

Processes Kinetics Modeling: A Numerical Study

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Introduction

The kinetics study of the reaction between Cu²⁺ and S₂O₃²⁻ in solutions is not entirely studied, being reported into the specialty literature just few papers which refer the reaction in aqueous solutions.

Aim

By using of a set of experimental data obtained from stopped flow spectrophotometrical installation build at Technical University of Cluj-Napoca, to investigate the kinetic of the reaction.

Assumption

The general form of the reaction is $A + B \rightleftharpoons X \rightarrow P$

Experimental procedure

The cooper and tiosulfate aqueous solutions were prepared in different concentrations varying from 0.001 M to 0.01 M.

The reaction was detected to be a very fast one: the existence of the X intermediary was found to be below 25 ms.

The wavelength of light detection diode was found (and is 430 nm) in order to prepare the detection of intermediary forming as the wavelength which assures the best stability of the light emission in time.

A microampere meter was set in order to be used for recording of the signal from detector and the baud rate of the recording was choused to be 0.04 ms.

A digital oscilloscope with buffer was used to plot and transfer the data to the computer.

In order to minimize the experimental interferences such as dilution of the intermediary, the size of the mixing chamber was varied; a small size one was selected and used for measurements. The mixing chamber has a volume equal to 0.35cm³ and the length of optical pathway traversed by the beam through measurement chamber is 0.4 cm.

Experiments

Three experiments with equal concentration of reactants (0.001, 0.005 and 0.01 M) are the subject of this investigation.

The recording of digital data was started always after the mixing moment but near to, because of limited memory buffer of the oscilloscope (64 Kb).

The number of relevant measurements corresponding to the reaction time it varies in 1500-8000 range.

Mathematical Methods

The Lambert-Beer law was used to correlate extinction with concentration; the unknown parameter was the molar extinction coefficient. The mathematical model of the assumed reaction mechanism was numerically written; the unknown parameters were four partial reaction orders and three reaction rates constants.

The subject of optimization was squared sum of differences between experimental extinction E and theoretical approach of extinction $a[X]$. Only a first part of the experimental data records entered into the optimization procedure (1100 for 0.001 M, 1300 for 0.005 M, and 6500 for 0.01M).

Results

The optimization procedure produced the best fit of the model to the experiment with 0.962, 0.955, and 0.980 respectively correlation coefficients.

Not all unknown parameters were possible to be obtained. Reaction rates: only to the right ones. Partial orders: all, except one of intermediary for the left direction reaction. Extinction coefficient: 212 ± 22 l/mol*cm. For all obtained parameters is no significant difference between parameters values from one experiment to another with a 95% confidence.

Conclusion

Reaction kinetics was almost complete determined. Reaction rates: 2000 ± 1000 , N/A, 2200 ± 200 , partial orders: 0.789 ± 0.05 , 0.781 ± 0.04 , N/A, 1.55 ± 0.04 .

The optimization procedure was proved to be a self consistent one, despite of the number of unknown parameters used.

Acknowledgments:

Research supported in part by UEFISCSU Romania, Grant No. ET/108/2006.

Thanks for providing the experimental data to Dr. Mihaela Ligia UNGUREȘAN from Technical University of Cluj-Napoca, Romania.

PROCESSES KINETICS MODELING: A NUMERICAL STUDY

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ABSTRACT

The kinetics study of the reactions between Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$ in solutions is not entirely studied, being reported just few papers that refer the reaction in aqueous solutions. The experimental measurements of the reaction between Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$ for three concentrations was obtained by using the stopped flow spectrophotometrical installation. For each pair of equal reactants concentrations (at 0.001, 0.005, and 0.01 M) the light intensity at 430 nm in time with a band rate of 40 ns was determined and the extinctions were calculated. Starting from the experimental determinations an original mathematical model was developed and assessed. The optimization procedure produced best fit of the model to the experiments obtaining correlation coefficients equal with 0.962, 0.955, and 0.980, respectively.

