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INFLUENCE OF DIELECTRIC CONSTANT (D), $[H^+]$ AND $[SO_4^{2-}]$ ON THE RATE OF REDOX REACTION BETWEEN TRIS (2,2′-BIPYRIDINE) IRON(II) AND CERIC SULPHATE IN AQUEOUS SULPHURIC ACID MEDIUM

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Abstract

Kinetic of the redox reaction between tris (2,2′-bipyridine)iron(II) cation and ceric sulphate has been studied in aqueous sulphuric acid medium. Different methods were employed for the determination of order of reaction. The order of reaction is found to be first with respect to reductant however retarding effect of increasing initial concentration of oxidant is found. Influence of $[H^+]$, $[SO_4^{2-}]$ and dielectric constant (D) on the rate of redox reaction has also been studied. Increase in $[H^+]$ and dielectric constant of the medium retard the rate while enhancement of the $[SO_4^{2-}]$ accelerates the rate first and then the reaction goes towards retardation. Effects of $[H^+]$ and $[SO_4^{2-}]$ were studied by using acetic acid-sodium acetate buffer for the first one and varying ionic concentrations of the salt sodium sulphate for the latter one, whereas dielectric constant was varied by using 0%, 10% and 20% ethanol-water mixtures. Results of effects of each one of the factors i.e., H^+, SO_4^{2-} and dielectric constant (D) have been compared and on the basis of these factors, $[Ce(SO_4)_3^{2-}]$ is suggested to be the active species of cerium(IV). However a rate law consistent with the observed kinetic data has also been derived supporting the proposed mechanism.

Keywords: Ceric Sulphate, dielectric constant, rate of redox reaction.

INTRODUCTION

The tris(2,2′-bipyridine)iron(II) cation is of much importance and frequently used. It is employed for the spectrophotometric determination of iron by the analytical chemists. The complex, due to its stability and high stability constant, is also used to remove the interferences of iron, while determining other metals. Intense red color of the tris bipyridine ferrous complex and very high molar extinction coefficient are responsible for the extensive use of the chelate ligand, 2,2′-bipyridine, as a colorimetric reagent and for the spectrophotometric determination of iron. It is also used as a redox indicator due to its high reduction potential (~1.02 V) [Jeffery *et al.* 1989]. The large cationic iron (II) complex is useful in the specific precipitation of anions in gravimetric procedures.

The redox reactions have drawn attention of the chemists and numerous kinetic investigators [Panda and Reddy 2006]. Studies involving electron transfer between ferrous/ferric and their complexes have been widely reported in recent years [Farrukh and Naqvi 2002]. The oxidation of iron(II) complexes with α,α′-diimine chelate ligands like 1,10-phenanthroline (Ferroin), 2,2′-bipyridine or 2,2′-bipyridyl and of substituted 1,10-phenanthroline and 2,2′-bipyridine, involves the loss of one electron from the complex cation, e.g.,

$$[Fe(o-phen)_3]^{2+} \rightarrow [Fe(o-phen)_3]^{3+} + \bar{e} \cdots\cdots \quad (A)$$

$$[Fe(bipy)_3]^{2+} \rightarrow [Fe(bipy)_3]^{3+} + \bar{e} \cdots\cdots \quad (B)$$

Such oxidations can readily be followed spectrophotometrically as the iron (II) complexes have large molar extinction coefficients at the wavelengths far removed from the less absorbing species of the iron (III). Hence the kinetics and mechanism for these types of reactions can spectrophotometrically be easily studied. Ayodele *et al*. [2000] had spectrophotometrically studied the kinetics and mechanism of the periodate oxidation of 4,4′-dimetyl derivative of the ferrous bipyridine complex in the acidic medium whereas Burgess and Prince [1966], had spectrophotometrically investigated the kinetics of peroxydisulphate oxidation of the iron(II) complexes with tris-2,2′-bipyridine, substituted tris-2,2′-bipyridine, tris-1,10-phenanthroline, substituted tris-1,10-phenanthroline and bis-2,2′:6′,2″-terpyridine or bis-2,2′:6′,2″-terpyridyl.

Cerium in the tetravalent state is a strong oxidizing agent which apparently reacts only via one-electron step.

$$Ce^{4+} + \bar{e} \rightarrow Ce^{3+} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (C)$$

Aqueous solutions containing cerium(IV) species are stable, despite the lower electrode potential for the H_2O/O_2 couple (1.23 V), probably for kinetic reasons. Cerium (IV) oxidation is a valuable tool in the organic chemistry and can be used for the quantitative volumetric oxidation reactions called the cerate oxidimetry in the analytical chemistry. It is widely used for the oxidation of many substrates in the different aqueous acidic mediums [Kumar and Prasad 1974, Kishan and Sundaram 1980, Jameel 1997].

Kinetics of the redox reaction between tris(2,2′-bipyridine)iron(II) sulphate and ceric sulphate in the aqueous sulphuric acid medium has been investigated in the present report. Influence of different factors on the rate of the redox reaction has also been studied and in the view of results a rate law is derived which supports the proposed mechanism. Further to that order of the reaction has been fixed by using different methods like isolation, integration and half-life. Stability of the complex, $[Fe(bipy)_3]SO_4$ in different mediums has also been investigated.

MATERIALS AND METHODS

All the chemicals including diammoniumiron(II) sulphate-6-hydrate, cerium(IV) sulphate-4-hydrate, sodium acetate-3-hydrate, 2,2′-bipyridine, sodium sulphate, acetic acid, sulphuric acid and ethanol were of Analar grade. However diammoniumiron(II) sulphate-6-hydrate, sodium acetate-3-hydrate and sodium sulphate were of (BDH) Analar grade whereas cerium(IV) sulphate-4-hydrate, 2,2′-bipyridine, acetic acid, sulphuric acid and ethanol were of Merck Analar grade. Deionized water was employed for preparation of the solutions.

DETERMINATION OF METAL TO LIGAND RATIO OR EMPIRICAL FORMULA OF THE IRON(II) BIPYRIDINE COMPLEX BY THE JOB'S METHOD OF CONTINUOUS VARIATION

Empirical formula of the complex of iron(II) with the chelate ligand 2,2′-bipyridine was established by the Job's method of continuous variation. For the purpose, at the wavelength of maximum absorption (λ_{max}) in the visible region, 522 nm for the complex ion, several solutions were spectrophotometrically examined (because aqueous solutions of required concentrations of the metal ions and the ligand were colorless), for all of which $[M]_t + [L]_t$ was a constant, although each had different values for $[M]_t$ and $[L]_t$. Here $[M]_t$ or $[L]_t$ represent the total concentration of metal or ligand, respectively that's free as well as complexed forms. Measurements of the intensity of absorption (optical density or absorbance) was plotted against composition (the ratio $[M]_t / ([M]_t + [L]_t)$; that was against $[M]_t$ / constant). The results are displayed in Table 1 and Fig. 1. From the position of the maximum at the plot, the ratio of metal to ligand or composition of the complex was determined. The maximum absorption was obtained when the ratio of metal to ligand was 1:3, thus empirical formula of the intense red colored complex cation is established as $[Fe(bipy)_3]^{2+}$.

