THE KINETIC STUDY OF IODIDE CATALYSED REACTION BETWEEN IRON(III)-THIOCYANATE COMPLEX ION BY NITRATE AND NITRITE IN SULPHURIC ACID

KITTIYA WONGKHAN

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.....
Miss Kittiya Wongkhan
Candidate

.....
Assoc. Prof. Prapin Wilairat,
Ph.D.
Major-Advisor

.....
Prof. Sauvarop Limcharoen,
Dr. rer. nat.
Co-Advisor

.....
Assoc.Prof.Rassmidara Hoonsawat,
Ph.D.
Dean
Faculty of Graduate Studies

.....
Prof. Sauvarop Limcharoen, Dr. rer. nat.
Chair
Master of Science Programme
in Physical Chemistry
Faculty of Science

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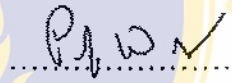
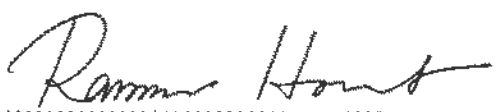
Miss Kittiya Wongkhan
Candidate



Assoc. Prof. Prapin Wilairat,
Ph. D.
Chair

Prof. Sauvarop Limcharoen,
Dr. rer. nat.
Member

Prof. Prapon Wilairat,
Ph. D.
Member



Assoc. Prof. Rassmidara Hoonsawat,
Ph. D.
Dean
Faculty of Graduate Studies
Mahidol University

Prof. Amaret Bhumiratana,
Ph. D.
Dean
Faculty of Public Health
Mahidol University

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Kittiya Wongkhan

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KITTIYA WONGKHAN 4336098 SCPC/M

M.Sc. (PHYSICAL CHEMISTRY)

THESIS ADVISORS : PRAPIN WILAIRAT, Ph. D.(PHYSICAL CHEMISTRY), SAUVAROP LIMCHAROEN, Dr. rer. nat.(PHYSICAL CHEMISTRY)

ABSTRACT

The kinetics of an iodide catalysed reaction between iron(III)-thiocyanate complex with nitrate and nitrite in sulphuric acid was studied by UV-VIS spectrophotometry. The reactants were divided into 2 solutions. The reactants contained in both solution A and B did not react together before mixing. Solution A contained iron(III), thiocyanate, nitrate and acid whereas solution B contained nitrite and iodide. The kinetics were studied by varying the total nitrate, nitrite, acid and iodide concentrations to give pseudo-first order kinetics for the decrease of the iron(III)-thiocyanate complex ion, as measured by its absorbance at 458 nm. The experiment observed rate law as given by:

$$\text{Rate} = -\frac{d[FeSCN^{2+}]}{dt} = k'[NO_3^-][I^-][H^+]^2(1 + k''[NO_2^-]^2)$$

where k' = 0.087 x 10^6 M^{-3} $min.^{-1}$ and k'' = 0.302 M^{-3} for nitrate, nitrite, sulphuric acid and iodide in the range 0.20-0.70, (2.0-7.0) x 10^{-3}, 0.125-0.60 and (1.968 – 4.724) x 10^{-6} M, respectively. The rate of reaction was directly proportional to the total iodide concentration, and can thus be employed to determine trace amounts of iodide. The rate reaction was independent of iron(III) concentration when the ratio of $[Fe^{3+}]/[SCN^-]$ was greater than 100. Various species of the iron(III)-thiocyanate complex ions and the hydrolysis of ferric ion in the acid may have different kinetic properties, leading to the observed variations of the rate of reaction.

KEY WORDS : IODIDE CATALYST/ SVEIKINA REACTION

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การศึกษาจลนศาสตร์ของปฏิกิริยาระหว่างเหล็ก(III)-ไทโอไซยาเนต ไนเตรตและไนไตรต์ในกรดซัลฟูริก โดยมีไอโอไดด์เป็นตัวเร่งปฏิกิริยา (THE KINETIC STUDY OF IODIDE CATALYSED REACTION BETWEEN IRON(III)-THIOCYANATE WITH NITRATE AND NITRITE IN SULPHURIC ACID)

กิตติยา วงษ์ขันธ์ 4336098 SCPC/M

วท.ม. (เคมีเชิงฟิสิกส์)

คณะกรรมการควบคุมวิทยานิพนธ์ : ประพิณ วิไลรัตน์, Ph. D. (Physical chemistry), เสาวรภย์ ลิ้มเจริญ, Dr. rer. nat. (Physical chemistry)