INTRODUCTION

The kinetics study of the reaction between Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$ in solutions is not entirely studied, being reported into the specialty literature just few papers that refer the reaction in aqueous solutions. First study of reaction between $\text{Cu}[\text{NH}_3]_4^{2+}$ and $\text{S}_2\text{O}_3^{2-}$ was reported in 1973 by Byerley et. al [1]. Almost twenty years later, Rabai and Epstein published results regarding kinetics of interaction between Cu^{2+} with $\text{S}_2\text{O}_3^{2-}$ in aqueous solution [2]. The kinetics of the reaction between Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$ investigated using a stopped flow spectrophotometrical installation [3] has been previous studied [4]. Starting with experience obtained from optimization of the mobile phase composition in HPTLC [5], an optimization procedure for the reaction between tiosulfate and copper ions has been developed and its performances are presented.

METHOD

Assumption: The general form of the investigated reaction is $\text{A} + \text{B} \xrightleftharpoons[k_2]{k_1} \text{X} \xrightarrow{k_3} \text{P}$ and the associated reaction rates are: $v = k_1[\text{A}]^{y_1}[\text{B}]^{y_2}$; $v = k_2[\text{X}]^{y_3}$; $v = k_3[\text{X}]^{y_4}$, where [A], [B], and [X] are the concentration of chemicals at a moment of reaction, k_j ($j = 1, 2, 3$) are the reaction rates constants, and y_i ($i = 1, \dots, 4$) are partial reaction orders.

Experimental Data

The cooper and tiosulfate aqueous solutions prepared in different equal concentrations varying from 0.001 M to 0.01 M (0.001 M – Exp.No.1, 0.005 M – Exp.No.2, and 0.01 M – Exp.No.3) were the subject of this investigation. The reaction was detected to be a very fast one: the existence of the X intermediary was found to be below 25 ms.

The wavelength of light detection diode was found (and is 430 nm) in order to prepare the detection of intermediary forming as the wavelength which assures the best stability of the light emission in time.

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A digital oscilloscope with buffer was used to plot and transfer the data to the computer.

The number of relevant measurements corresponding to the reaction time varied between 1500 and 8000 range.

Mathematical Methods

The Lambert-Beer law was used to correlate extinction with concentration; the unknown parameter was the molar extinction coefficient: $\varepsilon = \hat{E}/X$, where ε = molar extinction coefficient, \hat{E} = estimated extinction by the model, X = intermediary concentrations

The mathematical model of the assumed reaction mechanism was developed; the unknown parameters were four partial reaction orders and three reaction rates constants.

The optimum was considering in case in which the method was convergence towards credible results, and the optimized values of variable become almost constant. Following criteria were imposed: (1) valid reaction rates; (2) the values of constants used in model belonging to the 95% confidence intervals; and (3) lower values for the variation of constant values used in optimization.

Because the reaction between copper (II) and tiosulfate ions is a very fast only the first part of the experimental data were included into optimization procedure: (1) 1100 determinations for the reaction at 0.001 M, (2) 1300 determinations for the reaction at 0.005 M, and (3) 6500 determinations for the reaction at 0.01M.

RESULTS

The results of the optimized variables and constants for partial reaction orders (y_0, y_1, y_2, y_3), reaction rate constants (k_0, k_1, k_2), and for the minimization function (S_{min}) are presented in Table 1. Graphical representations of the variation of optimized parameters for experiment number 1 (from five to five iterations) are presented in figure 1- 8.

The parameters of the performing regression equations, for each experiment, were presented in Table 2 (where a and b are coefficients of the regression equation $E = aX + b$, r is the correlation coefficient between experimental and estimated by the optimization model values, and IC is the iteration cycle).

