been determined according to standard procedures [10] using saturated calomel (SCE) and platinum (contact) electrode assembly connected through KNO_3 salt bridge. The formal reduction potentials of H_2A/A have been determined by partially oxidising the substrate with the addition of Tl(III) and then recording emf potentiometrically [10].

2.4. Polymerisation test

The addition of deaerated olefinic monomer (acrylamide and/or acrylonitrile) to the reaction mixture, has induced vinyl polymerisation indicating the formation of free radicals in the system.

3. Results and discussion

3.1. Salient features of the study

3.1.1. Stoichiometry and product analysis

When the reaction was conducted under the conditions [Fe(III)L] ≫ [Substrate] or (H_2A), it was noticed that one mole of dihydroxy compound consumed two moles of oxidant to give a dienone type compound as the product of oxidation. Products were analysed by characteristic spot tests according standard literature procedures [9,10].

$$2Fe(III)L + R\langle^{OH}_{OH} \rightarrow 2Fe(II)L + R\langle^{O}_{O} + 2H^+$$

where $R\langle^{OH}_{OH}$ indicates dihydroxy compound.

3.1.2. Under the conditions [L] ≫ [Fe(III)] and [H_2A] ≫ Fe(III)

Plots of $\ln[A_\infty/(A_\infty - A_t)]$ as function of time (where A_∞, A_t represent absorbance at infinite time and time t) were linear, passing through origin indicating order with respect to [Fe(III)] to be unity (Fig. 1).

3. Order in [H_2A] is found to be fractional from the log–log plots of k' vs. [H_2A]. Further, the reciprocal plots of $1/k'$ vs. $1/[H_2A]$ are linear with a positive slope and positive intercept on $1/k'$ axis indicating the formation of a precursor. Similar observations were made in anionic, cationic as well as non-ionic micellar media (Table 1, Fig. 2).

4. Effect of variation of [Salt], [Acid] and Methanol % (Table 2, Table 3, Table 4) indi-

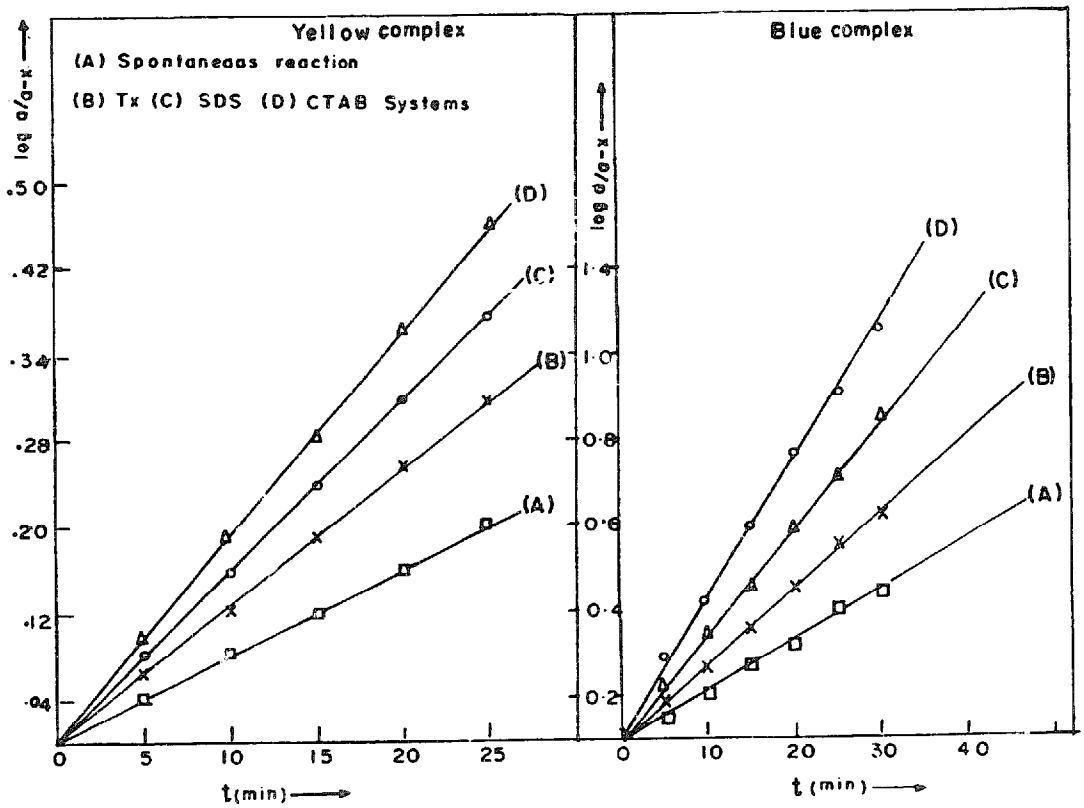


Fig. 1. Resorcinol in aqueous acid and micellar media. (A) Plot of $\log\{a/(a-x)\}$ versus time, Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Resorcinol] = 1.00 mol · dm^{-3}; [H^+] = 0.100 mol · dm^{-3}. (B) Plot of $\log\{a/(a-x)\}$ versus time, Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Resorcinol] = 1.00 mol · dm^{-3}; [H^+] = 0.100 mol · dm^{-3}; 10^2[Tx] = 3.00 mol · dm^{-3}. (C) Plot of $\log\{a/(a-x)\}$ versus time, Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Resorcinol] = 1.00 mol · dm^{-3}; [H^+] = 0.100 mol · dm^{-3}; 10^3[SDS] = 8.00 mol · dm^{-3}. (D) Plot of $\log\{a/(a-x)\}$ versus time, Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Resorcinol] = 1.00 mol · dm^{-3}; [H^+] = 0.100 mol · dm^{-3}; 10^4[CTAB] = 9.00 mol · dm^{-3}.

cated different trends from yellow complexes of Fe(III) to blue complexes of Fe(III). The trends are given in Table 5. (H_2A = Asc. acid, benzene diol hydroquinone, catechol or resorcinol).