Table 1: Determination of Metal to Ligand Ratio or Empirical Formula of the Iron(II) bipyridine Complex ion by the Job's Method of Continuous Variation.
Diammoniumiron(II) sulphate-6-hydrate = 2.8 × 10^{-4} M, 2,2′-bipyridine = 2.8 × 10^{-4} M, medium = deionized water, λ_{max} = 522 nm, Temperature = 28 °C

	Composition of the reaction mixture			
Sr. No.	$\frac{[Fe^{2+}]_t}{([Fe^{2+}]_t + [bipy]_t)}$	$\frac{[bipy]_t}{([Fe^{2+}]_t + [bipy]_t)}$	Absorbance	Empirical Formula found, for the Complex Ion
1.	0.00	1.00	0.003	$[Fe(bipy)_3]^{2+}$
2.	0.10	0.90	0.258	
3.	0.15	0.85	0.378	
4.	0.20	0.80	0.502	
5.	0.25	0.75	0.609	
6.	0.30	0.70	0.565	
7.	0.45	0.55	0.450	
8.	0.60	0.40	0.408	
9.	0.75	0.25	0.203	
10.	0.90	0.10	0.086	
11.	1.00	0.00	0.010	

Ferrous solutions of the required concentrations were prepared by dilution of the stock solution which was prepared by dissolving required amount of the diammmoniumiron(II) sulphate-6-hydrate in the deionized water. Dilutions were made up by deionized water too. Whereas dilutions of the required concentrations of the ligand (2,2′-bipyridine) were prepared from the stock solution of the ligand that was prepared by dissolving required amount of 2,2′-bipyridine in 1cm^3 ethanol and making up to the required volume by deionized water.

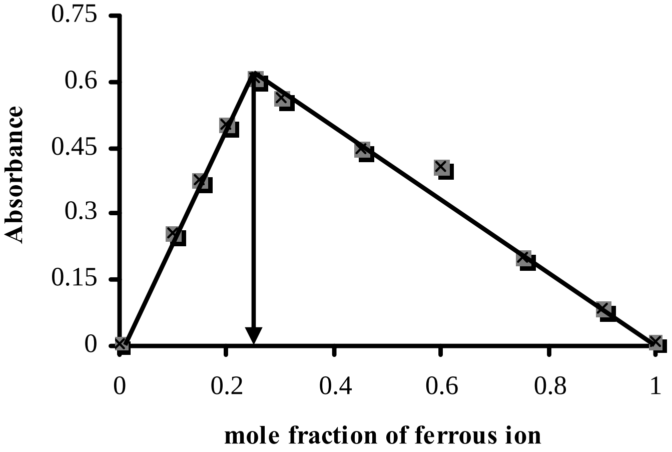

Fig. 1: The Job's Plot for $[Fe(bipy)_3]^{2+}$ Complex Species formed between Ferrous Ion and Bipyridine.

SYNTHESIS OF THE TRIS(2,2′-BIPYRIDINE) IRON(II) SULPHATE

Tris(2,2′-bipyridine)iron(II) sulphate was synthesized by mixing same volumes of solutions of both of diammoniumiron(II) sulphate-6-hydrate and 2,2′-bipyridine. The ratio of concentrations was maintained at 1:3 between the two reactants respectively. The complex was crystallized out in the form of sulphate salt by adding sodium sulphate and ethanol to the reaction mixture. In this stage ethanol was added to minimize the dielectric constant of the system and thus helping in precipitation of the complex. Intense red colored crystals of the complex compound were recrystallized by using ethanol as a solvent for recrystallization. The crystals obtained were firstly dried with ether and then in desiccators.

CHARACTERIZATION OF THE SYNTHESIZED COMPLEX COMPOUND, $[FE(BIPY)_3]SO_4$ AND PRODUCT ANALYSIS

Tris(2,2′-bipyridine)iron(II) sulphate was characterized by its UV-Visible spectrum or absorption spectrum (Figs. 2, 3). The characteristic wavelengths of maximum absorption (λ_{max}) for the complex compound in the ultra violet and visible regions were in excellent agreement with the values reported in the literature [Burgess and Prince 1965, Stolzenberg 1995] and those established for the complex cation through the Job's method of continuous variation. However for further confirmation and characterization, solution of the complex cation; $[Fe(bipy)_3]^{2+}$ and of the complex compound; $[Fe(bipy)_3]SO_4$, was first oxidized, according to equations (B, C and K), in $[Fe(bipy)_3]^{3+}$ by ceric sulphate. The product was then examined for its color and value of the characteristic wavelength of maximum absorption (λ_{max}) in the visible region. These results, were matched with the previous ones [Burgess and Prince 1965, Stolzenberg 1995], and were in good agreement (Fig. 4). These results are reported in Table 2.

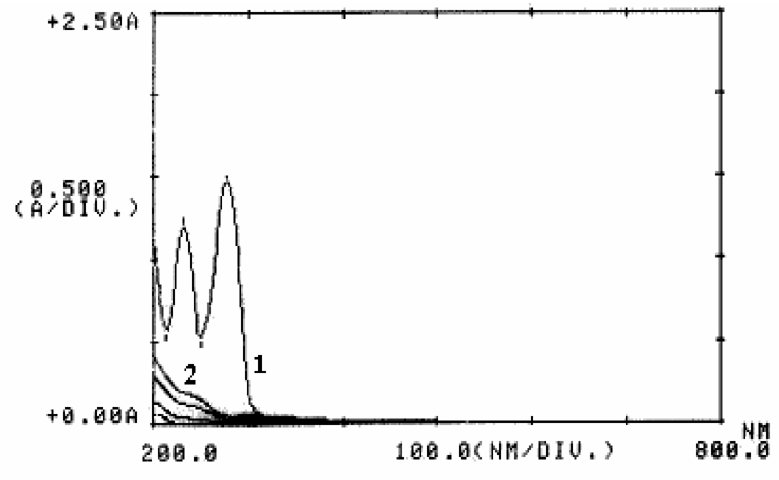

Fig. 2: Absorption Spectra of (1) 2,2′-bipyridine, (2) Ferrous Ammonium Sulphate hexahydrate at various Concentrations.