Table 1. The values of the optimized parameters

	Exp.No.1	Exp.No.2	Exp.No.3
y_1	0.823	0.799	0.745
y_2	0.807	0.791	0.745
y_3	N.R.	N.R.	N.R.
y_4	1.509	1.571	1.571

N.R. = not reliable; S_{min} = the minimization function
 y_0, \dots, y_3 = partial reaction orders; k_0, k_1, k_2 = reaction rates

Table 2. Statistical characteristics of the regression equations

Exp. No	E = a·X + b					η_{IC}	
	a	a_{SI}	b	b_{SI}	r		
Exp.No.1 (0.001 M)	218.5	27	-0.0005	26	0.9801	23	107
Exp.No.2 (0.005 M)	189.4	28	-0.0821	20	0.9551	18	99
Exp.No.3 (0.01M)	226.7	27	-0.1300	20	0.9616	18	99

a_{SI} = coefficient a stabilized at iteration; b_{SI} = coefficient b stabilized at iteration;
 r = correlation coefficient; r_{SI} = r stabilized at iteration; η_{IC} = iteration no

The variances of the regression coefficients (a and b), for each experiment, reported to the iteration are in Figure 9 and 10, respectively.

The plot of the experimental determination versus time and the optimized values by the model for iteration cycle of 107 is presented in Figure 11.

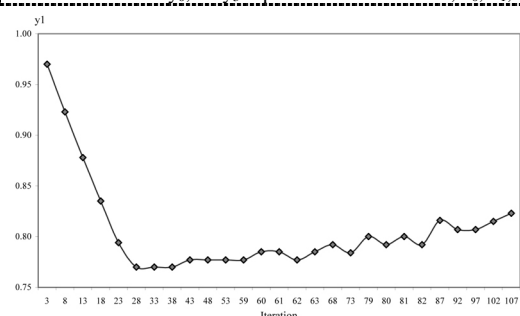


Figure 1. y_1 vs iteration (Exp.No.1)

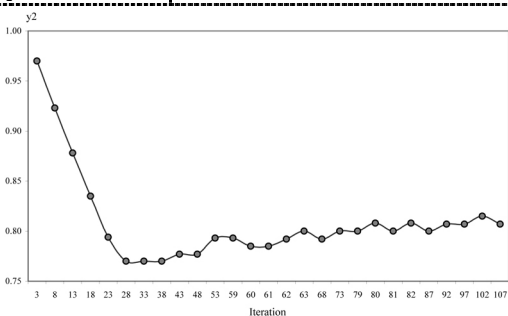


Figure 2. y_2 vs iteration (Exp.No.1)

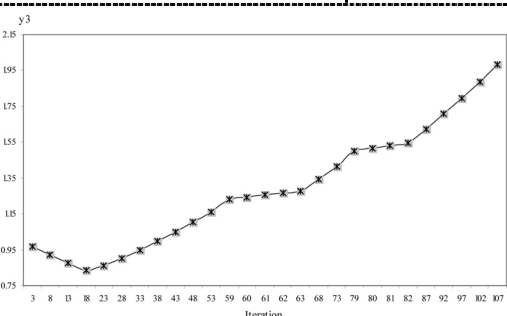


Figure 3. y_3 vs iteration (Exp.No.1)

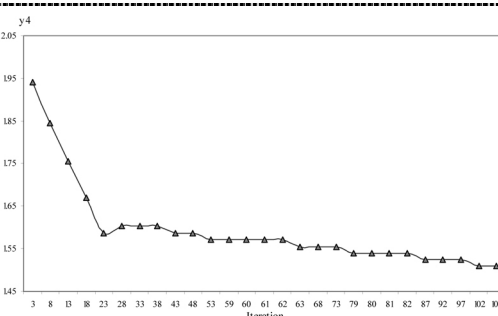


Figure 4. y_4 vs iteration (Exp.No.1)

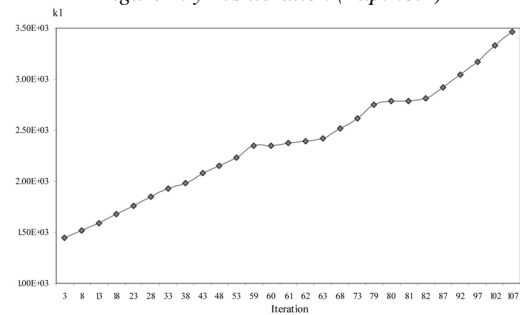


Figure 5. k_1 vs iteration (Exp.No.1)