บทคัดย่อ

งานวิจัยนี้ได้ทำการศึกษาจลนศาสตร์ของปฏิกิริยาระหว่างสารประกอบเชิงซ้อนของเหล็ก(III)-ไทโอไซยาเนตไอออนกับ ไนเตรตและไนไตรต์ในกรดซัลฟูริกซึ่งมีไอโอไดด์เป็นตัวเร่งปฏิกิริยาเมื่อมีการเปลี่ยนแปลงความเข้มข้นของไนเตรตไอออน ไนไตรต์ไอออน กรดไอออน และไอโอไดด์ไอออน ขณะที่อุณหภูมิคงที่ (30.0 องศาเซลเซียส) สารละลายจะแบ่งเป็น 2 ส่วน คือ สารละลาย A ประกอบด้วย เหล็ก(III) ไทโอไซยาเนต ไนเตรต และกรด สายละลาย B ประกอบด้วย ไนไตรและไอโอไดด์ พบว่าสามารถหากฎอัตราโดยการวัดความเปลี่ยนแปลงความเข้มข้นของสารประกอบเชิงซ้อนเหล็ก(III)-ไทโอไซยาเนตไอออน ได้ดังนี้

$$\text{Rate} = -\frac{d[FeSCN^{2+}]}{dt} = k'[NO_3^-][I^-][H^+]^2(1 + k''[NO_2^-]^2)$$

ซึ่งความเข้มข้นที่เปลี่ยนแปลงของสารประกอบเชิงซ้อนของเหล็ก(III)-ไทโอไซยาเนตไอออนสามารถติดตามได้ที่ค่าการดูดกลืนแสงที่ความยาวคลื่น 458 นาโนเมตร โดยที่ k' = 0.087 x 10^6 M^{-3} $min.^{-1}$ และ k'' = 0.302 M^{-3} ซึ่งความเข้มข้นของ ไนเตรตไอออน ไนไตรต์ไอออน กรดซัลฟูริกและไอโอไดด์ไอออนที่มีค่าอยู่ในช่วง 0.20-0.70, (2.0-7.0) x 10^{-3}, 0.125 - 0.60 และ (1.968 – 4.724) x 10^{-6} โมลาร์ ตามลำดับ โดยเป็นปฏิกิริยาเสมือนเป็นอันดับหนึ่งในสารประกอบเชิงซ้อนเหล็ก(III)-ไทโอไซยาเนตไอออนเมื่ออัตราส่วนระหว่างความเข้มข้นของเหล็ก(III) ไอออนต่อไทโอไซยาเนตไอออนมีค่าสูง และมากเกินพอที่อัตราส่วนเท่ากับ 100 ซึ่งอัตราการเกิดปฏิกิริยาไม่ขึ้นกับเหล็ก(III) ไอออน นอกจากนี้อัตราการเกิดปฏิกิริยาสัมพันธ์โดยตรงกับความเข้มข้นของไนเตรตและไอโอไดด์ ซึ่งการวัดอัตราการเกิดปฏิกิริยาดังกล่าวสามารถนำไปใช้หาปริมาณไอโอไดด์ได้ เนื่องจากสารประกอบเชิงซ้อนของเหล็ก(III)-ไทโอไซยาเนตและการเกิดโฮโดรไลซิสของเหล็ก(III)ในสารละลายกรดมีสมบัติทางจลนศาสตร์ที่แตกต่างกัน ทำให้มีอัตราการเกิดปฏิกิริยาที่วัดได้มีค่าต่างกัน

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LIST OF ABBREVIATIONS

Abs	=	Absorbance
g	=	Gram
L	=	Liter
μM	=	Micromolar
mg	=	Milligram
mM	=	Millimolar
M	=	Molar
min.	=	Minute
nm	=	Nanometer
k	=	Rate constant
s	=	Second
t	=	Time
^{o}C	=	Temperature in Degree Celsius
UV	=	Ultraviolet
VIS	=	Visible

THE RELEVANCE OF THE RESEARCH WORK TO THAILAND

The iodine requirement of human is 100-200 μg/day. In Thailand, there are many people with iodine deficiency. The catalytic effect of iodide on the oxidation-reaction between thiocyanate ion and nitrite in nitric acid has been used for many years for the determination of trace amounts of iodide but many questions concerning the kinetics of this reaction remain unanswered. Therefore the main objective of this research is to study the kinetics of the iodide catalysed reaction between nitrite, nitrate with iron(III)-thiocyanate complex in sulphuric acid solution.

CHAPTER I
INTRODUCTION

The reaction between iron(III)-thiocyanate complex, nitrate and nitrite in acid can be catalysed by iodide ion. This reaction is often called the Sveikina reaction [1]. It is autocatalytic in nitrous acid. An autocatalytic reaction is characterized by an induction period, the length of which depends on the concentration of the catalytic species, nitrous acid in this case. Since 1964 the catalytic effect of iodine on the oxidation-reaction between thiocyanate ion and nitrite in nitric acid has been used for many years for the determination of trace amounts of iodide because of its specificity and high sensitivity. Examples which have employed this reaction are the determination of total iodine in food [2], iodine and iodate in sea water [3], iodine in silicate rocks [4], total inorganic iodine and free iodine in water [1]. The reac tion can also be employed for the determination of trace amount of nitrite [5,6].