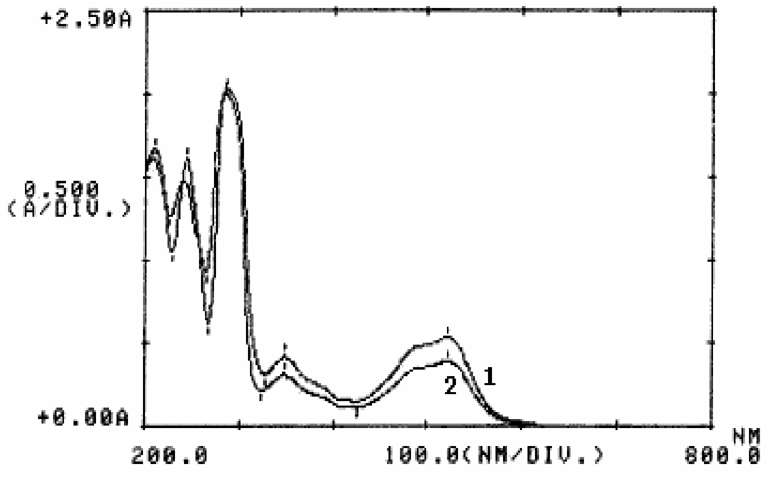

Fig. 3: Absorption Spectra of (1) Tris(2,2′-bipyridine)iron(II) Sulphate, (2) Tris(2,2′-bipyridine) iron(II) Cation, while Concentrations for both the reagents were altered to show the difference between the Spectra.

$$\left[Fe(bipy)_3\right]^{2+} + Ce^{4+} \rightarrow \left[Fe(bipy)_3\right]^{3+} + Ce^{3+} \cdots\cdots\cdots (K)$$

The ceric sulphate was used for the characterization of the complex compound because of the property that oxidized (Ce^{4+}) and reduced (Ce^{3+}) both forms of the cerium approximately do not absorb in the visible region (Fig. 5).

Matching between the values of molar extinction coefficients of the synthesized complex compound and its oxidized form with the values given in the literature [Burgess and Prince 1965, Stolzenberg 1995] also confirms the synthesized complex as $[Fe(bipy)_3]SO_4$.

Table 2: Absorption Spectral Data of the Complex Cation and the Complex Compound in the Reduced and the Oxidized Forms.

Complex Ion or Complex Compound	Visible Color	Observed Values wavelength maxima (λ_{max})		Literature* Values wavelength maxima (λ_{max})	
		UV	Visible	UV	Visible
$[Fe(bipy)_3]^{2+}$ (reduced form, spectrum 2 in Fig. 8)	Intense red	284 nm	522 nm	297 nm	522 nm
$[Fe(bipy)_3]^{3+}$ (oxidized form, spectrum 2 in Fig. 9)	Pale blue	–	610 nm	–	610 nm
$[Fe(bipy)_3]SO_4$ (reduced form, spectrum 1 in Fig. 8)	Intense red	285 nm	522 nm	–	–
$[Fe(bipy)_3]^{3+}$ (oxidized form, spectrum 1 in Fig. 9)	Pale blue	–	610 nm	–	–

* [Burgess and Prince 1965, Stolzenberg 1995].

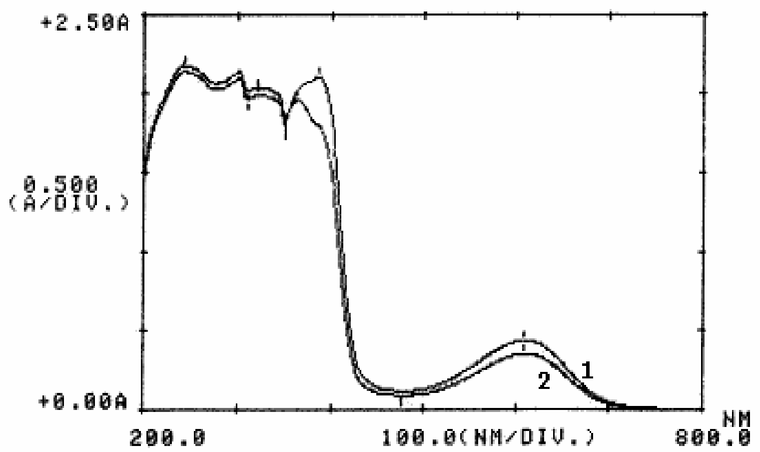

Fig. 4: Absorption Spectra of, (1) Oxidation Product of the Tris(2,2′-bipyridine)iron(II) Sulphate that's Tris(2,2′-bipyridine)iron(III) cation, (2) Oxidation Product of the Tris(2,2′-bipyridine)iron(II) Cation that'sTris(2,2′-bipyridine)iron(III) Cation, while Concentrations for both the Reagents were altered, to show the difference between the Spectra.

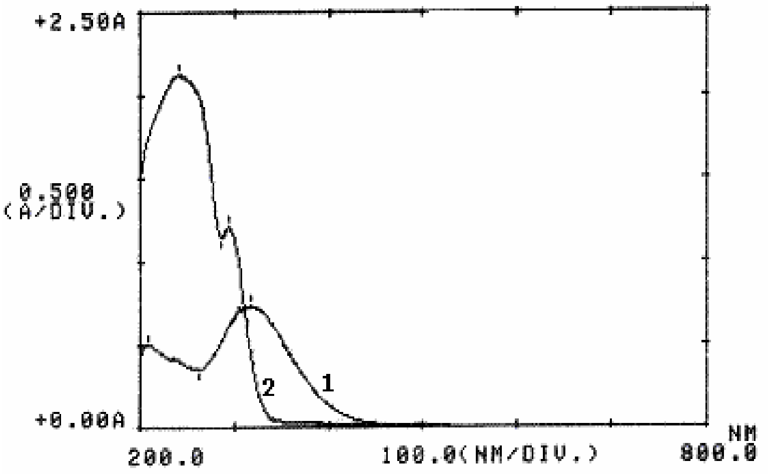

Fig. 5: Absorption Spectra of (1) Cerium (IV) Sulphate Tetrahydrate, (2) Cerium (III) Nitrate Hexahydrate

STABILITY OF THE TRIS(2,2′-BIPYRIDINE)IRON(II) SULPHATE IN DIFFERENT MEDIUMS

Kinetics of the reaction was spectrophotometrically followed at the wavelength of maximum absorption (λ_{max}) of the tris(2,2′-bipyridine)iron(II) sulphate in the visible region. Hence it was necessary to check stability of the complex compound in different mediums, used in the study of the kinetics of the redox reaction. Stability of the complex compound was studied at room temperature, 28 °C in different mediums like mixtures of ethanol in water and at different pH values.