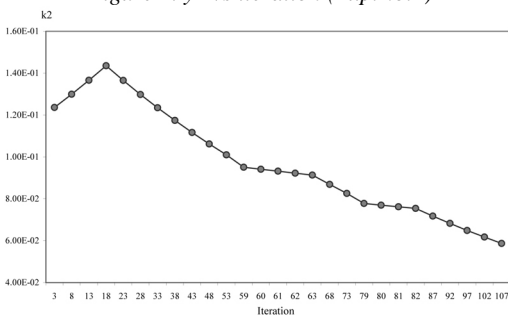


Figure 6. k_2 vs iteration (Exp.No.1)

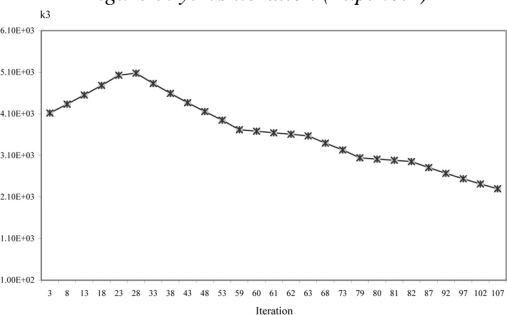


Figure 6. k_3 vs iteration (Exp.No.1)

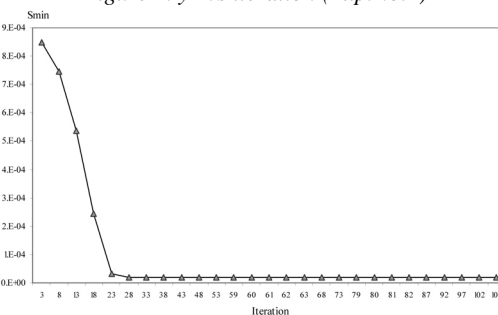


Figure 6. S_{min} vs iteration (Exp.No.1)