3.2. Reactive species and mechanism of oxidation

From the salient kinetic features cited in the previous section it has been observed that the plots of $1/k'$ vs. $1/[H_2A]$ were linear with positive slope and definite intercept on $1/k'$ axis, which generally indicate the formation of an intermediate complex in the pre-equilibrium step. The precursor thus formed may slowly decompose to give products. On the basis of effect of variation of $[H^+]$, [Salt] and solvent on the rate of the reaction nature of active oxidising and reducing species can be determined. Consequently the linear plot of k' vs. $1/[H^+]$ with positive slope, may probably indicate that the active reducing species is HA^- according to the following equilibrium,

$$H_2A \overset{K_d}{\rightleftharpoons} HA^- + H^+$$

At constant $[H^+]$, the increase in $NaClO_4$ did not affect the rate. However, under similar conditions the rates are marginally inhibited $KHSO_4$. On the basis of results obtained from ion-exchange and spectrophotometric techniques Whitekar and Davidson [3] proposed that Fe(III) complex mainly exists as $Fe(SO_4)_2^-$ when $[SO_4^{2-}] > 0.01$ mol · dm^{-3}. Since $[SO_4^{2-}] \geq 0.100$ mol · dm^{-3} in this study Fe $(SO_4)_2^-$ has been considered as the active species. Under the conditions [Phen] ≫ [Fe(III)] Gaines and coworkers [4] have reported the formation of a 1:2

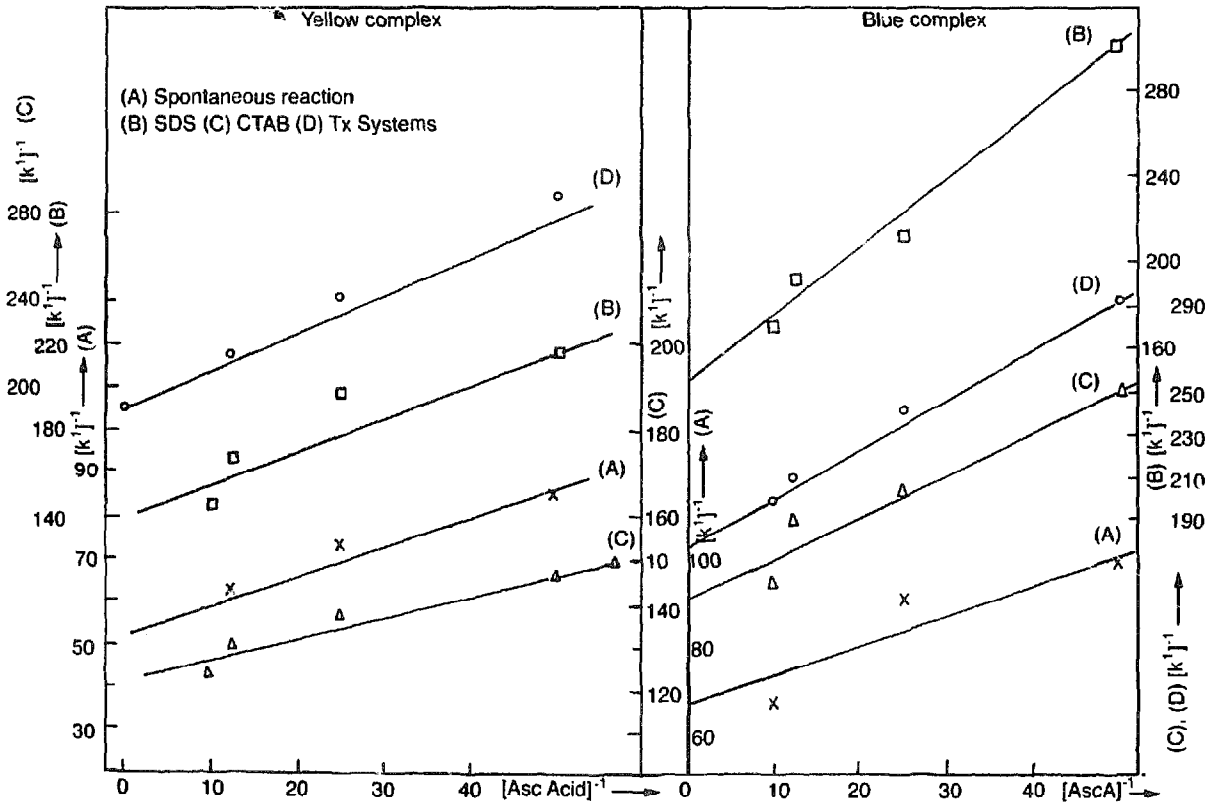


Fig. 2. Ascorbic acid in aqueous acid and micellar media. (A) Plot of $[k']^{-1}$ versus [Ascorbic acid]$^{-1}$; Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; $[H^+]$ = 0.100 mol · dm^{-3}; (B) Plot of $[k']^{-1}$ versus [Ascorbic acid]$^{-1}$; Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; $[H^+]$ = 0.100 mol · dm^{-3}; 10^3[SDS] = 8.00 mol · dm^{-3}. (C) Plot of $[k']^{-1}$ versus [Ascorbic acid]$^{-1}$; Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; $[H^+]$ = 0.100 mol · dm^{-3}; 10^4[CTAB] = 9.00 mol · dm^{-3}. (D) Plot of $[k']^{-1}$ versus [Ascorbic acid]$^{-1}$; Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; $[H^+]$ = 0.100 mol · dm^{-3}; 10^2[Tx] = 3.00 mol · dm^{-3}.

complex of Fe(III) with the ligand. Hence, in the presence of sulphate ions, the equilibrium could be represented by

$$Fe(SO_4)_2^- + 2\,Phen \rightleftharpoons [Fe(Phen)_2]^{3+} + 2SO_4^{2-} \quad (2)$$

The complex of Fe(III) and phen of the present study has been shown to be entirely different from ferrin by Harris [5] et al., from the magneto chemical studies. Ferrin cannot be obtained by direct mixing of Fe(III) and phen, but only by the oxidation of ferroin [1–5]. From the foregoing discussions, the plausible mechanism in phen catalysed Fe(III)–H_2A reaction can be proposed as an equilibrium reaction between $[Fe(Phen)_2]^{3+}$ and HA^- to give a mixed ligand complex $[Fe(Phen)_2(HA)]^{2+}$, which dissociates in the slow step. The reaction between $[Fe(Phen)_2]^{3+}$ and HA^- can be further supported from the solvent effect studies. The results are in accordance with Amis theory for a positive ion–dipole type reaction [20]. Hence the mechanistic pathway could be traced as shown in the scheme:

$$H_2A \overset{K_d}{\rightleftharpoons} HA^- + H^+ \quad (1)$$

$$[Fe(Phen)_2]^{3+} + H_2A \rightleftharpoons [Fe(Phen)_2(H_2A)]^{3+} \quad (3a)$$

$$[Fe(Phen)_2]^{3+} + HA^- \overset{K}{\rightleftharpoons} [Fe(Phen)_2(HA)]^{2+} \quad (3b)$$

Table 1
Effect of variation of [ascorbic acid]