EFFECT OF MEDIUMS

Stability of the complex compound in different mediums like 0%, 10% and 20% ethanol-water mixture was studied. The data were spectrophotometrically collected at 522 nm with the time interval of one minute for 3.5 hours. Results established that the complex compound is stable in the particular mediums.

EFFECT OF pH

Stability of the complex compound was also checked at different pH values like 3.71, 4.15 and 4.82. pH was maintained by using acetic acid-sodium acetate buffer. Standard solutions of the buffers were prepared as described [Jeffery *et al*. 1989]. The data were collected in the same manner as for the study of effect of the mediums. From the results it is inferred that the complex compound is stable at a pH value of 4.82.

KINETIC MEASUREMENTS

The reaction was followed by monitoring the rate of change in the absorbance with the time at the wavelength of maximum absorption (λ_{max} 522 nm) of tris(2,2′-bipyridine)iron(II) sulphate. Kinetic study of the redox reaction between tris(2,2′-bipyridine)iron(II) sulphate and ceric sulphate was carried out in the sulphuric acid medium, under the pseudo-first order conditions with the ceric sulphate concentration always in at least 3.33, 6.67, 10, 20 and 30-fold excess of the complex compound. The pseudo-first order rate constants were obtained from the slopes of the plots of $ln\frac{(A_o - A_\infty)}{(A_t - A_\infty)}$ against time. The plots were always linear.

INSTRUMENTATION

All the spectra and the kinetic measurements were recorded on the spectrum and the photometric mode respectively, of a Shimadzu UV-160, UV-Visible spectrophotometer, using quartz cells whereas pH measurements were carried out on a METTLER MP-220 model pH meter.

RESULTS AND DISCUSSION

Course of the reaction was followed under the condition of isolation, as if;

$$\text{Rate} = k\,[\text{reductant}]\,[\text{oxidant}]_t \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(I)}$$

Where [reductant] <<< $[\text{oxidant}]_t$

Effect of the [reductant] on the rate of the redox reaction could be studied independently of the $[\text{oxidant}]_t$, because under the condition employed, the

$[\text{oxidant}]_t$ will be effectively constant and effect of the [reductant] on the rate of the redox reaction could be studied independently of the $[\text{oxidant}]_t$, hence

Rate = k_{obs} [reductant] ……………………………………… (II)

$\therefore k_{obs} = k\,[\text{oxidant}]_t$ ………………………………………... (III)

k_{obs} = pseudo-first order rate constant having the unit s^{-1}.

Equations (II) and (III) will thus help to evaluate value of the rate constant and also to investigate order of the reaction with respect to the [reductant] and the $[\text{oxidant}]_t$, respectively.

DEPENDENCE OF THE RATE OF REDOX REACTION ON THE REDUCTANT

Order of the redox reaction and value of the pseudo-first order rate constant (k_{obs}), with respect to the reductant $[Fe(bipy)_3]SO_4$, was determined by employing Integration and Half-life method. Both the methods showed the first-order dependence of the rate of the redox reaction on the tris(2,2′-bipyridine)iron(II) sulphate. Similar results were obtained while different initial concentrations of the oxidizing agent were employed, keeping all the other factors constant. Results are recorded in Table 3. Matching of the values of k_{obs} substantiates our claim that the first order kinetics is being followed.

Table 3: Dependence of the Rate of the Redox Reaction on the Reductant and the Oxidant. $[Fe(bipy)_3SO_4] = 0.75 \times 10^{-5}$ M, $[H_2SO_4] = 9.0 \times 10^{-2}$ M, Temperature = 28 °C

Set No.	$10^4\,[Ce^{IV}]_t$ (M)	0% ethanol-water mixture		Effect of H^+ ions on k_{obs}	
		Integration method $10^1\,k_{obs}\,(s^{-1})$	Half-life method $10^1\,k_{obs}\,(s^{-1})$	Integration method $10^1\,k_{obs}\,(s^{-1})$	Half-life method $10^1\,k_{obs}\,(s^{-1})$
1.	0.25	0.725	0.719	0.540	0.529
2.	0.50	1.450	1.446	1.100	1.121
3.	0.75	1.891	1.898	1.469	1.260
4.	1.50	2.493	2.475	1.778	1.848
5.	2.25	1.969	1.540	1.548	1.429

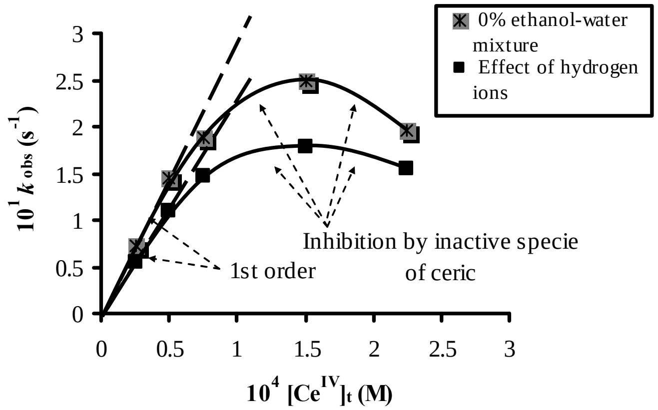

Fig. 6: Plot of k_{obs} versus $[Ce^{IV}]_t$ in 0% Ethanol-Water Mixture in Acidic Medium.

DEPENDENCE OF THE RATE OF REACTION ON THE OXIDANT

Order of the reaction with respect to the ceric sulphate; $[\text{oxidant}]_t$ was established through equation (III). The kinetic runs were carried out by varying initial concentration of the oxidant, keeping the remaining conditions unaltered. Values of the pseudo-first order rate constant (Table 3) were found to be dependent upon the ratio between the two reactants, tris(2,2′-bipyridine)iron(II) sulphate and ceric sulphate. A plot of k_{obs} versus $[Ce^{IV}]_t$ was found to be a curve (Fig. 6) indicating the complex kinetics with respect to the oxidant.