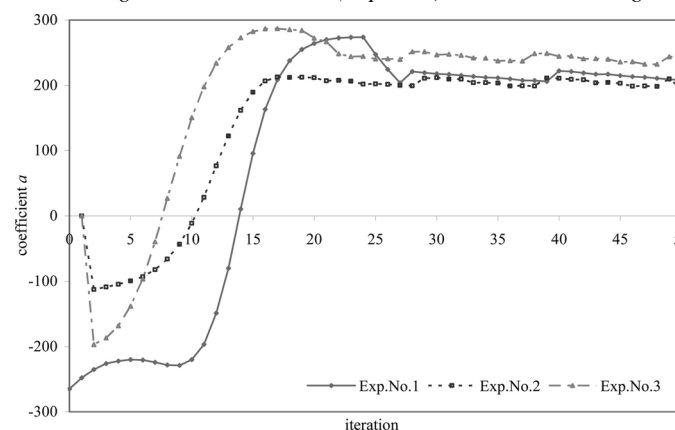


Figure 9. The distribution of regression coefficient 'a' vs iteration

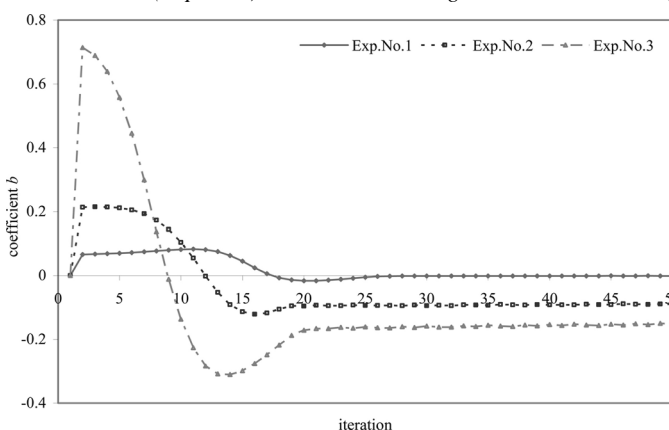


Figure 10. The distribution of the regression coefficient 'b' vs iteration

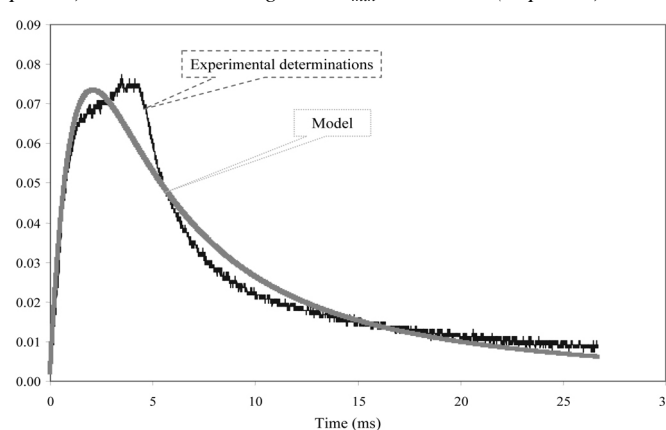


Figure 11. Optimized and experimental extinction versus time for Exp. No. 1 [$\text{Cu}^{2+}(1 \cdot 10^{-3}\text{M}) + \text{S}_2\text{O}_3^{2-}(1 \cdot 10^{-3}\text{M})$]

CONCLUSION

Reaction kinetics was almost complete determined. Reaction rates: 2000 +/- 1000, N/A, 2200 +/- 200, partial orders: 0.789 +/- 0.05, 0.781 +/- 0.04, N/A, 1.55 +/- 0.04.

Despite of the number of unknown parameters used, the proposed optimization procedure proved to be self-consistent.

ACKNOWLEDGEMENTS

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- [1] Byerley, J. J.; Fouda, S. A.; Rempe, G. L. *J. Chem. Soc.* 8 (1973) 889–893. [2] Rabai, G.; Epstein, I. R. *Inorg. Chem.* 31 (1992) 3239–3242. [3] Niac, G.; Giurgiu, M. *Studia Universitatis Babeş-Bolyai, Series Chemia* 1 (1971) 43–49. [4] Ungureșan, M.L. *Fast redox reactions of reduction of Cu(II) ion with thio-compounds*. PhD Thesis, unpublished (2006). [5] Cimpoiu, C.; Jäntschi, L.; Hodișan, T. *J. Liq. Chromatogr. Related Technol.* 22 (1999) 1429–1441.

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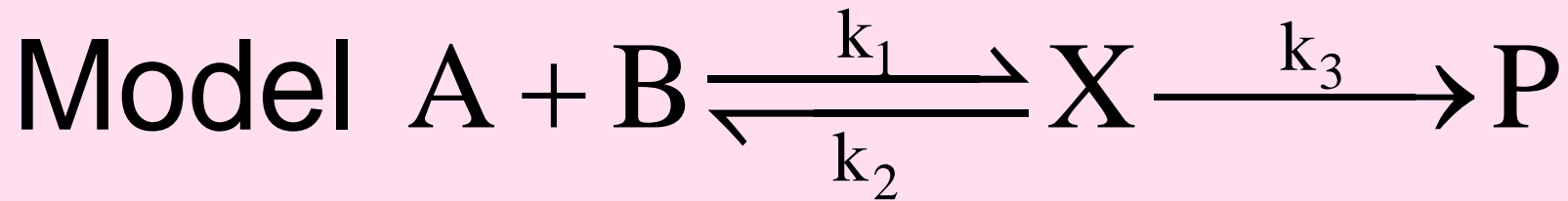
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Experimental: Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$

- The copper and tiosulfate aqueous solutions prepared in different equal concentrations varying from 0.001 M to 0.01 M (0.001 M – Exp.No.1, 0.005 M – Exp.No.2, and 0.01 M – Exp.No.3) were the subject of this investigation. The reaction was detected to be a very fast one: the existence of the X intermediary was found to be below 25 ms.
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Results –next slide