The net reaction is given by

$$2SCN^- + 3NO_2^- + 3NO_3^- + 2H^+ \rightarrow 2CN^- + 2SO_4^{2-} + 6NO + H_2O \qquad (1.1)$$

Virtually all of the kinetic data reported to date have been based upon observation of the reaction after a certain time period [3,4,5]. While this type of information may be perfectly adequate for analytical purposes, it is not very useful for studying the mechanism of the reaction.

In 1969, Stedman and Whincup [7] studied the reaction of thiocyanate ion with nitric and nitrous acid without iron(III) ion and iodide. The net reaction is given by

$$SCN^- + HNO_2 + NO_3^- + 2H^+ \rightarrow OHSCN + 2HNO_2 \qquad (1.2)$$

The reaction did not use iodide ion as catalyst. Iron(III) ion was employed to determine the thiocyanate that remained in the reaction at various time interval.

Although there have been many articles for this reaction in the literature, many questions concerning the kinetics of this reaction remain unanswered. Most of the studies have been directed at solving a specific analytical problem; consequently, attention has been focused upon these factors rather than a complete understanding of the reaction.

CHAPTER II
OBJECTIVE

It has been found that the orange color of iron(III)-thiocyanate complex, which was formed by the reaction of thiocyanate with an excess of iron(III) salt, in dilute nitric acid solution, faded more rapidly in the presence of iodide than in its absence[5]. The catalytic effect of iodide ion on the oxidation–reduction reaction of between thiocyanate with nitrate, nitrite in acidic medium has been used for many years for determination of ultra-trace quantities of iodide because of its specificity and high sensitivity [4]. The net reaction has been reported as

$$2SCN^- + 3NO_2^- + 3NO_3^- + 2H^+ \rightarrow 2CN^- + 2SO_4^{2-} + 6NO + H_2O \qquad (2.1)$$

The main aim of the present study is to study the kinetics of the iodide catalysed reaction between nitrite, nitrate with iron(III)-thiocyanate complex in sulphuric acid solution.

In papers describing the Sveikina reaction to analyse iodide or nitrite ions the rate of the color-fading of iron(III)-thiocyanate complex has been employed but in the equation for net reaction there is no iron(III)-thiocyanate represented in the scheme. Although there are some reports about the effect of the concentration of each reactant, effect of temperature and effect of various other ions [1-6] on the kinetics, but many questions concerning the kinetics of this reaction remain unanswerd especially the effect of iron(III) in the reaction.

The scope of this thesis is:

1. To find the condition giving rise to the pseudo-first order kinetics for the iodide catalysed reaction of nitrite and nitrate with iron(III)-thiocyanate complexes in acidic condition.

2. To follow the kinetics of the iodide catalysed reaction using UV-VIS spectrophotometer.

3. To investigate the rate law of the iodide catalysed reaction in order to elucidate its mechanism.

CHAPTER III
LITERATURE REVIEW

3.1 Mechanism of the oxidation of metal thiocyanate by nitric and nitrous acid

There are many reports on the oxidation of metal thiocyanate by various reagents. In 1969, G. Stedman and Whincup studied the oxidation of sodium thiocyanate in nitric and nitrous acid [7]. They presented a mechanism of the oxidation reaction of metal thiocyanate by nitric and nitrous acid, which gave an adequate interpretation of all of their experiment results. They proposed that

a. The final product is sulfuric acid, hydrogen cyanide, sulphur dicyanide and nitrous acid, as shown in Figure 3.1.

b. The stoichiometry varies during the course of the oxidation, and in the early stages corresponds to the formation of sulphuric acid and hydrogen cyanide, as shown in Figure 3.2.

c. The variation of rate constant has two distinct parts depending on with thiocyanate concentration.

At low concentrations of thiocyanate, the rate increases approximately linearly with thiocyanate concentration which is designated as the “thiocyanate-dependent” region, as shown in Figure 3.3. The rate law is given by: $v_1=k'[H^+]^2[HNO_2][NO_3^-][SCN^-]$.

At high concentration of thiocyanate, the rate is almost independent of thiocyanate, the "thiocyanate- independent" region, as shown in Figure 3.3. The rate law of the reaction is given by: $v_2 = k"[H^+][HNO_2][NO_3^-]$.

The derivation of the rate law from the mechanism as reported by Stedman and Whincup [ ] is given in Appendix I.