DEPENDENCE OF THE RATE OF THE REACTION ON THE FACTORS LIKE DIELECTRIC CONSTANT (D), $[H^+]$ AND $[SO_4^{2-}]$ OF THE SYSTEM

Effect of The Dielectric Constant of The Medium

Effect of the dielectric constant of the medium on the observed rate constant; k_{obs}, was studied by decreasing the dielectric constant of the medium gradually through addition of the ethanol in the medium. 0%, 10% and 20% ethanol-water mixtures were used for that purpose. The remaining conditions were kept unaltered.

Results (Table 4) reveal that value of the pseudo-first order rate constant (k_{obs}) increases on decreasing the dielectric constant of the medium however a plot (Fig. 7) of log k_{obs} versus (1/D) was found to be a straight line with a positive slope (85.144) and an intercept (-1.8087) on y-axis through which it is clearly judged that the rate determining step involves the reacting specie with the unlike charges.

Table 4: Dependence of k_{obs} on the Dielectric Constant (D) of the System.
$[Fe(bipy)_3SO_4] = 0.75 \times 10^{-5}$ M, $[Ce^{IV}]_t = 2.25 \times 10^{-4}$ M, $[H_2SO_4] = 9.0 \times 10^{-2}$ M, Temperature = 28 °C

Medium	Dielectric Constant (D)	10^4 1/D	10^1 k_{obs} (s^{-1})	10^4 log k_{obs}
0% ethanol-water mixture	78.54	127.32	1.969	-7057.5
10% ethanol-water mixture	65.80	151.97	2.824	-5491.3
20% ethanol-water mixture	54.90	182.15	5.723	-2423.7

*Values of the dielectric constant aren't recalculated for presence of the sulphuric acid in the medium and used as they were reported in the literature [Tarui 2002].

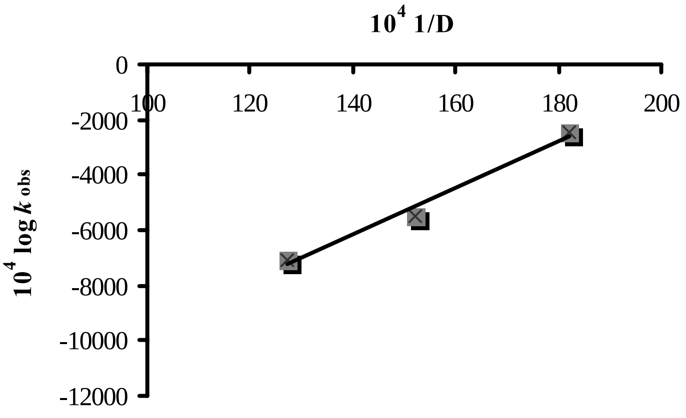

Fig. 7: Effect of the Dielectric Constant of the System on the Rate of the Redox Reaction between Tris(2,2′-bipyridine)iron(II) Sulphate and Ceric Sulphate.

Although cerium(IV) is well known to oxidize the alcohols in the different aqueous acidic mediums under particular conditions [Ardon 1957, Muhammad and Rao 1963, Jameel 1997, Handi *et al*. 2000], but at the experimental conditions employed in this study, the rate of the oxidation of ethanol by ceric sulphate in the aqueous sulphuric acid medium is known to be very slow [Muhammad and Rao 1963, Ardon 1957] and negligible if compared with the one under observation. Thus ethanol was used (complex compound is stable in 10% and 20% ethanol-water mixture) to investigate effect of the dielectric constant of the medium on the rate of the redox reaction.

Effect of [H$^+$]

Wiberg and Ford [1969] have shown the existence of the equilibrium in 85% aqueous acetic acid solution:

$$CeOH^{3+} + HOAc \leftrightarrow CeOAc^{3+} + H_2O \cdots\cdots\cdots\cdots\cdots\cdots \quad (D)$$

But there is no evidence for the formation of any species like $CeOH^{3+}$ and $CeOAc^{3+}$ of cerium(IV) in the mixture of acetic acid-sodium acetate buffer and aqueous sulphuric acid. From the literature survey [Hardwick and Robertson 1951, Wiberg and Ford 1969, Kishan and Sundaram 1980], it can be concluded that in the mixture of acetic acid-sodium acetate buffer and aqueous sulphuric acid, cerium(IV) exists in the form of sulphate complexes, however acetate buffer just increases concentration of the hydrogen ions of the mixture.

Hence in order to study the effect of [H$^+$] on the rate of reaction, kinetic runs were carried out by using acetic acid-sodium acetate buffer of the pH value 4.82, for making the solution of $[Fe(bipy)_3]SO_4$ instead of 0% ethanol-water mixture. All the remaining conditions were kept constant. Table 3 and Fig. 6 narrate effect of [H$^+$] on the pseudo-first order rate constant. Values of the rate constant (k_{obs}) were found to decrease on increasing concentration of hydrogen ions of the system.

Table 5: Dependence of k'_{obs} on $[SO_4^{2-}]$. Medium = 0% ethanol–water mixture, $[Fe(bipy)_3SO_4] = 0.75 \times 10^{-5}$ M, $[Ce^{IV}]_t = 2.25 \times 10^{-4}$ M, $[H_2SO_4] = 15.9 \times 10^{-2}$ M, Temperature = 28 °C

S. No.	10^2 $[Na_2SO_4]$ (M)	10^2 $[SO_4^{2-}]_a$ (M)	10^2 $[SO_4^{2-}]_a^{-1}$ (M^{-1})	10^1 k_{obs} (s^{-1})	k'_{obs} ($M^{-1}s^{-1}$)	10^5 $1/k'_{obs}$ (M s)
1.	30	33.767	296.147	1.830	813.3	122.955
2.	40	43.767	228.482	2.213	983.5	101.677
3.	50	53.767	185.987	2.534	1126.2	88.794
4.	60	63.767	_	2.680	1191.1	83.956
5.	70	73.767	_	2.390	1062.2	94.144
6.	80	83.767	_	1.860	826.6	120.977
7.	90	93.767	_	1.257	558.6	179.019

Effect of $[SO_4^{2-}]$

Influence of the $[SO_4^{2-}]$ on the rate of the reaction was investigated by varying $[SO_4^{2-}]_a$, using sodium sulphate (Na_2SO_4) as a source of sulphate ions, keeping [H$^+$] almost constant and the other factors also unaltered. Results (Table 5, Fig. 8) show that on increasing $[SO_4^{2-}]_a$ in the medium, k'_{obs} accelerates first and then goes toward retardation. Here,

k'_{obs} = second order rate constant having the unit $mol^{-1}\ dm^3\ s^{-1}$ or $M^{-1}\ s^{-1}$.

