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Kinetic Determination of Trace Amounts of Thiosulfate Based on Its Inhibitory Effect

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The sulfur containing ligand *viz.*, thiosulfate is found to inhibit the Ag(I) catalyzed substitution of cyanide in hexacyanoferrate(II) by phenylhydrazine. The inhibitory effect of thiosulfate is attributed due to its tendency to form complexes with Ag(I), leading to the production of inhibitor-catalyst complexes. The reactions, followed spectrophotometrically in aqueous medium at 488 nm, was possible by the increase in absorbance of the cherry-red product, $[Fe(CN)_5PhNHNH_2]^{3-}$ at pH 2.8 (±0.02), at 30 (±0.1) °C, and an ionic strength (μ) of 0.02 M (KNO_3). The linear calibration curves were obtained using the absorbance measured at different times (A_t) and thiosulfate concentrations under specified conditions. The calculated detection limit was 4.9×10^{-7} M. The Michaelis-Menten constant (K_m) and equilibrium constants for the formation of complexes between catalyst and inhibitor (K_{CI}), and the catalyst and substrate (K_S) were computed from the kinetic data. A general mechanistic scheme is proposed for this reaction.

Keywords: Kinetics, Silver(I), Thiosulfate, Inhibition, Spectrophotometry

INTRODUCTION

Numerous kinetic studies relate to the kinetics and mechanisms of metal-catalyzed ligand-substitution reactions between hexacyanoferrate(II) and nitrogen heterocyclic ligands [1-4]. The kinetic determination of ultra trace quantities of inorganic ions have been the subject of interest of several investigators [5-14] including our group [15-18]. A complexing agent added to a metal ion-catalyzed reaction may alter the catalytic activity of the catalyst through the formation of strong complexes with metal catalysts, resulting either in ligand inhibition or rate promotion [5]. Such change in catalytic activity is highly dependent on the concentration of the complex formed between the catalyst and the added ligand concentration. This often provides a linear relationship between the rate of specific indicator reactions and the concentration of added ligand, which in turn makes it possible to determine the concentration of the complexing ligand by the so-called kinetic method of analysis using a much cheaper UV-Vis spectrophotometer.

Our recent investigation on the kinetic determination of Ag(I) at trace levels [19] using the catalytic effect of Ag(I) on ligand substitution reactions between hexacyanoferrate(II) and phenylhydrazine in the presence of several foreign ions showed that thiosulfate ions retard or inhibit the reaction rate considerably [19]. This was attributed to the complex-forming tendencies of the inhibiting ligand or complexing agent, *i.e.*, low concentrations of thiosulfate with the silver(I) catalyst in the present case, which usually form more stable complexes with sulfur-containing ligands than those having N and O donor atoms even at low pH values.

Sodium thiosulfate has been as a ligand of choice [20] in the treatment of certain acute and chronic heavy-metal poisoning. The terminal sulfur atom in sodium thiosulfate can

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easily bind with soft metals possessing high affinity. Sodium thiosulfate is also used as an antidote to cyanide poisoning [21,22], in pharmaceutical preparations as an anionic surfactants aiding dispersion mediums [21,22] and as an analytical reagent in determining the concentrations of a few compounds in solution (*e.g.*, hydrogen peroxide) and the chlorine content in commercial bleaching powder and in water.

There are a limited number of investigations available in the literature related to the determination of these complexing agents called inhibitors using metal-catalyzed reactions [23-29]. The determination of thiosulfate has also been made through kinetic measurements based on costly equipment, such as stopped-flow [30] and cathodic-stripping voltammetry [31].

Therefore, it is evident that the development of simple, less-expensive kinetic methods for the determination of low levels of thiosulfate is still desirable. The present paper describes the development of kinetic methods for the sensitive determination of thiosulfate based on the Ag(I)-catalyzed ligand substitution reaction between hexacyanoferrate(II) and phenylhydrazine.

EXPERIMENTAL

Materials

The chemicals $K_4[Fe(CN)_6].3H_2O$, (Merck), $AgNO_3$ (AR, Galaxo Laboratories) phenylhydrazine hydrochloride (S.D. Fine-Chem Ltd., Mumbai, India), and sodium thiosulfate (BDH) were used for this work. All other chemicals used were of analytical grade. Double-distilled water was used throughout this study.

Stock solutions of hexacyanoferrate(II), silver nitrate, phenylhydrazine and buffer solution were prepared as reported elsewhere [2]. Thiosulfate was iodometrically standardized against a standard $K_2Cr_2O_7$ solution [32]. The pH of the reaction mixture was maintained at a desired value using a potassium phthalate-sodium hydroxide buffer.