System	10^2[Ascorbic acid] (mol · dm^{-3})	$10^3 k_w$ (min^{-1})	$10^3 k_\psi$ (min^{-1}) (A)	(B)	(C)
Fe(III) phenanthroline (yellow)	1.00	10.8	3.45	4.60	3.12
	2.00	11.5	4.60	5.26	3.45
	4.00	13.4	5.07	5.77	4.14
	8.00	15.9	5.99	6.20	4.60
	10.0	18.4	6.90	6.90	5.07
Fe(III) bipyridyl (yellow)	1.00	13.8	10.8	11.5	10.2
	2.00	17.2	12.2	13.4	10.8
	4.00	20.7	16.0	15.8	11.5
	8.00	27.6	18.4	17.2	12.2
	10.0	34.5	20.2	18.4	13.4
Fe(III) nitrophenanthroline (yellow)	1.00	10.2	11.5	12.5	10.8
	2.00	10.8	12.5	13.6	11.5
	4.00	12.2	14.9	15.4	12.5
	8.00	13.2	16.1	16.0	13.6
	10.0	14.9	18.4	17.2	15.4
Fe(III) phenanthroline (blue)	1.00	9.21	2.76	4.80	3.22
	2.00	9.91	3.45	5.26	3.45
	4.00	10.8	4.60	5.99	4.14
	8.00	12.7	5.06	6.02	4.77
	10.0	14.9	5.81	6.90	5.06
Fe(III) bipyridyl (blue)	1.00	10.8	5.81	6.20	4.60
	2.00	11.5	6.21	6.90	4.77
	4.00	13.2	6.90	7.28	5.26
	8.00	16.0	8.06	8.06	5.76
	10.0	18.4	8.82	9.21	6.20

10^3[OX] = 1.00 mol · dm^{-3}; [H^+] = 0.100 mol · dm^{-3}; Temp = 298 K; (A) 10^3[SDS] = 8.00 mol · dm^{-3}; (B) 10^4[CTAB] = 9.20 mol · dm^{-3}; (C) 10^2[Tx] = 3.00 mol · dm^{-3}.

$$[Fe(Phen)_2(H_2A)]^{3+} \rightarrow [Fe(Phen)_2]^{2+} + HA^{\cdot} + H^+ \quad (4a)$$

$$[Fe(Phen)_2(HA)]^{2+} \xrightarrow[\text{slow}]{k} [Fe(Phen)_2]^{2+} + HA \quad (4b)$$

$$[Fe(Phen)_2]^{3+} + HA^{\cdot} \xrightarrow{\text{fast}} [Fe(Phen)_2]^{2+} + A + H^+ \quad (5)$$

(where A = product of oxidation).

Steps (3a) and (4a) can be neglected because the plot of k' against $[H^+]^{-1}$ is linear passing through origin indicating that only the acid dependent path is operative in the mechanism of electron transfer. Consequently, reaction between $[Fe(Phen)_2]^{3+}$ and $HA^{\cdot}$ only should be considered. The rate law, for the above mechanism, therefore is

$$\frac{-d\left[Fe(Phen)_2^{3+}\right]}{dt} = \frac{kKK_d\left[Fe(Phen)_2^{3+}\right][H_2A]}{[H^+] + KK_d[H_2A]} \quad (6)$$

This can be conveniently rearranged as

$$k' = \frac{-d\left[Fe(Phen)_2^{3+}\right]/dt}{\left[Fe(Phen)_2^{3+}\right]}$$

$$k' = \frac{kKK_d[H_2A}{[H^+] + KK_d[H_2A]} \quad (7)$$

Table 2
Effect of variation of $[H^+]$

System	$10^2[H^+]$ (mol · dm^{-3})	10^3k_w (min^{-1})	10^3k_ψ (min^{-1}) (A)	(B)	(C)
Fe(III) phenanthroline (yellow)	1.00	6.42	6.00	8.86	4.60
	2.00	6.64	5.54	8.06	4.14
	4.00	9.60	5.06	7.78	3.99
	8.00	10.2	4.45	6.90	3.45
	10.0	10.8	3.45	4.60	3.12
Fe(III) bipyridyl (yellow)	1.00	9.91	20.2	16.0	14.4
	2.00	10.0	18.4	15.6	13.4
	4.00	11.4	16.0	14.4	12.2
	8.00	12.4	10.2	12.2	11.5
	10.0	13.8	10.8	11.5	10.2
Fe(III) Nitrophenanthroline (yellow)	1.00	5.07	11.5	No	6.54
	2.00	5.763	10.0	Change	7.76
	4.00	6.45	9.57	in k'	8.10
	8.00	8.14	8.86	values	9.58
	10.0	10.2	7.46	observed	10.80
Fe(III) phenanthroline (blue)	1.00	12.2	4.45	10.2	8.82
	2.00	11.5	4.30	9.91	8.06
	4.00	9.96	3.61	9.21	7.24
	8.00	9.45	2.92	6.90	6.90
	10.0	9.21	2.76	4.80	3.22
Fe(III) bipyridyl (blue)	1.00	50.7	23.0	29.9	20.0
	2.00	46.0	20.0	27.6	18.2
	4.00	34.5	18.8	23.0	17.4
	8.00	22.6	10.0	20.0	12.6
	10.0	10.8	5.81	6.20	4.60

10^2[Ascorbic acid] = 1.00 mol · dm^{-3}; 10^3[OX] = 1.00 mol · dm^{-3}; Temp = 298 K; (A) 10^3[SDS] = 8.00 mol · dm^{-3}; (B) 10^4[CTAB] = 9.20 mol · dm^{-3}; (C) 10^2[Tx] = 3.00 mol · dm^{-3}.

Reciprocals of Eq. 7 yield

$$\frac{1}{k'} = \frac{[H^+]}{kKK_d[H_2A]} + \frac{1}{k}$$

Plots of $1/k'$ vs. $1/[H_2A]$ have been found linear with positive slope (m_1) and intercept (C_1) on $1/k'$ axis. When the values of m are graphically correlated as a function of $[H^+]$ the resultant plots were linear passing through origin and yielding again a positive slope (m_2). From the values of C_1 and m_2 specific constants k and K have been evaluated. The values of thermodynamic parameters involving k, K are presented in Tables 6–10. The catalysis of 1,10-phenanthroline could be explained as due to the π-electron cloud present in the Lewis base which facilitates the electron transfer more rapidly. Furthermore this type of ligands are known to stabilise the lower valency states rather than the higher [2–5,14].