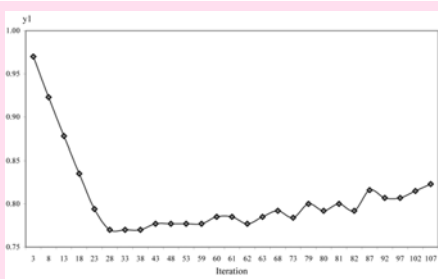
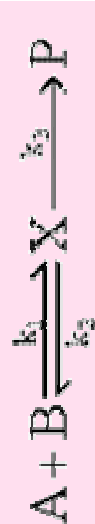


Figure 1. y_1 vs iteration (Exp.No.1)

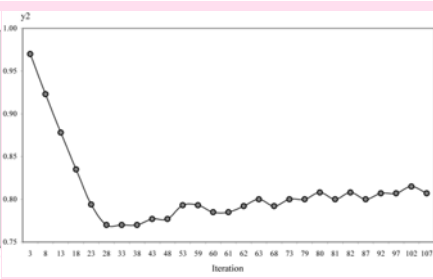


Figure 2. y_2 vs iteration (Exp.No.1)

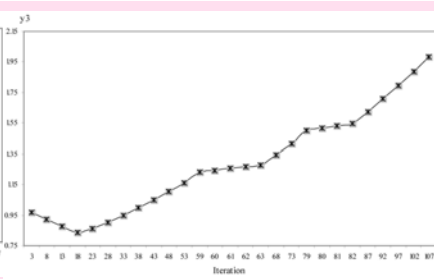


Figure 3. y_3 vs iteration (Exp.No.1)

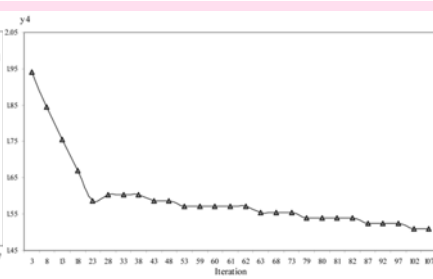


Figure 4. y_4 vs iteration (Exp.No.1)

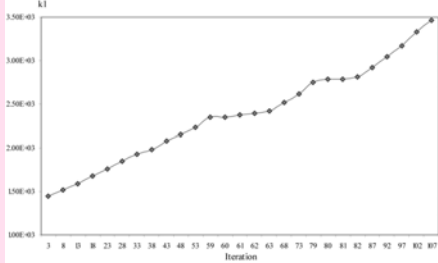


Figure 5. k_1 vs iteration (Exp.No.1)

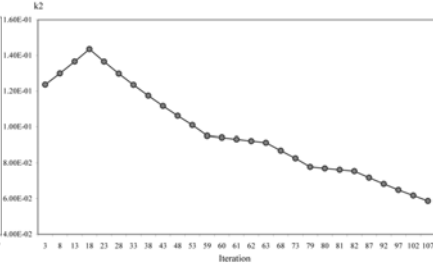


Figure 6. k_2 vs iteration (Exp.No.1)

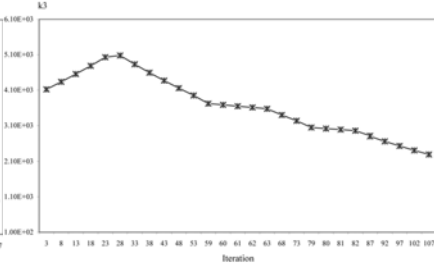


Figure 6. k_3 vs iteration (Exp.No.1)

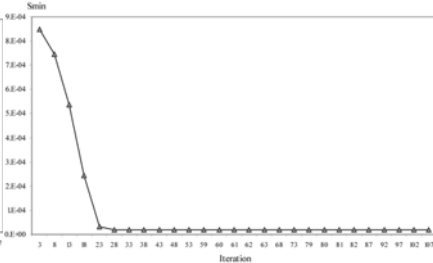


Figure 6. S_{min} vs iteration (Exp.No.1)