Apparatus and Kinetic Measurement

A SISCO visible spectrophotometer (model DIGI-110), fitted with a water circulation for thermostating the cell compartment, was used to monitor the progress of reaction. The pH measurements were made on a Toshniwal digital pH meter (model CL-46). The standard BDH buffers were used to calibrate the pH meter. All the solutions were thermally equilibrated using a thermostat for at least half an hour at 30 ± 0.1 °C before starting each kinetic run.

The spectrophotometer cuvettes were washed regularly with acetone to avoid any possible deposition of the colored complex, $[Fe(CN)_5PhNHNH_2]^{3-}$, on the walls of the cuvettes during the course of the reaction.

Procedure

After thermal equilibration, all reagent solutions were mixed in the following sequence: 1.0 ml of $AgNO_3$ solution at the desired concentration, 1.0 ml of various concentrations of inhibitor or complexing agent, which were mixed and kept for 15 min to ensure complete formation of catalyst-inhibitor complex (CI). Then, 2.0 ml of the potassium hydrogen phthalate buffer (pH 2.8 ± 0.02) was added, followed by 2.0 ml of phenylhydrazine and 1.0 ml KNO_3 (1 M). The reaction was finally initiated by adding 2.0 ml of the $[Fe(CN)_6]^{4-}$ solution. The reaction mixture was mixed by vigorous shaking and then transferred to a cuvette (10 mm path length), which was kept in a cell compartment maintained at 30 ± 0.1 ^{o}C by circulating water from a thermostatted bath. The reaction rate was measured by following the increase in the absorbance resulting from the formation of a cherry-red colored complex, $[Fe(CN)_5PhNHNH_2]^{3-}$, at 488 nm. The fixed-time procedure was adopted as a measure of the initial rate to establish the calibration curves.

The inhibitory effect of thiosulfate on the Ag(I)-catalyzed replacement of CN^- ion in $[Fe(CN)_6{}^{4-}]$ by phenylhydrazine was studied under the following conditions: $[Fe(CN)_6{}^{4-}] = 2.5 \times 10^{-3}$ M, $[PhNHNH_2] = 1.0 \times 10^{-5}$ M, $[Ag^+] = 8.0 \times 10^{-7}$ M and 2.0 ml of potassium hydrogen phthalate-NaOH buffer to maintain a final pH of 2.8 ± 0.02 in the reaction mixture.

RESULTS AND DISCUSSION

The phenylhydrazine substitution of the coordinated cyanide in hexacyanoferrate(II) is homogeneously catalyzed by $[Ag]^+$ ions in an acidic medium at normal temperature. A detailed kinetic and mechanistic study of this reaction under various conditions has been reported by Naik *et al*. [2]. The traces of $[Ag]^+$ ions enhanced the reaction rate considerably and the variation in rate was followed spectrophotometrically [19]. The reaction product, $[Fe(CN)_5PhNHNH_2]^{3-}$, has a strong absorption band at 488 nm (MLCT transitions) with no interference from the reactants Ag^+, $K_4[Fe(CN)_6]$ and phenylhydrazine.

The change in absorbance depends on the concentration of the reactants, pH, temperature and ionic strength [2]. Therefore, the effects of these variables on the reaction rate are prerequisite. The corresponding plots of the initial rate (V_i) evaluated at fixed times revealed the dependence of rate on $[PhNHNH_2]$, $[Fe(CN)_6{}^{4-}]$, temperature and ionic strength.

Effect of pH on Reaction Medium

The dependence of rate on pH was studied first within the pH range 1-8, in order to select a pH value corresponding to the optimum rate of the reaction using fixed-time procedure. The change in absorbance at 488 nm as a function of the pH of the media, at three time points (A_t, where t = reactant mixing times of 7, 10 and 12 min) is shown in Fig. 1.

Here, the reaction rate is slow at lower pH values, attains a maximum value at pH 2.8 ± 0.02 and then decreases again. The decrease in absorbance at the higher pH is probably due to a deficiency in the number of protons needed to regenerate the catalytic species and/or to decrease the $[Ag^+]$ as a result of its hydrolytic precipitation as hydroxides.

Hence, the pH 2.8 ± 0.02 is quite critical to this system, and should be maintained at this optimum value to avoid losing the sensitivity required for the determination using phthalate-sodium hydroxide buffer [33].