However, in the case of benzene diol systems reactive species appeared to be different. Effect of variation of [Acid] enhanced the reaction rates thus pointing out the participation of

Table 3
Effect of variation of [Additive]

System	10^2[Additive] (mol · dm^{-3})	10^3k_w (min^{-1})	10^3k_ψ (min^{-1}) (A)	(B)	(C)
	[SO_4^{-2}]				
Fe(III)Phenanthroline (yellow)	1.00	20.0	8.06	9.21	8.76
	2.00	18.2	8.75	9.91	9.02
	8.00	16.7	10.3	10.8	9.91
	10.0	14.9	12.6	11.5	10.2
Fe(III) bipyridyl (yellow)	1.00	41.5	23.0	27.3	20.0
	2.00	36.8	20.0	23.0	18.4
	8.00	23.0	18.4	19.8	16.0
	10.0	18.4	16.0	17.4	14.4
Fe(III) phenanthroline (blue)	1.00	14.6	3.91	10.2	3.45
	2.00	12.5	4.60	9.91	4.14
	8.00	11.5	6.90	9.21	4.77
	10.0	10.3	7.59	8.75	5.26
Fe(III) bipyridyl (blue)	1.00	69.0	41.5	52.6	34.5
	2.00	50.6	34.5	47.7	27.6
	8.00	32.2	23.0	30.5	20.0
	10.0	27.6	20.0	24.6	18.4
	[Phen]				
Fe(III) phenanthroline (yellow)	1.00	27.6	–	–	–
	2.00	46.1	–	–	–
	4.00	55.3	–	–	–
	8.00	62.0	–	–	–
	10.0	69.1	–	–	–
	[Bipy]				
Fe(III) bipyridine (yellow)	1.00	7.34	–	–	–
	2.00	7.58	–	–	–
	4.00	8.24	–	–	–
	8.00	8.86	–	–	–
	10.0	9.21	–	–	–

10^2[Ascorbic acid] = 1.00 mol · dm^{-3}; 10^3[OX] = 1.00 mol · dm^{-3}; [H^+] = 0.10 mol · dm^{-3}; Temp = 298 K; (A) 10^3[SDS] = 8.00 mol · dm^{-3}; (B) 10^4[CTAB] = 9.20 mol · dm^{-3}; (C) 10^2[Tx] = 3.00 mol · dm^{-3}.

Table 4
Effect of variation of % MeOH

System	MeOH %	$10^3 k_w$ (min^{-1})	$10^3 k_\psi$ (min^{-1}) (A)	(B)	(C)
Fe(III) phenanthroline (yellow)	5	20.1	8.21	10.8	8.06
	10	18.2	9.62	10.2	7.78
	15	16.7	10.3	9.91	6.90
	20	15.4	11.9	9.21	6.20
Fe(III)bipyridyl (yellow)	5	16.6	10.8	12.2	10.2
	10	13.8	10.2	11.5	9.98
	15	9.2	8.06	8.86	6.90
	20	6.6	5.26	5.07	4.77
Fe(III) phenanthroline (blue)	5	11.7	8.47	10.2	9.91
	10	10.8	6.90	9.91	9.21
	15	10.5	5.94	9.21	8.06
	20	9.8	3.46	8.86	7.78
Fe(III) bipyridyl (blue)	5	5.76	3.46	4.77	4.14
	10	4.14	3.24	4.06	3.45
	15	3.45	2.76	3.24	2.30
	20	2.30	2.02	2.02	1.84

10^2[Ascorbic acid] = 1.00 mol · dm^{-3}; 10^3[OX] = 1.00 mol · dm^{-3}; [H^+] = 0.10 mol · dm^{-3}; Temp = 298 K; (A) 10^3[SDS] = 8.00 mol · dm^{-3}; (B) 10^4[CTAB] = 9.20 mol · dm^{-3}; (C) 10^2[Tx] = 3.00 mol · dm^{-3}.

undissociated benzene diol (H_2A) as reactive species. This observation coupled with the observed linearity of Amis plot ($\log k'$ vs. $1/[D]$) point out the participation of a cation in rate limiting step (Fig. 3). The most plausible reaction path could be, thus, given as follows:

$$[Fe(phen)_2]^{3+} + H_2A \overset{K}{\rightleftharpoons} [Fe(phen)_2(H_2A)]^{3+}$$

$$[Fe(phen)_2(H_2A)]^{3+} \underset{\text{slow}}{\overset{k}{\rightarrow}} [Fe(phen)_2]^{2+} + H^+ + HA^{\cdot}$$

Table 5
Differentiating kinetic features

Effect of [Additive]	Substrate	Table	Observation Aqueous	SDS	CTAB	Tx
(A) Yellow Complexes of Fe(III)						
1. $[(NH_4)_2SO_4]$	Ascorbic acid	3	−	−	−	−
	Benzene diol		+	+	+	+
2. [Acid]	Ascorbic acid	2	+	−	−	−
	Benzene diol		+	+	+	+
3. [Methanol (%)]	Ascorbic acid	4	−	−	−	−
	Benzene diol		+	+	+	+
(B) Blue complexes of Fe(III)						
1. $[(NH_4)_2SO_4]$	Ascorbic acid	3	−	−	−	−
	Benzene diol		+	+	+	+
2. [Acid]	Ascorbic acid	2	−	−	−	−
	Benzene diol		+	+	+	+
3. [Methanol (%)]	Ascorbic acid	4	−	−	−	−
	Benzene diol		+	+	+	+

[a] Note: (+) Indicates rate enhancement. (−) Indicates rate retardation.