$[\ ]_a$ = actual concentration of the species for which the dissociation constant of bisulphate ions is considered.

From the earlier reports [Hardwick and Robertson 1951, Krishna and Tewari 1961] it appears that in the aqueous sulphric acid medium cerium(IV) can exist in several forms, depending upon the concentration of cerium(IV) and sulphuric acid like, Ce^{4+}, $Ce(SO_4)^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$, $HCe(SO_4)_3^{-}$ and $H_2Ce(SO_4)_4^{2-}$.

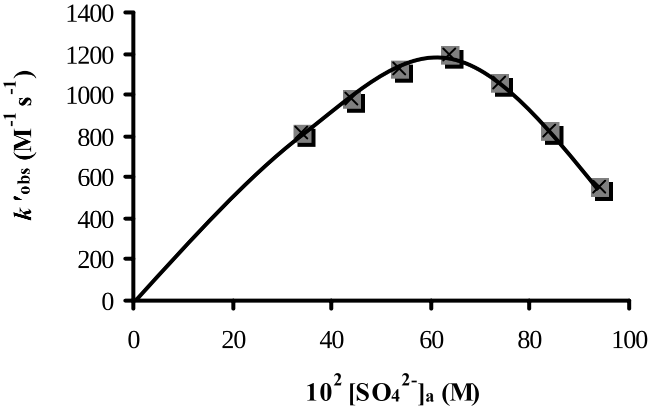

Fig. 8: Plot of k'_{obs} versus [SO$_4^{2-}$]$_a$, showing Influence of the Sulphate Ions in the Electron-transfer reaction between Tris(2,2′-bipyridine)iron(II) Sulphate and Ceric Sulphate.

Some of the equilibria [Hardwick and Robertson 1951, Krishna and Tewari 1961] leading to the formation of sulphato complexes of cerium (IV) include,

$$Ce^{4+} + HSO_4^{-} \leftrightarrow CeSO_4^{2+} + H^{+} \cdots\cdots\cdots\cdots\cdots\cdots \quad (E)$$

$$CeSO_4^{2+} + HSO_4^{-} \leftrightarrow Ce(SO_4)_2 + H^{+} \cdots\cdots\cdots\cdots \quad (F)$$

$$Ce(SO_4)_2 + HSO_4^{-} \leftrightarrow Ce(SO_4)_3^{2-} + H^{+} \cdots\cdots\cdots \quad (G)$$

$$Ce(SO_4)_2 + HSO_4^{-} \leftrightarrow HCe(SO_4)_3^{-} \cdots\cdots\cdots\cdots\cdots \quad (H)$$

$$Ce(SO_4)_3^{2-} + H^{+} \leftrightarrow HCe(SO_4)_3^{-} \cdots\cdots\cdots\cdots\cdots \quad (I)$$

$$HCe(SO_4)_3^{-} + HSO_4^{-} \leftrightarrow H_2Ce(SO_4)_4^{2-} \cdots\cdots \quad (J)$$

In the oxidation of different substrates by cerium (IV) in aqueous sulphuric acid medium, one or more of the equilibria can be involved in the kinetics of the reaction and one or more of the specie can be considered to be the reactive specie of cerium(IV).

Through the effects of dielectric constant, H$^+$ and SO$_4^{2-}$ of the medium on the rate of the reaction, difficulty of choice of the active and the inactive specie among the above mentioned ones for the study of the kinetics of a particular reaction of cerium(IV) under the experimental conditions employed, can easily be overcome.

Under the experimental conditions of the present work, the most relevant equilibria appear to be (G), (H), (I) and (J) and through effects of the different factors active and inactive specie involved in the reaction kinetics, have been suggested.

Influence of the dielectric constant on k_{obs} shows that the reacting specie have unlike charges whereas literature survey [Basolo *et al.* 1954, Burgess and Prince 1966, Ayodele *et al.* 2000] indicates that under the experimental conditions the reductant exists in the form of a complex cation like $[Fe(bipy)_3]^{2+}$ and hence reacts as $[Fe(bipy)_3]^{2+}$. It is expected that the reactive species of cerium (IV) is one of $Ce(SO_4)_3^{2-}$, $HCe(SO_4)_3^{-}$ and $H_2Ce(SO_4)_4^{2-}$ and inactive species is $Ce(SO_4)_2$. But effect of the $[H^+]$ on the rate of the reaction clearly supports the fact of participation of $Ce(SO_4)_3^{2-}$ as an active species and $Ce(SO_4)_2$, $HCe(SO_4)_3^{-}$ and $H_2Ce(SO_4)_4^{2-}$ as inactive specie in the redox reaction between tris(2,2′-bipyridine)iron(II) sulphate and ceric sulphate. Further to that the conclusion is also favoured by the influence of $[SO_4^{2-}]_a$ on k'_{obs}, like initially on lower concentration of the sulphate ions, value of the second order rate constant increases because of the formation of the active species through equilibrium (G), but at higher concentrations it is decreased because of the conversion of the reactive species $Ce(SO_4)_3^{2-}$ into the inactive species $H_2Ce(SO_4)_4^{2-}$ through the equilibria (H), (I) and (J).

PROPOSED MECHANISM

Stoichiometry of the reaction is given as:

$$[Fe(bipy)_3]^{2+} + Ce^{4+} \rightarrow [Fe(bipy)_3]^{3+} + Ce^{3+}$$

Keeping the various aspects in view as well as the kinetic evidence obtained for the existence of different forms of cerium (IV) in the present investigation, we propose the following mechanism which involves the following reactions:

$$Ce(SO_4)_2 + HSO_4^- \xleftrightarrow{K_1} Ce(SO_4)_3^{2-} + H^+ \cdots\cdots\cdots (1)$$

$$Ce(SO_4)_2 + HSO_4^- \xleftrightarrow{K_2} HCe(SO_4)_3^- \cdots\cdots\cdots\cdots\cdots (2)$$

$$Ce(SO_4)_3^{2-} + H^+ \xleftrightarrow{K_3} HCe(SO_4)_3^- \cdots\cdots\cdots\cdots\cdots\cdots (3)$$

$$HCe(SO_4)_3^- + HSO_4^- \xleftrightarrow{K_4} H_2Ce(SO_4)_4^{2-} \cdots\cdots\cdots (4)$$

$$[Fe(bipy)_3]^{2+} + Ce(SO_4)_3^{2-} \xrightarrow{k} [Fe(bipy)_3]^{3+} + Ce^{3+} + 3SO_4^{2-} \cdots\cdots (5)$$