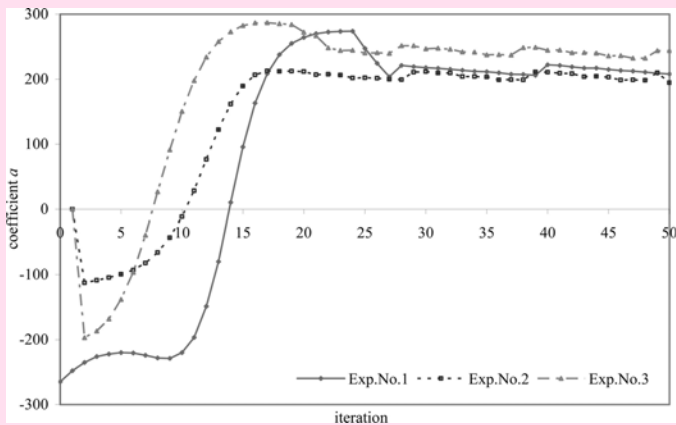


Figure 9. The distribution of regression coefficient \hat{a} vs iteration

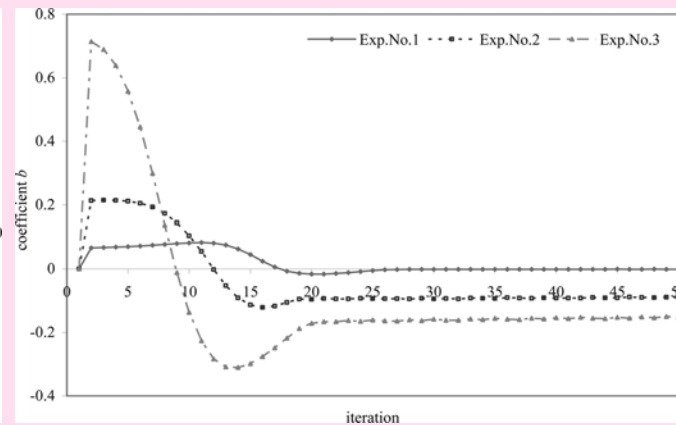


Figure 10. The distribution of the regression coefficient \hat{b} vs iteration

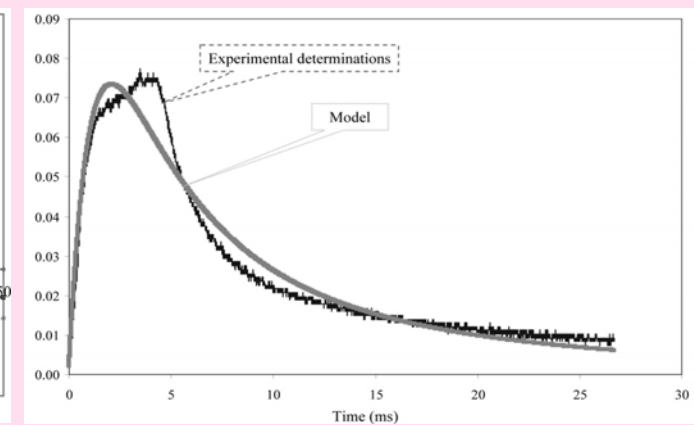


Figure 11. Optimized and experimental extinction versus time for Exp. No. 1 [$Cu^{2+}(1 \cdot 10^{-3}M) + S_2O_3^{2-}(1 \cdot 10^{-3}M)$]

Reaction kinetics was **almost complete determined**. Reaction rates: $k_1=2000 \pm 1000$, $k_2=N/A$, $k_3=2200 \pm 200$, partial orders: $y_1=0.789 \pm 0.05$, $y_2=0.781 \pm 0.04$, $y_3=N/A$, $y_4=1.55 \pm 0.04$. Despite of the number of unknown parameters used, the proposed optimization procedure proved to be self-consistent.

Acknowledgements

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- Thank you for your attention



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