Table 6
Kinetic parameters k and K at 298 K in aqueous acid and micellar media

Oxidant	Substrate	Aq. H_2SO_4		SDS		CTAB		Tx	
		k (min^{-1})	K	k (min^{-1})	K	k (min^{-1})	K	k (min^{-1})	K
Fe(III) phenanthroline (yellow)	Ascorbic acid	0.030	0.0185	0.035	0.066	0.037	0.0092	0.024	0.0786
	Hydroquinone	0.008	0.026	0.032	0.037	0.064	0.008	0.018	0.063
	Catechol	0.125	0.021	0.012	0.011	0.022	0.008	0.007	0.042
	Resorcinol	0.027	0.021	0.009	0.013	0.058	0.0092	0.052	0.077
Fe(III) bipyridyl (yellow)	Ascorbic acid	0.012	0.010	0.050	0.010	0.072	0.020	0.013	0.009
	Hydroquinone	0.012	0.033	0.069	0.051	0.068	0.010	0.011	0.048
	Catechol	0.012	0.023	0.066	0.014	0.0912	0.0094	0.052	0.024
	Resorcinol	0.022	0.041	0.011	0.014	0.022	0.0093	0.012	0.075
Fe(III) phenanthroline (blue)	Ascorbic acid	0.016	0.002	0.007	0.012	0.023	0.040	0.013	0.0062
	Hydroquinone	0.013	0.052	0.098	0.057	0.014	0.046	0.011	0.047
	Catechol	0.010	0.019	0.070	0.008	0.009	0.040	0.006	0.011
	Resorcinol	0.021	0.012	0.016	0.038	0.046	0.052	0.009	0.007
Fe(III) bipyridyl (blue)	Ascorbic acid	0.021	0.012	0.049	0.014	0.070	0.046	0.092	0.022
	Hydroquinone	0.021	0.012	0.009	0.018	0.020	0.018	0.072	0.020
	Catechol	0.010	0.021	0.019	0.018	0.069	0.072	0.010	0.025
	Resorcinol	0.055	0.015	0.012	0.092	0.013	0.040	0.0091	0.017

$$[Fe(phen)_2]^{3+} + HA^{\cdot} \rightarrow[\text{fast}] [Fe(phen)_2]^{2+} + H^+ + A$$

(In all the steps phen is taken as a specific example. Similar type of discussion holds good with other ligands).

In the case of the blue complexes of Fe(III)L also Michaelis–Menten type of mechanism and rate law are operative expecting the difference

Table 7
Thermodynamic parameters involving k and K at 298 K

Substrate	Oxidant	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
Ascorbic acid	Fe(III) phen (yellow)	24.6	45.9	−71.4	50.4	82.4	−107.4
Hydroquinone		32.7	78.9	−155.0	42.0	81.7	−133.2
Catechol		11.9	83.9	−239.3	80.2	87.8	−25.5
Resorcinol		45.6	82.6	−124.3	9.6	82.1	−243.3
Ascorbic acid	Fe(III) bipy (yellow)	48.6	83.5	−117.1	62.5	81.8	−64.8
Hydroquinone		16.7	60.3	−146.3	34.6	81.1	−156.0
Catechol		9.5	66.6	−191.6	9.6	82.4	−243.7
Resorcinol		20.4	60.3	−133.8	64.0	63.1	−302.0
Ascorbic acid	Fe(III) phen (blue)	23.2	85.2	−208.1	18.5	83.0	−144.3
Hydroquinone		20.4	81.4	−204.6	12.9	79.1	−222.0
Catechol		19.2	80.3	−205.0	18.0	81.4	−215.2
Resorcinol		16.7	79.1	−209.4	19.2	85.4	−222.1
Ascorbic acid	Fe(III) bipy (blue)	15.4	83.2	−227.1	16.5	82.8	−215.8
Hydroquinone		19.2	86.5	−225.8	23.1	80.8	−193.6
Catechol		12.8	82.2	−232.8	8.1	81.7	−235.0
Resorcinol		15.6	84.2	−230.2	23.1	85.2	−208.1

Table 8
Thermodynamic parameters involving k and K at 298 K in SDS medium

Substrate	Oxidant	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
Ascorbic acid	Fe(III) phen (yellow)	30.7	61.5	−103.8	9.61	85.2	−253.4
Hydroquinone		24.6	62.8	−128.4	6.7	81.4	−250.8
Catechol		19.2	78.9	−200.3	9.9	83.4	−243.7
Resorcinol		15.4	79.1	−213.8	19.3	83.1	−204.0
Ascorbic acid	Fe(III) bipy (yellow)	15.3	60.9	−153.0	8.4	82.4	−248.3
Hydroquinone		28.3	64.3	−120.8	48.0	80.1	−107.7
Catechol		28.8	79.9	−171.5	8.24	83.0	−255.0
Resorcinol		24.0	78.7	−183.6	8.42	77.5	−231.8
Ascorbic acid	Fe(III) phen (blue)	42.4	75.5	−111.1	64.0	85.7	−72.8
Hydroquinone		49.9	52.9	−100.6	63.2	79.3	−54.0
Catechol		48.0	80.1	−107.8	67.0	81.1	−47.3
Resorcinol		8.01	83.1	−100.1	64.0	76.1	−46.3
Ascorbic acid	Fe(III) bipy (blue)	19.9	74.3	−182.6	19.3	83.9	−216.7
Hydroquinone		21.5	82.8	−181.2	18.2	83.1	−217.8
Catechol		20.4	80.1	−200.3	15.0	80.0	−218.1
Resorcinol		9.5	66.6	−191.6	20.4	80.1	−200.3

in Fe(III)L species i.e., $[Fe(phen)_3]^{3+}$ instead of $[Fe(phen)_2]^{3+}$.

3.3. Marcus theory of linear free energy relationship

Marcus theory [8,16–19] depicts that the free energy of activation $\Delta G^{\#}$ for an 'outersphere' or 'innersphere' electron-transfer reaction is correlated to specific rate constants. The free energy of activation, $\Delta G^{\#}$ for reaction can be obtained by the following expressions

$$k = Z\exp(\Delta G^{\#}/RT) \quad (8)$$

$$\Delta G^{\#} = \lambda/4(1 + \Delta G/\lambda)^2 \quad (9)$$

Where Z is the collision number in solution

Table 10
Thermodynamic parameters involving k and K at 298 K in Tx medium

Substrate	Oxidant	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
Ascorbic acid	Fe(II) phen (yellow)	35.8	64.3	−95.6	63.2	79.3	−54.0
Hydroquinone		64.5	93.2	−96.5	56.0	69.2	−44.3
Catechol		55.2	79.2	−80.5	24.6	45.9	−71.4
Resorcinol		41.6	66.6	−82.5	69.3	77.6	−27.9
Ascorbic acid	Fe(II) bipy (yellow)	16.7	62.8	−154.8	19.2	58.0	−146.3
Hydroquinone		11.9	60.3	−162.4	34.7	80.9	−155.0
Catechol		16.7	66.6	−167.4	22.0	61.9	−133.8
Resorcinol		12.8	60.8	−161.2	34.5	77.1	−143.3
Ascorbic acid	Fe(II) phen (blue)	26.2	62.8	−122.7	50.7	61.2	−126.8
Hydroquinone		20.4	60.3	−133.8	38.0	75.7	−127.5
Catechol		45.6	82.7	−124.3	50.8	85.3	−117.1
Resorcinol		28.2	61.5	−111.8	16.7	60.3	−146.3
Ascorbic acid	Fe(II) bipy (blue)	35.2	78.7	−145.9	20.2	80.0	−191.9
Hydroquinone		42.0	83.3	−138.6	16.8	79.9	−207.5
Catechol		42.0	79.7	−126.5	12.8	84.8	−239.3
Resorcinol		17.9	61.6	−146.6	20.2	81.1	−201.3