Effects of Reagent Concentration, Temperature and Ionic Strength

The effect of phenylhydrazine concentration was studied at the optimum pH and a $[PhNHNH_2]$ range of 1.25×10^{-4} to 2.0×10^{-3} M. On the basis of the plot of initial rate *vs*. $[PhNHNH_2]$ (not shown), the rate increases linearly with $[PhNHNH_2]$ up to a concentration of 1.0×10^{-3} M, and finally levels off at $[PhNHNH_2] \geq 1.0 \times 10^{-3}$ M. Thus, the $[PhNHNH_2]$ of 1.0×10^{-3} M was selected as optimal.

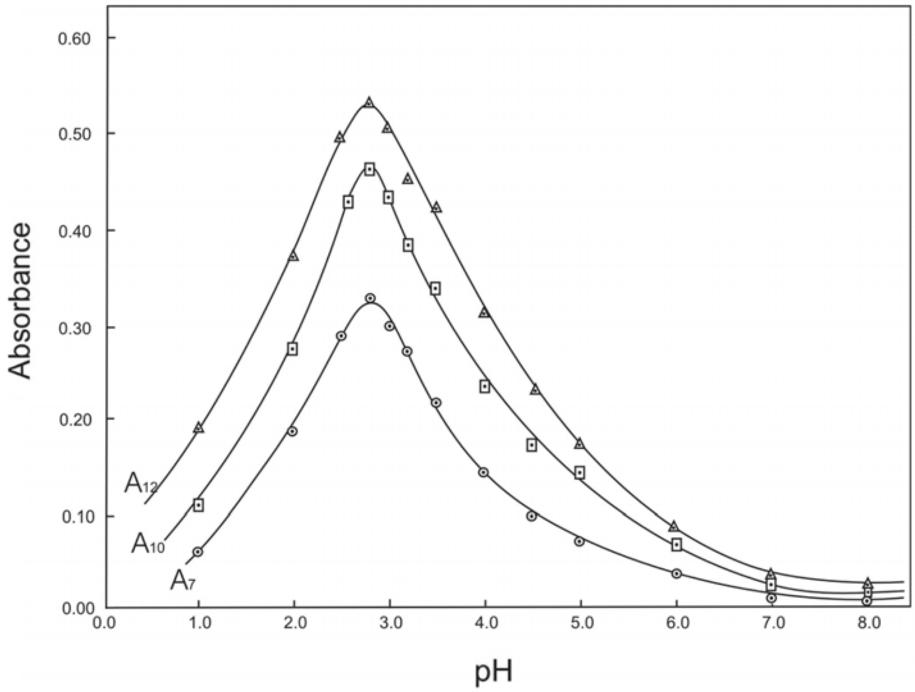


Fig. 1. Effect of pH on the Ag(I)-catalyzed substitution of CN^- in hexacyanoferrate(II) by phenylhydrazine. Conditions: $[Fe(CN)_6]^{4-} = 1.25 \times 10^{-2}$ M, $[PhNHNH_2] = 1.25 \times 10^{-3}$ M, $[Ag^+] = 1.0 \times 10^{-5}$ M, μ = 0.1 M, KNO_3 and temperature = 30 ± 0.1 °C.

The effect of $[Fe(CN)_6]^{4-}$ on the initial rate was studied in the range of 2.0×10^{-4} to 1.5×10^{-2} M, keeping all other experimental variables at constant known values. The plot of log(initial rate) *vs*. $\log[Fe(CN)_6]^{4-}$ (not shown), reveals a variable-order dependence on $[Fe(CN)_6]^{4-}$, changing from first-order at lower concentrations to a fractional order at the higher concentrations, but certainly not tending toward zero order. A $[Fe(CN)_6]^{4-}$ of 2.5×10^{-3} M was chosen as optimal.

The influence of temperature on the rate of the catalyzed and uncatalyzed reactions was studied in the range of 15-45 °C. The reaction obeyed Eyring's equation, and was found to proceed at a reasonable rate at 30 ºC, and was therefore selected for subsequent studies. The effect of ionic strength (μ) on the rate of the catalyzed reaction was studied in a range of 0.01 to 0.2 M, adjusted using KNO_3. As the ionic strength increases, the rate of reaction decreases. An ionic strength of 0.02 M gives a measurable change in absorbance values. Hence, $\mu = 0.02$ M was selected for further studies.