Equilibria (1), (2), (3) and (4) are involved in the mechanism and lead to the formation of different specie like,

$$[Ce(SO_4)_2]_a = \frac{[Ce(SO_4)_3^{2-}]_a [H^+]_a}{K_1 [HSO_4^-]_a} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

$$[HCe(SO_4)_3^-]_a = \frac{K_2 [Ce(SO_4)_3^{2-}]_a [H^+]_a}{K_1} \cdots\cdots\cdots\cdots\cdots (7)$$

$$\left[HCe(SO_4)_3^{\;-}\right]_a = K_3\left[Ce(SO_4)_3^{\;2-}\right]_a\left[H^+\right]_a \;\cdots\cdots\cdots\cdots\cdots\; (8)$$

$$\left[H_2Ce(SO_4)_4^{\;2-}\right]_a = K_4\left[HCe(SO_4)_3^{\;-}\right]_a\left[HSO_4^{\;-}\right]_a \cdots\cdots\; (9)$$

$$\therefore \left[H_2Ce(SO_4)_4^{\;2-}\right]_a =$$

$$K_4\left[Ce(SO_4)_3^{\;2-}\right]_a\left[HSO_4^{\;-}\right]_a\left[H^+\right]_a\left\{\frac{K_2+K_1K_3}{K_1}\right\}\cdots\cdots\; (10)$$

The total cerium (IV) concentration is

$$\left[Ce^{IV}\right]_t = \left[Ce(SO_4)_2\right]_a + \left[Ce(SO_4)_3^{\;2-}\right]_a + \left[HCe(SO_4)_3^{\;-}\right]_a + \left[H_2Ce(SO_4)_4^{\;2-}\right]_a \cdots (11)$$

Where [ ]$_t$ = total concentration of the species.
[ ]$_a$ = actual concentration of the species.

Dissociation constant of the bisulphate ion is also considered [Hill and Petrucci 1996] when ion concentrations in the aqueous sulphuric acid are being calculated under the experimental conditions employed.

$$\left[HSO_4^{\;-}\right]_a = \frac{\left[H^+\right]_a\left[SO_4^{\;2-}\right]_a}{K_d}\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\; (12)$$

Where K_d = Dissociation constant of the bisulphate ion.
The use of equations (6), (7), (8), (10), (11) and (12) leads to

$$\left[Ce(SO_4)_3^{\;2-}\right]_a =$$

$$\frac{K_1K_d\left[Ce^{IV}\right]_t\left[SO_4^{\;2-}\right]_a}{K_d^{\;2}+\left[SO_4^{\;2-}\right]_a\left[K_d\,(K_1+[H^+]_a\{K_2+K_1K_3)+(K_4[H^+]_a[SO_4^{\;2-}]_a)(K_2+K_1K_3)\}\right]}\;(13)$$

The rate of the redox reaction, equal to k [Fe(bipy)$_3^{2+}$] [Ce(SO$_4$)$_3^{2-}$]$_a$, is

$$-\frac{d\left[Fe(bipy)_3^{\;2+}\right]}{dt} =$$

$$\frac{k\,K_1K_d\left[Fe(bipy)_3^{\;2+}\right]\left[Ce^{IV}\right]_t\left[SO_4^{\;2-}\right]_a}{K_d^{\;2}+\left[SO_4^{\;2-}\right]_a\left[K_d\,(K_1+[H^+]_a\{K_2+K_1K_3)+(K_4[H^+]_a[SO_4^{\;2-}]_a)(K_2+K_1K_3)\}\right]}\;(14)$$

Expression (14) explains unit order in [Fe(bipy)$_3^{2+}$], unit order in [Ce^{IV}]$_t$, acceleration as well as inhibition by [SO$_4^{2-}$]$_a$ and inhibition by [H$^+$]$_a$.
On combining equations (II) and (14), we obtain

$$k_{obs} = \frac{k K_1 K_d \left[Ce^{IV}\right]_t \left[SO_4{}^{2-}\right]_a}{K_d{}^2 + \left[SO_4{}^{2-}\right]_a \left[K_d \left(K_1 + \left[H^+\right]_a \{K_2 + K_1 K_3 \right) + \left(K_4 \left[H^+\right]_a \left[SO_4{}^{2-}\right]_a \right) (K_2 + K_1 K_3)\} \right]} \quad (15)$$

Under the experimental conditions, $[SO_4^{2-}]_a >>>> [Ce^{IV}]_t >>> [Fe(bipy)_3^{2+}]$

$$k_{obs} = k'_{obs} \left[Ce^{IV}\right]_t \;\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \; (16)$$

$$\therefore k'_{obs} = \frac{k K_1 K_d \left[SO_4{}^{2-}\right]_a}{K_d{}^2 + K_i \left[SO_4{}^{2-}\right]_a} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \; (17)$$

Where

k'_{obs} = the second order rate constant having the unit conc.$^{-1}$ time^{-1} that's M^{-1} s^{-1}.

K_i = Inhibition constant and is

$$K_i = \left[K_d \left(K_1 + \left[H^+\right]_a \{K_2 + K_1 K_3 \right) + \left(K_4 \left[H^+\right]_a \left[SO_4{}^{2-}\right]_a \right) (K_2 + K_1 K_3)\} \right]$$

There are two limiting cases for k_{obs} and k'_{obs}:

k_{obs} depends on $[Ce^{IV}]_t$ in a complex manner (Fig. 6).

- for k_{obs} the excess of cerium (IV) is only small, when $Ce(SO_4)_3^{2-}$ is the only species of cerium (IV) present at significant concentration under the experimental conditions employed, i.e. at low concentration of SO_4^{2-} [Hardwick and Robertson 1951], thus

  $K_d^2 + K_i \left[SO_4{}^{2-}\right]_a \rightarrow K_d^2$ and

$$k_{obs} = \frac{k K_1 \left[Ce^{IV}\right]_t \left[SO_4{}^{2-}\right]_a}{K_d} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \; (18)$$

Also the reaction rate is proportional to $[Ce^{IV}]_t$, i.e. is first order in ceric sulphate.