Table 9
Thermodynamic parameters involving k and K at 298 K in CTAB medium

Substrate	Oxidant	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	ΔH kJ mol^{-1}	ΔG kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
Ascorbic acid	Fe(III) phen (yellow)	28.2	60.5	−110.7	38.8	81.9	−144.6
Hydroquinone		35.8	64.3	−95.6	35.2	78.9	−144.6
Catechol		46.8	80.4	−107.7	35.9	77.5	−139.6
Resorcinol		45.5	82.0	−123.0	42.3	83.2	−137.2
Ascorbic acid	Fe(III) bipy (yellow)	12.8	60.9	−161.4	30.2	80.2	−167.8
Hydroquinone		22.2	62.8	−154.8	28.2	82.0	−180.5
Catechol		26.3	79.9	−179.9	21.5	81.2	−152.0
Resorcinol		21.5	78.7	−191.9	35.2	81.9	−156.7
Ascorbic acid	Fe(III) phen (blue)	48.9	85.1	−121.5	16.7	78.9	−208.7
Hydroquinone		51.1	82.6	−105.7	26.3	79.9	−179.9
Catechol		28.2	61.5	−117.1	21.5	78.7	−191.9
Resorcinol		47.3	79.9	−109.4	9.5	66.6	−191.6
Ascorbic acid	Fe(III) bipy (blue)	16.7	62.8	−154.8	26.?	79.9	−179.9
Hydroquinone		11.9	60.3	−162.4	12.8	60.9	−161.4
Catechol		16.7	66.6	−167.4	22.2	62.8	−154.8
Resorcinol		12.8	60.8	−161.2	32.7	78.9	−155.0

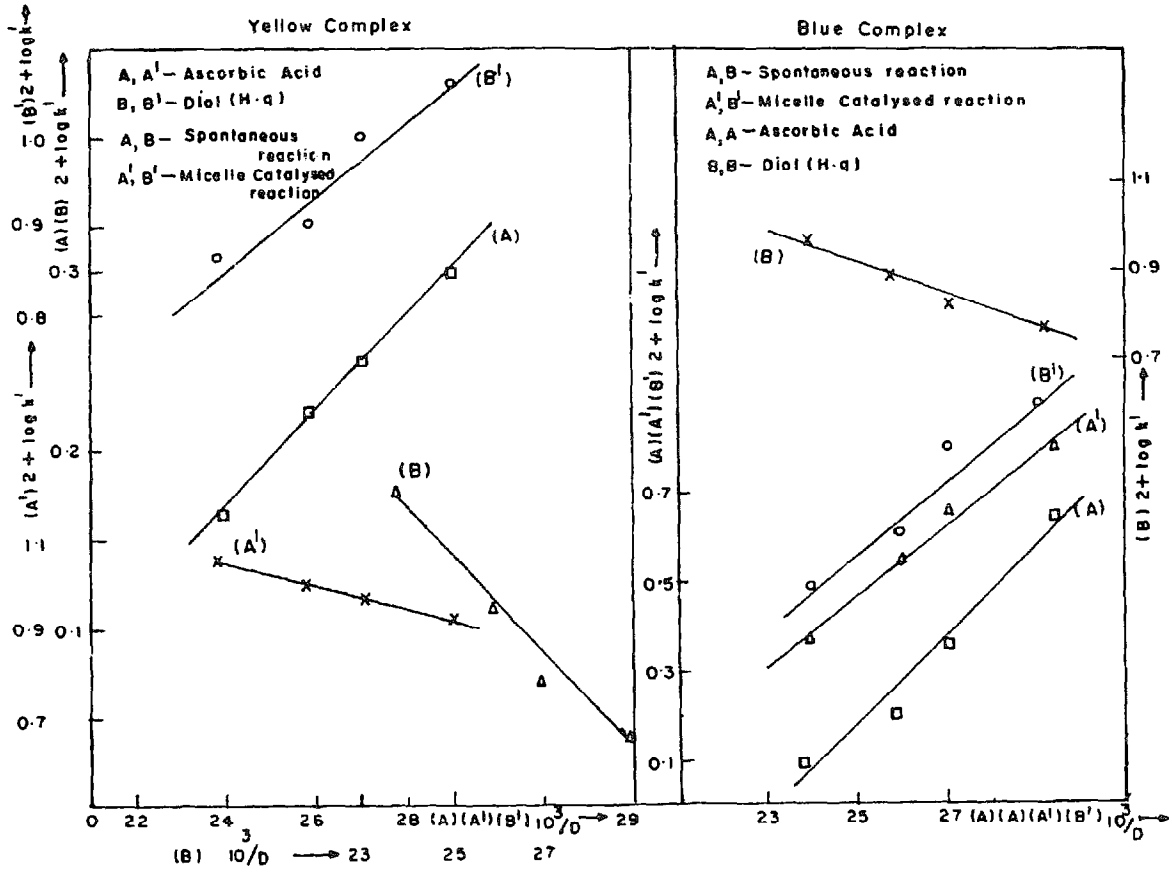


Fig. 3. Ascorbic acid and hydroquinone in aqueous acid and micellar media. Plots of $\log k'$ versus $10^3/[D]$, Temp. = 298 K (A) 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Ascorbic acid] = 1.00 mol · dm^{-3}; [H$^+$] = 0.100 mol · dm^{-3}; (A') 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Ascorbic acid] = 1.00 mol · dm^{-3}; [H$^+$] = 0.100 mol · dm^{-3}; 10^3[SDS] = 8.00 mol · dm^{-3}. (B) 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Hydroquinone] = 1.00 mol · dm^{-3}; [H$^+$] = 0.100 mol · dm^{-3}; (B') 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Hydroquinone] = 1.00 mol · dm^{-3}; [H$^+$] = 0.100 mol · dm^{-3}; 10^3[SDS] = 8.00 mol · dm^{-3}.

(assumed as 10^{11} $dm^3 \cdot mol^{-1}$) and λ is defined as reorganisation parameter of the inner and outer coordination spheres of the reacting complex. When the reorganisation term $\lambda \gg \Delta G$, the quadratic can be neglected in Eq. (9) which can be further simplified [8] to

$$\Delta G^{\#} = (\lambda/4) + (0.50\Delta G) \quad (10)$$

Since the overall free energy change ΔG is proportional to the difference in the redox potentials of oxidising and reducing couples, $\Delta G^{\#}$ can be related to $\log k$ according to the expression,

$$\log k = 8.5(E_2 - E_1) + \text{constant} \quad (11)$$

where E_2 and E_1 are redox potentials for oxidising and reducing couples respectively.