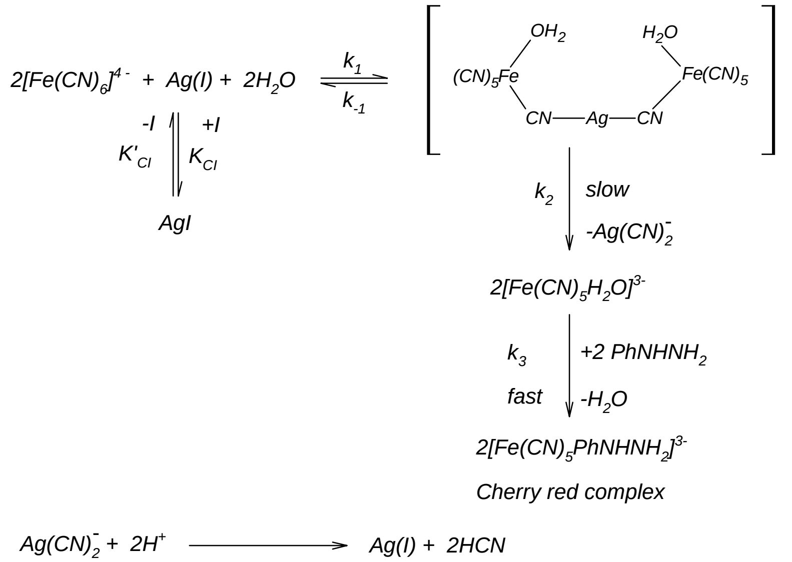
For analytical applications, the catalytic effect of $[Ag^+]$ on the rate of the catalyzed reaction was studied in a range 1.0×10^{-7} to 9.0×10^{-7} M under the following conditions: $[Fe(CN)_6]^{4-} = 5.0 \times 10^{-4}$ M, $[PhNHNH_2] = 2.0 \times 10^{-3}$ M, pH = 2.8 ± 0.02 , temperature = 30 ± 0.1 ºC and $\mu = 0.02$ M (KNO_3). The plot of absorbance after 7 min (A_7) *vs*. $[Ag^+]$ was found to be linear in the $[Ag^+]$ range of 4.0×10^{-7} to 9.0×10^{-6} M [2]. The linear regression equations correlating A_t (t = 12 and 15 min) to $[Ag^+]$ between 1.0×10^{-7} to 9.0×10^{-7} M are used to graph the calibration for the kinetic determination of $[Ag^+]$ [19]. A $[Ag^+]$ of 8.0×10^{-7} M provides sufficient absorbance change, and hence was used for the determination of thiosulfate.

Kinetic Role of Inhibiting Ligands

Regarding the silver(I)-catalyzed phenylhydrazine substitution of cyanide in hexacyanoferrate(II), the kinetic role of thoisulfate as an inhibitor can be understood if we assume that the inhibitor is competitive with the catalyst and reversible [34], thereby effectively depleting the concentration of catalyst and reducing the reaction rate.

In order to include the role of inhibitor (I), the mechanistic scheme proposed earlier [2] for the indicator reaction has been modified to the form shown in Scheme 1. Here, the path of the uncatalyzed reaction is ignored for simplicity. If the nonrate-limiting concentration of $[Fe(CN)_6]^{4-}$ is represented by [S] and its initial concentration by $[S]_0$, then it is simple to derive a kinetic equation by treating it similarly to that used for a single-substrate enzyme-catalyzed reaction in the presence of an inhibitor. The reaction rate in the presence of catalyst only is represented by Eq. (1):

$$V_o = \frac{V_{max}}{1 + \frac{K_m}{[S_0]}} \tag{1}$$



Scheme 1. The mechanistic pathway for the Ag(I) catalyzed substitution of cyanide in hexacyanoferrate(II) by phenylhydrazine.

This equation can be further transformed to the Lineweaver-Burk [35] form in Eq. (2).

$$\frac{1}{V_0}=\frac{1}{V_{max}}+\frac{K_m}{V_{max}}\cdot\frac{1}{[S_0]} \qquad (2)$$

where V_0 is the initial rate in the presence of catalyst only, V_{max} is the maximum attainable rate at a specific catalyst concentration in the presence of a nonrate-limiting quantity of substrate, and K_m is the Michaelis-Menten constant, which is roughly equivalent to the dissociation constant of the catalyst-substrate complex.