- the excess of cerium (IV) is large, when all the specie i.e. active and inactive ones of cerium (IV) are present at significant concentration [Hardwick and Robertson 1951, Krishna and Tewari 1961] under the experimental conditions employed, i.e. at high concentration of SO_4^{2-} , hence

  $K_d^2 + K_i \left[SO_4{}^{2-}\right]_a \rightarrow K_d^2 + K_i \left[SO_4{}^{2-}\right]_a$ and

$$k_{obs} = \frac{k K_1 K_d \left[Ce^{IV}\right]_t \left[SO_4{}^{2-}\right]_a}{K_d^2 + K_i \left[SO_4{}^{2-}\right]_a} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \; (19)$$

By taking the reciprocal of both the sides of equation (19), we get

$$\frac{1}{k_{obs}} = \frac{K_d}{k K_1 \left[Ce^{IV}\right]_t \left[SO_4{}^{2-}\right]_a} + \frac{K_i}{k K_1 K_d \left[Ce^{IV}\right]_t} \cdots\cdots\cdots (20)$$

and the reaction rate is inhibited by ceric sulphate at higher concentrations.

- for k'_{obs} the excess of sulphate ions is very large, and

$$K_d^2 + K_i\left[SO_4^{2-}\right]_a \rightarrow K_i\left[SO_4^{2-}\right]_a \quad \text{and}$$

$$k'_{obs} = \frac{k K_1 K_d}{K_i} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (21)$$

On rearranging equation (21)

$$\frac{1}{k'_{obs}} = \frac{K_i}{k K_1 K_d} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (22)$$

$$\frac{1}{k'_{obs}} = \frac{K_1 + \left[H^+\right]_a (K_2 + K_1 K_3)}{k K_1} + \frac{\left[SO_4^{2-}\right]_a \left(K_4 \left[H^+\right]_a^2\right)(K_2 + K_1 K_3)}{k K_1 K_d} \cdots \quad (23)$$

Equation (23) can be simplified as

$$\frac{1}{k'_{obs}} = \left(\frac{1}{k} + b\right) + \frac{K_4 b \left[H^+\right]_a \left[SO_4^{2-}\right]_a}{K_d} \cdots\cdots\cdots\cdots\cdots\cdots \quad (24)$$

$$\therefore b = \frac{K'\left[H^+\right]_a}{k K_1} \; and \; K' = (K_2 + K_1 K_3)$$

- the excess of sulphate ions is only small, when

$$K_d^2 + K_i\left[SO_4^{2-}\right]_a \rightarrow K_d^2 + K_1 K_d\left[SO_4^{2-}\right]_a \quad \text{and}$$

$$k'_{obs} = \frac{k K_1 K_d \left[SO_4^{2-}\right]_a}{K_d^2 + K_1 K_d \left[SO_4^{2-}\right]_a} \cdots\cdots\cdots\cdots\cdots\cdots \quad (25)$$

Equation (25) can be simplified by taking the reciprocal thus

$$\frac{1}{k'_{obs}} = \frac{K_d}{k K_1 \left[SO_4^{2-}\right]_a} + \frac{1}{k} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (26)$$

According to the equation (26) a plot of $1/k'_{obs}$ versus $1/\ [SO_4^{2-}]_a$ should be linear with a positive slope, $K_d/k\,K_1$ and an intercept, $1/k$ on y-axis.

This plot is linear (Fig. 9), with an intercept $1/k$, 30.926×10^{-5} M s and a slope = $K_d\ /k\ K_1 = 31.05 \times 10^{-5}\ M^2$ s. These values confirm the proposed mechanism. From the intercept and slope of such a plot the value of k, a second order rate constant and K_1 are derived and found as, $k = 32.335 \times 10^2\ M^{-1}\ s^{-1}$ and $K_1 = 11.653 \times 10^{-3}$, whereas $K_d = 1.17 \times 10^{-2}$ M at 28 °C.

However a linear correlation between the inverse of the rate constant, $1/k'_{obs}$ and $[SO_4^{2-}]_a$ is consistent with the rate law (24) and shown in Fig. 10. The agreement is qualitative only because the extent of retardation produced by the sulphate and the hydrogen ions might not be similar (equilibria 1 to 4) and thus the plot (Fig. 10) shows a negative intercept = $(1/k) + b = -126.25 \times 10^{-5}$ M s and a positive slope = $K_4 b[H^+]_a/K_d = 31.202 \times 10^{-4}$ s that gives negative mathematical values for K' and K_4 respectively. However a negative mathematical value of an equilibrium constant, have no physical or quantitative existence.

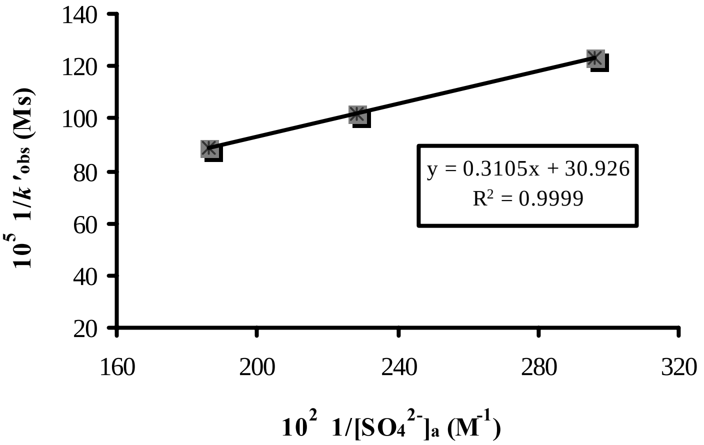

Fig. 9: Plot of $1/k'_{obs}$ versus $1/[SO_4^{2-}]_a$, showing the Catalytic Effect of the added Sulphate Ions in the Redox Reaction.

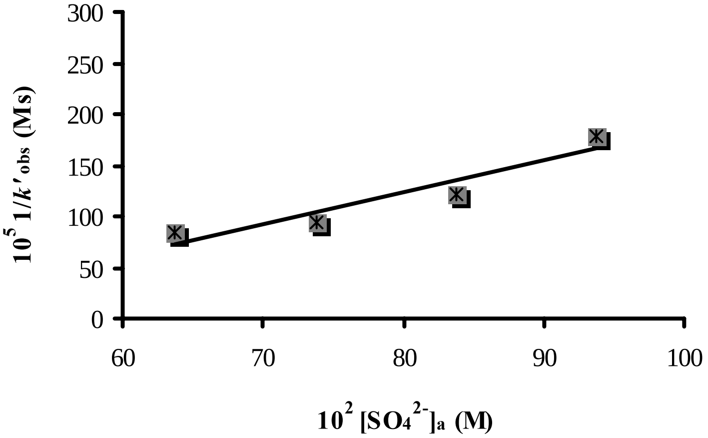

Fig. 10: Plot of $1/k'_{obs}$ versus $[SO_4^{2-}]_a$, showing the Retarding Effect of the added Sulphate Ions in the Redox Reaction between Tris(2,2′-bipyridine)iron(II) Sulphate and Ceric Sulphate.

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