In the oxidation of closely related compounds by the same oxidant redox potential (E_2) for oxidising couple remains constant while the value of E_1 varies with the structure of compound. Thus the rate constant can be related to E_1 according to the modified equation.

$$\log k = 8.5E_1 + \text{constant} \quad (12)$$

Plot of $\log k$ as a function of E_1 is linear with positive slope and intercept on $\log k$ axis. Deviation from the value of 8.5 was observed in the case of yellow complexes indicating an inner sphere electron transfer mechanism and a strong ion–ion interaction between $[HA]^-$ and Fe(III)L while forming a precursor complex. However, in case of blue complexes the slopes are with in the range of 8.5 which is supporting the substitution inertness of blue complexes and outer sphere electron transfer mechanism (Fig. 5).

Perusal of the activation parameters, Tables 7–10,calculated according Eyring's theory for specific rate constants reveal that activation entropies are highly negative indicating greater

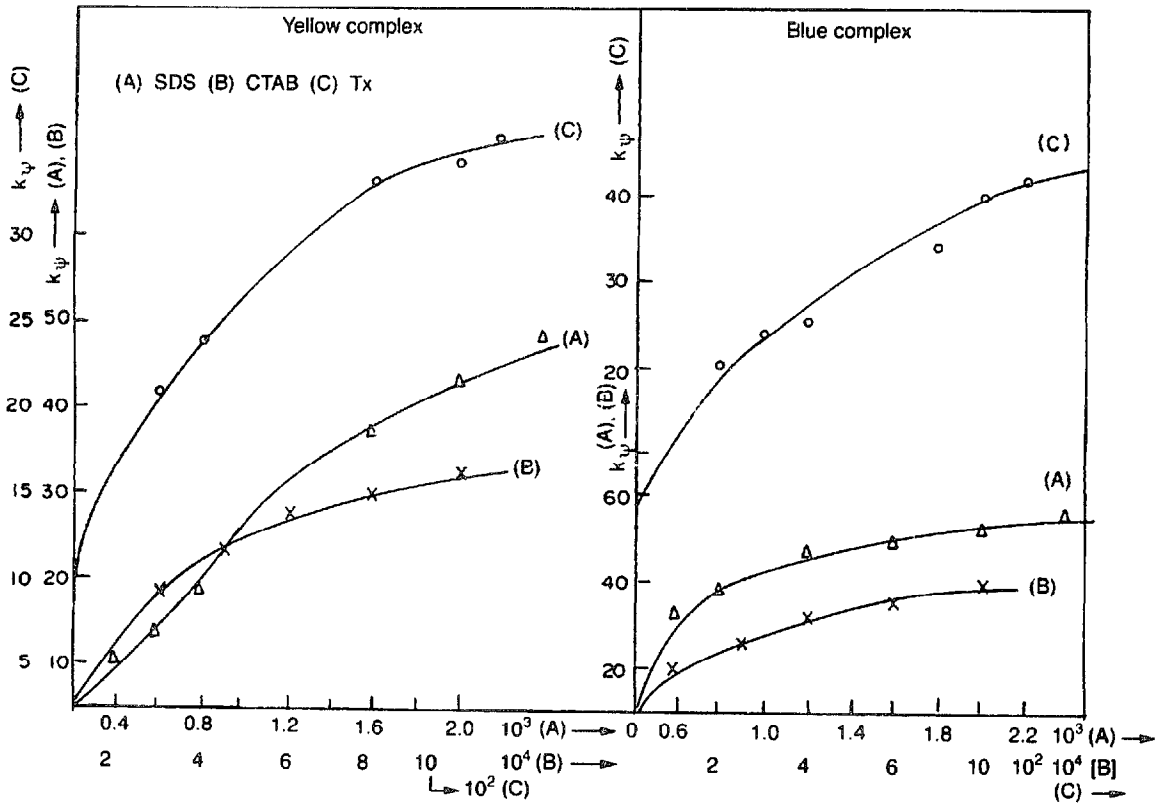


Fig. 4. Variation of micelle. (A) Plots of $\log k_\psi$ versus [D] or [SDS]; Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Hydroquinone] = 1.00 mol · dm^{-3}; $[H^+]$ = 0.100 mol · dm^{-3} (B) Plots of $\log k_\psi$ versus [CTAB]; Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Hydroquinone] = 1.00 mol · dm^{-3}; $[H^+]$ = 0.100 mol · dm^{-3} (C) Plots of $\log k_\psi$ versus [Tx]; Temp. = 298 K 10^3[Fe(III)] = 1.00 mol · dm^{-3}; 10^2[Hydroquinone] = 1.00 mol · dm^{-3}; $[H^+]$ = 0.100 mol · dm^{-3}.

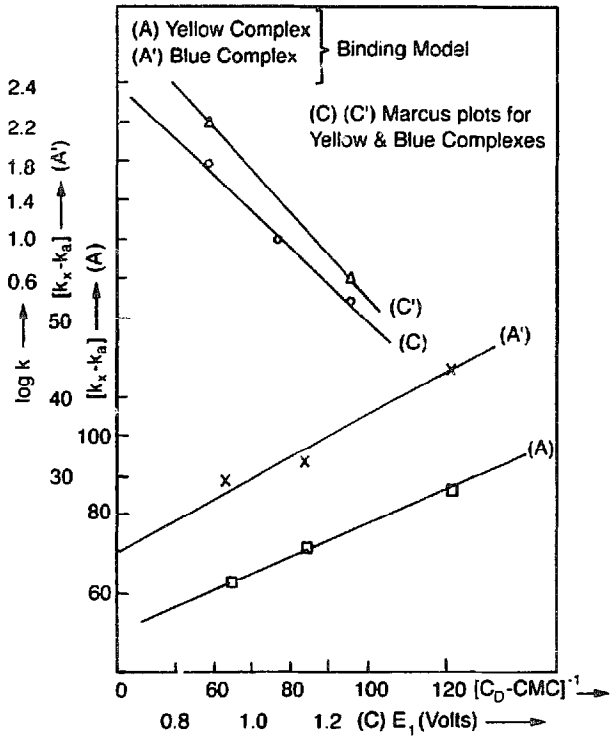


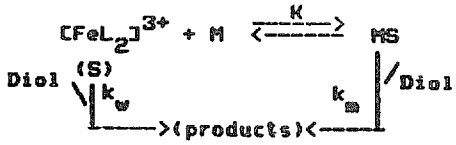
Fig. 5. Binding model and Marcus plots. (A) Binding model for yellow complex of [Fe(III)]L. Plots of $[k_\psi - k_0]^{-1}$ versus $[C_D - CMC]^{-1}$ (A'). Binding model for blue complex of [Fe(III)]. Plots of $[k_\psi - k_0]^{-1}$ versus $[C_D - CMC]^{-1}$. (B) Marcus plot for yellow complex of [Fe(III)] chelates. Plots of k versus E_1 (V). (B') Marcus plot for blue complex of [Fe(III)]. Plots of k versus E_1 (V).

solvation in the transition state. Further the $\Delta S^{\#}$ values of the present system are in accordance with literature values representing greater hydration in the transition state.