In the presence of inhibitor, the rate of reaction can be represented as shown in Eq. (3)

$$V_i=\frac{V_{max}}{1+\frac{K'_m}{[S_0]}} \qquad (3)$$

It can be easily shown that

$$K'_m = K_m\left[1+\frac{[\mathrm{I}]_0}{\mathrm{K}'_{\mathrm{CI}}}\right] \qquad (4)$$

Now, with the K'_m in Eq. (4), the initial rate can be conveyed as in Eq. (5).

$$V_i=\frac{V_{\max}}{1+\frac{K_m}{[S]_0}\left(1+\frac{[I]_0}{K'_{CI}}\right)} \qquad (5)$$

Here, V_i is the reaction rate in the presence of the inhibitor (at a fixed catalyst concentration), and K'_{CI} is the dissociation constant of the catalyst-inhibitor (C-I) complex.

Equation (5) can be transformed to Eq. (6) in Lineweaver-Burk form as:

$$\frac{1}{V_i}-\frac{1}{V_{\max}}=\frac{K_m}{V_{\max}[S]_0}+\frac{K_m}{V_{\max}[S]_0}\frac{[I]_0}{K'_{CI}} \qquad (6)$$

In Eq. (6), V_{max} is not an experimental quantity, but it is obtained from the intercept of the plot of $1/V_o$ *vs.* $1/[S_o]$ from Eq. (2) in absence of inhibitor as shown in Fig. 2. The slope of the above plot gives a K_m of 15.48 mM ($R \geq 0.9719$, $s \leq 0.3493$).

Equation (6) also works when the inhibitor 'I' forms a C-I type of chelate with the catalyst 'C', and for this reaction no substrate inhibition is seen. Under these conditions a plot of $(1/V_i)$ - $(1/V_{max})$ *vs.* $[I]_o$ gives a straight line as shown in Fig. 3

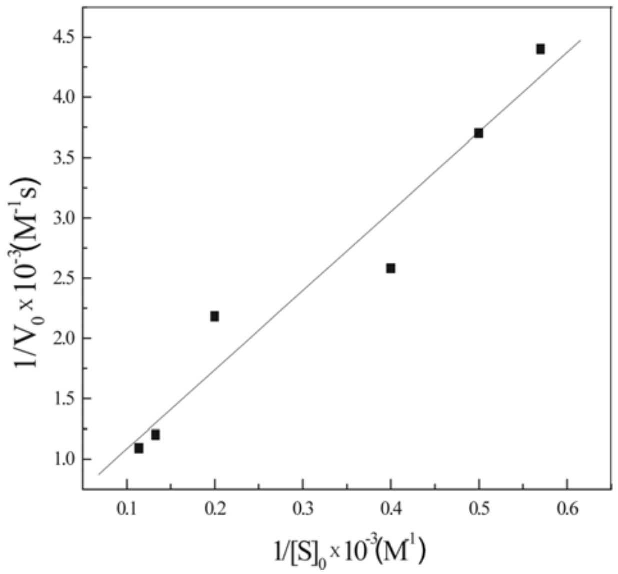


Fig. 2. Linear plot of $1/V_o$ *vs.* $1/V_o$. Conditions: $[Ag^+] = 1 \times 10^{-6}$ M, $[PhNHNH_2] = 2.0 \times 10^{-3}$ M, pH = 2.8 ± 0.02, temperature = 30 ± 0.1 °C and $\mu = 0.02$ M, KNO_3.

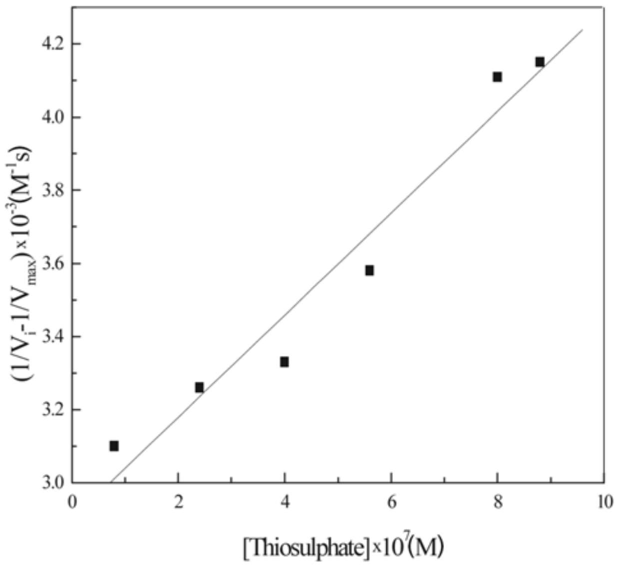


Fig. 3. Determination of K'_{CI} and K_m in presence of inhibitor thiosulphate under conditions: $[Fe(CN)_6]^{4-} = 2.5 \times 10^{-2}$ M, $[PhNHNH_2] = 1.0 \times 10^{-3}$ M, $[Ag^+] = 8.0 \times 10^{-7}$ M, pH = 2.8 ± 0.02, ionic strength, $\mu = 0.02$ M (KNO_3) and temperature = 30 ± 0.1°C.

for thiosulfate ($R \geq 0.9776$, $s \leq 0.1054$). The intercepts of this plot give a K_m that agrees with the value calculated here by plotting $1/V_o$ *vs.* $1/[S_o]$, the slope of which gives a K'_{CI} that corresponds to the thiosulfate complex of silver(I), as listed in Table 1.

The reciprocal of this K_m is approximately equal to the stability constant K_s ($\log K_s = 1.81 \pm 0.05$) of the catalyst-substrate complex. Also given in Table 1 are the values of the stability constant (K_{CI}) of the CI complexes and its reciprocal K'_{CI}, both of which are actually conditional constants. The competitive, non-competitive and uncompetitive behavior of inhibiting ligands can also be differentiated, although this is beyond the scope of this study.

Application of Calibration Graphs to Sample Analysis

The experimental observations reveal that thiosulfate inhibits the catalytic action of Ag(I), as it binds with the metal catalyst through the sulfur atom. The degree of inhibition is dependent upon the ratio of inhibitor to catalyst. This inhibition increases linearly with thiosulfate concentrations up to 8.8×10^{-7} M, which is a molar ratio ([I]/[C]) range of 0.1 to 1.1. At a higher ratio, the rate would approach that of the uncatalyzed reaction.

The calibration graph for thiosulfate was obtained using the standard procedure under optimum reaction conditions. The kinetic graphs established in the first 15-25 min of the reaction using the initial rate as well as the absorbance measured at different fixed times were linear. Absorbance values were measured at t = 12 and 15 min as a function of [thiosulfate], keeping all other experimental variables fixed The plot of the absorbance decrease measured at different times, A_t *vs.* [thiosulfate], showed a linear dependence when the thiosulfate concentration was in the range of 0.80 to 8.80×10^{-7} M. The linear regression expressions relating A_t to the [thiosulfate] are given through Eqs. (7) and (8).

$$A_{12} = 0.188 - 4.45 \times 10^4[\text{Thiosulfate}] \tag{7}$$

$$A_{15} = 0.230 - 4.87 \times 10^4[\text{Thiosulfate}] \tag{8}$$

The values of correlation coefficients (R) and standard deviations corresponding to the regression/calibration equations given in Eqs. (7) and (8) are $R \geq 0.9974$, $s \leq 0.0012$ and $R \geq 0.9944$, $s \leq 0.0017$, respectively.

Table 1. Conditional Formation Constants Under Optimal Conditions

A	Silver-Inhibitor Complexes	
	Inhibitor	$\log K_{CI}$
	Thiosulphate	5.68 ± 0.03
B	Michaelis-Menten Constant	
	Inhibitor	$\log K_m$
	Thiosulphate	1.23 ± 0.02
C	Catalyst-Substrate Complex	$\log K_S$
		1.81 ± 0.05

It is also important to note that, while all other experimental variables are fixed at optimum values, absorbance values, with respect to [thiosulfate], are treated as a close measure of the initial rate of reaction. The average percent error in thiosulfate determination for A_{12} is less than that of A_{15}. The shorter fixed times were also investigated, but the small absorbance changes caused larger errors. Therefore, only A_{12} and A_{15} regression equations were used for [thiosulfate] determinations.

If $[Ag^+] \leq 8.0 \times 10^{-7}$ M, the extent of catalysis in the presence of inhibiting ligand is too slow to be measured under experimental conditions. Furthermore, a higher catalyst concentration enhances the sensitivity of the reaction with a corresponding increase in [thiosulfate], thus allowing for determination over a wide range.

Analytical Applications

The validity of the proposed method was tested by performing recovery experiments on spiked water samples. The amount of thiosulfate contained in aqueous solutions was determined using the standard calibration equations stated above. The results obtained on three thiosulfate determination replicates, standard deviations, percent error and quantitative recoveries obtained from linear regression equations or linear least square calibration fits are listed in Table 2.