3.4. Mechanism of oxidation in micellar media

Electron transfer from diols such as hydroquinone, catechol, resorcinol to Fe(III) chelates appeared to be catalysed by anionic (SDS), cationic (CTAB) and non-ionic (Tx) micelles, as shown in Table 6 and Fig. 4. When the data were cast in to binding model of micellar mechanistic scheme, the plots were linear with positive slope and intercepts (Fig. 5).

The present kinetic results have been to be in accordance with the binding model. Anionic micelles are stabilised by the cationic form of Fe(III) chelates due to oppositely charged electrostatic interactions. The observed kinetic results could be explained by the following scheme [11].



For the above mechanism the rate law could be given as

$$k_{obs} = \frac{k_w + k_m K[M]}{1 + K[M]}$$

$$\text{where } [M] = \frac{C_D - CMC}{N}$$

(N = aggregation number of micelle, C_D = concentration of micelle)

The electron transfer from diols to Fe(III) chelates was catalysed by SDS very well compared to other micelles. The catalysis could probably be explained due to the electrostatic interactions between cationic forms of Fe(III) chelates and negatively charged SDS. The binding model was explained by the kinetic results obtained in this reaction. The marginal catalysis of Tx could be explained due to the interaction of cationic forms of Fe(III) chelates and slight negative charge developed on polyoxyethylene.

3.5. Mechanism of micellar effects in ascorbic acid

As a typical case the authors observed rate retardation in oxidation of ascorbic acid in micellar media. All the micelles retarded the oxidation reaction. The observed retardation in the case of Ascorbic acid was probably due to the electrostatic repulsion of the reactants from the micelle such as repulsion between HA^- and anionic SDS, cationic Fe(III)L and CTAB and slight negatively charged polyoxyethylene and HA^-. An indication of this is the competitive inhibition of micellar catalysis produced by the

introduction of gegenions leading to neutralisation of the surface charge on the micelle. The transition state of the reaction was destabilised by the presence of micelle.

4. Conclusions

1. An inner sphere electron transfer from L-ascorbic acid or diols to Fe(III) chelates was proposed according to Marcus theory, when Blau's yellow complexes are used as oxidants.
2. In the case of blue complexes, an outer sphere mechanism was suggested because the observed slopes are nearly equal to the theoretical values (i.e., 8.5).
3. SDS catalysis in case of diols was explained due to the electrostatic interactions of cationic form of Fe(III) chelates and negatively charged SDS. Observed kinetic results are in good agreement with binding model. Similar type of explanation was offered in the case of blue complexes also.
4. CTAB catalysis is explained due to the interactions of negative substrate ion and positively charged CTAB. Similar observations were recorded in blue complexes also.
5. Triton-X marginally enhanced the rate in the case of diols as explained due to the interactions of positively charged Fe(III) chelates and slight negative charge developed on Tx.
6. Observed retardation in the presence of micelles in the case of ascorbic acid can be explained due to the repulsion of similarly charged reactants and micelles.

References

[1] F. Blau, Monatsh. 19 (1898) 6472.
[2] G.S. Laurence and K.J. Ellis, J. Chem. Soc., Dalton, (1972) 1167.
[3] R.A. Whiteker and N. Davidson, J. Am. Chem. Soc., 75,(1953) 3081 .
[4] A. Gaines (Jr), L.P. Hammett and G.H. Walden (Jr), J. Am. Chem. Soc., 58 (1936) 1668.
[5] C.M. Harris and T.N. Lockyer, Chem. and Ind., 12 (1958) 31.
[6] P.V. Subba Rao, B.A.N. Murthy and R.V.S. Murthy, Z. Phys. Chem. (Leipzig), 257 (1976) 813.
[7] P.V. Subba Rao, B.A.N. Murthy, R.V.S. Murthy and K.S. Murthy, J. Indian Chem. Soc., 55 (1978) 207.
[8] M.S. Frank, A. Kodanda Ramaiah and P.V. Krishna Rao, Indian J. Chem. 18A (1979) 369.
[9] A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, ELBS and Longman, London, 1978, p. 361.
[10] E. Mentasti and E. Pelizetti, Int. J. Chem. Kinet. 9 (1977) 215, and references cited there in.
[11] J.H. Fendler and E.J. Fendler, Micellar Catalysis in Organic Reaction: Kinetic Mechanistic Implication, Academic Press, New York 1975.
[12] C. Tanford, The Hydrophobic Effect, Wiley, New York, 1971.
[13] (a) N. Sutin, in G.I. Eichhorn (Ed.), Inorganic Biochemistry, Vol. 2, Elsevier, Amsterdam, 1973, chap. 19. (b) W.L. Reynolds and R.W. Lumry, Mechanism of Electron Transfer, Ronald Press, New York, 1966.
[14] C. Minero, E. Premauro, E. Pelizetti and D. Meisel, J. Phys. Chem., 87 (1983) and references cited there in 399.
[15] C.A. Bunton and G. Cerichelli, Int. Natl. J. Chem. Kinet., 11 (1980) 519.
[16] A.L. Carbone, F.P. Cavasino, C. Sbriziolo and E. Pelizetti, J. Phys. Chem., 89 (1985) 3578.
[17] M.J. Carney, J.S. Lesnik, M.D. Likar and J.R. Pladziewicz, J. Am. Chem. Soc., 106, (1984) 2565.
[18] E. Pramauro, E. Pelizetti, S. Diekmann and J. Frahm, Inorg. Chem., 21 (1982) 2432.
[19] G. Akerlof, J. Am. Chem. Soc., 54 (1932) 4125.
[20] E.A. Amis, Solvent Effects of Reaction Rates and Mechanisms, Academic Press, New York, 1966.