To check the applicability of the proposed method, recovery experiments were also performed on synthetic mixtures (SMs) of water spiked with thiosulfate and

Table 2. Accuracy of the Recommended Procedure for Determination of Thiosulfate in Aqueous Samples[a]

[Thiosulfate] ($\times 10^7$ M)	A_{12} [Thiosulfate][b] ($\times 10^7$ M)	A_{12} %Error	A_{15} [Thiosulfate][b] (found ± s) ($\times 10^7$ M)	A_{15} %Error
0.80	0.80 ± 0.02	+0.00	0.83 ± 0.01	+3.75
2.40	2.45 ± 0.03	+2.08	2.47 ± 0.01	+2.92
4.00	3.95 ± 0.02	-1.25	3.85 ± 0.02	-3.75
5.60	5.67 ± 0.03	+1.25	5.65 ± 0.03	+0.89
8.00	7.98 ± 0.04	-0.25	8.05 ± 0.04	+0.63
8.80	8.85 ± 0.05	+0.57	8.91 ± 0.05	+1.25

[a]Conditions: $[Fe(CN)_6]^{4-} = 2.5 \times 10^{-3}$ M, $[PhNHNH_2] = 1.0 \times 10^{-3}$ M, $[Ag^+] = 8.0 \times 10^{-7}$ M, pH = 2.8 ± 0.02, temperature = 30 ± 0.1 °C and ionic strength, $\mu = 0.02$ M (KNO_3). [b]±s values represent the relative standard deviation of the mean for three determinations.

Table 3. Determination of 0.3 and 0.6 μM of $[S_2O_3^-]$ in Synthetic Mixtures Under Optimum Conditions Using A_{15} Calibration Graphs at the Experimental Conditions Given in Table 2

Synthetic mixtures (SM)	Composition of SM (μM)	Found (μM) proposed method	Recovery (%)	Found (μM) CSV method [30]
SM-1	$S_2O_3^{2-}$ (0.3) + S^{2-} (0.3)	0.30	100.0	0.31
SM-2	$S_2O_3^{2-}$ (0.3) + S^{2-} (1.0)	0.31	103.3	0.32
SM-3	$S_2O_3^{2-}$ (0.6) + S^{2-} (1.0)	0.61	101.7	0.62
SM-4	$S_2O_3^{2-}$ (0.9) + S^{2-} (1.0)	0.92	102.2	0.91

commonly found sulfide ions, as shown in Table 3. The synthetic mixtures results in reasonably good agreement with the analysis by cathodic stripping voltammetry [30]. Under the specified conditions, the detection limit for thiosulfate was found to be 8.8×10^{-7} M.

Interference and Effects of Co-existing Substances

The influence of various ions on the determination of 0.4 μM thiosulfate was examined using A_{15} regression equations, the results of which are given in Table 4. Here, it is clear that inorganic ions, such as sodium, lead and magnesiumpresent in 10 percent excess over the $[Ag^+]$, do not noticeably effect the accuracy of the thiosulfate determination. The Cu^{2+} and Ni^{2+} ions are found to cause positive interference. The excess of anions, such as $C_2O_4^{2-}$, SO_4^{2-}, IDA^{2-}, NTA^{3-}, $HEDTA^{3-}$ and $DTPA^{5-}$ form strong complexes with Ag(I) and, hence, inhibit its catalytic activity causing negative interference. However, there should be no complexing agents that form complexes with higher stability constants than Ag(I) present in the

Table 4. Effects of Diverse Ions on Determination of 0.4 μM Thiosulfate[a]

Foreign ion	Tolerance limit (ng ml^{-1})
Na(I)	230
Pb(II)	2072
Cu(II)	635
Hg(II)	206
Mg(II)	243
Ni(II)	587
$(COO^-)_2$	88
$(SO_4)^{2-}$	96
IDA^{2-}	1321
$EDTA^{4-}$	2922
NTA^{3-}	1911
$HEDTA^{3-}$	2783
$DTPA^{5-}$	3933

[a]Using the A_{15} calibration equation under the conditions: $[Fe(CN)_6]^{4-} = 5.0 \times 10^{-3}$ M, $[PhNHNH_2] = 2.0 \times 10^{-3}$ M, pH= 2.8 ± 0.02, Ionic Strength, $\mu = 0.02$ M, KNO_3, temperature = 25 ± 0.1 °C.

solution except the one of analytical interest. It has also been observed that the inhibitory effect of thiosulfate starts at an [I]/[C] ratio of 0.10.

REFERENCES

[1] R.M. Naik, S. Prasad, R.K. Tewari, P.K. Singh, A.K. Tewari, Trans. Met. Chem. 30 (2005) 968.

[2] R.M. Naik, R.K. Tewari, P.K. Singh, S.B.S. Yadav, Int. J. Chem. Kin. 39 (2007) 447.

[3] R.M. Naik, J. Sarkar, D.D. Chaturvedi, Int. J. Chem. Kin. 37 (2005) 222.

[4] S. Prasad, Trans. Met. Chem. 28 (2003) 1.

[5] H.A. Mottola, Kinetic Aspects of Analytical Chemistry, John Wiley, New York, 1988.

[6] H.A. Mottola, D. Perez-Bendito, Anal. Chem. 68 (1996) 257R (and references therein).

[7] S.R. Crouch, T.F. Cullen, A. Scheeline, E.S. Kirkore, Anal. Chem. 70 (1998) 53R (and references therein).

[8] S.R. Grouch, A. Scheeline, E.S. Kirkor, Anal. Chem. 72 (2000) 53R (and references therein).

[9] S. Prasad, Anal. Chim. Acta 540 (2005) 173.

[10] S. Prasad, J. Anal. Chem. 60 (2005) 587.

[11] S. Prasad, Anal. Lett. 37 (2004) 2851.

[12] S. Prasad, T. Halafihi, Mikrochim. Acta 142 (2003) 237.

[13] T. Kawashima, S. Nakano, M. Tabata, M. Tanaka, TrAc., Trends Anal. Chem. 16 (1997) 132.

[14] Y.L. Feng, H. Narasaki, L.C. Tian, S.M. Wu, H.Y. Chen, Anal. Sci. 15 (1999) 915.

[15] R.M. Naik, P.K. Singh, R. Rastogi, R. Singh, A. Agarwal, Annali di Chemica. 97 (2007) 1169.

[16] R.M. Naik, A. Srivastava, S. Prasad, Spectrochimica Acta Part A 69 (2008) 193.

[17] S. Prasad, R.M. Naik, A. Srivastava, Spectrochimica Acta Part A 70 (2008) 958.

[18] R.M. Naik, J. Sarkar, Ind. J. Chem. Tech. 12 (2005) 563.

[19] R.M. Naik, R.K. Tiwari, P.K. Singh, S.B.S. Yadav, A. Asthana, Trans. Met. Chem. 33 (2008) 615.

[20] F.R. George, J.H. Andrew, Calif. West Med. 23 (1925) 853.

[21] A.F. Holleman, E. Wiberg, Inorganic Chemistry, Academic Press, San Diego, 2001.

[22] M.G. Aylmore, D.M. Muir, Minerals Eng. 14 (2001) 135.

[23] A. Giannousios, C. Papadopoulos, Analyst 121 (1996) 413.

[24] M.H. Cordoba, P. Vinas, C.S. Pedreno, Talanta 32 (1985) 221 (and references therein).

[25] A.M. Eleni, A.K. Michael, Analyst 112 (1987) 757.

[26] M. Marquez, M. Silva, D. Perez-Bendito, Analyst 113 (1988) 1373.

[27] D.P. Nikolelis, T.P. Hadjiioannon, Anal. Chem. 50 (1978) 205.

[28] M. Phull, P.C. Nigam, Talanta 30 (1983) 401.

[29] M.S. Gareia, C.S. Pedreno, M.I. Albero, Analyst 115 (1990) 989.

[30] J. Kurzawa, K. Janowicz, A.A. Suszka, Anal. Chim. Acta 431 (2001) 149.

[31] J. Krista, M. Kopanica, L. Novotny, Anal. Chim. Acta 386 (1999) 221.

[32] A. Vogel, A Text book of Quantitative Inorganic Analysis, Longmans Green and Co. Ltd., London, 1962, p. 350.

[33] R.C. Weast, CRC Handbook of Chemistry and Physics, 49th ed., The Chemical Rubber Co., Ohio, 1969, Sect. D-79.

[34] J. Maslowska, J. Leszezynska, Talanta 32 (1985) 883.

[35] H. Lineweaver, D. Burk, J. Am. Chem. Soc. 56 (1934) 568.

[36] J.I. Tinoco, K. Sauer, J.C. Wang, Physical Chemistry, Principles and Applications in Biological Sciences, Prentice-Hall Inc., New Jersey, 1978, p. 351.

[37] D. Klockow, J. Auffarth, C. Kopp, Anal. Chim. Acta 89 (1977) 37.