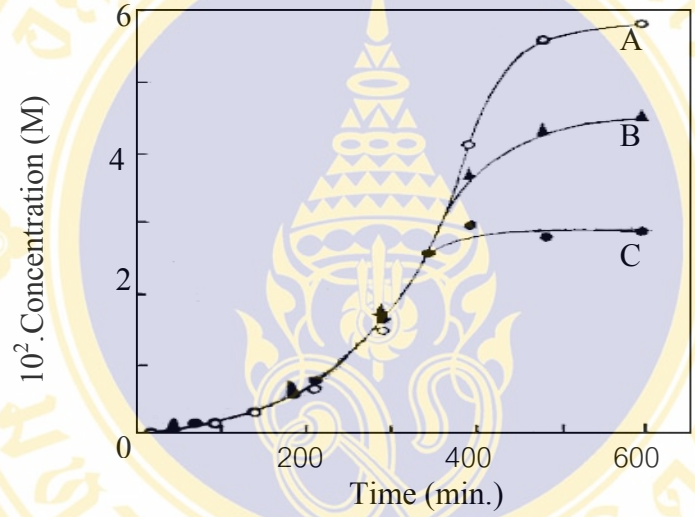


Figure 3.1 Oxidation of thiocyanate by nitric and nitrous acids in presence of initial hydrogen cyanide. $[H^+] = 0.90M$, $[NO_3^-] = 0.956M$, $[HCN]_0 = 0.0556M$, $[SCN]_0 = 0.045M$, $[nit]_0 = 0.00220M$, A. △[nit], B. △[SCN], C. △$[S(CN)_2]$.

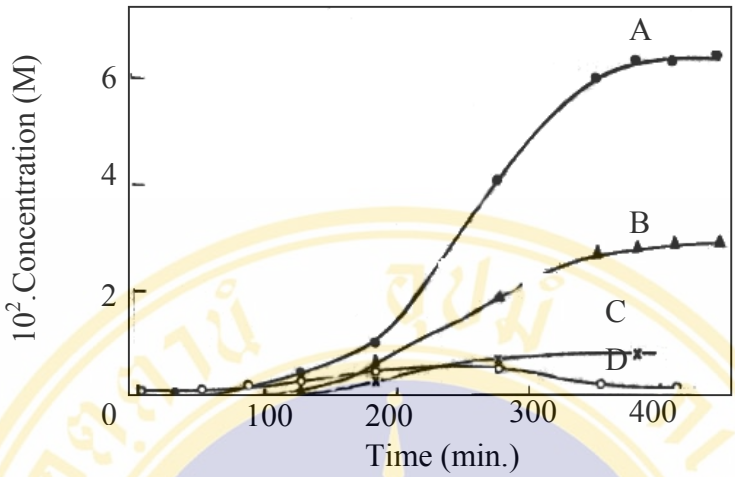


Figure 3.2 Oxidation of thiocyanate by nitric and nitrous acids in absence of initial hydrogen cyanide at 0°C. $[H^+] = [NO_3^-] = 0.85M$, $[SCN]_0 = 0.029M$, $[nit]_0 = 0.00227M$, A = △ [nit], B = △ [SCN], C = △ $[S(CN)_2]$, D = △ [NOSCN].

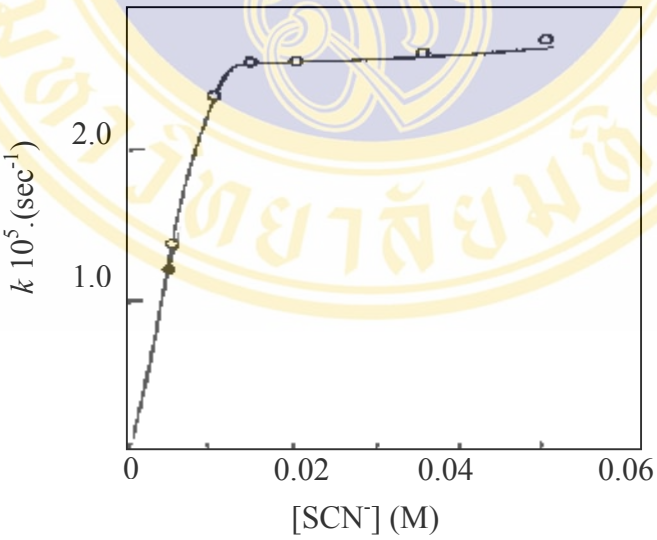


Figure 3.3 Variation of k with $[SCN^-]$, 0°C. $[H^+] = [NO_3^-] = 0.80M$; Ionic strength = 1.0M.

3.2 The iodide catalysed reaction of iron(III)-thiocyanate complex with nitrite ion in nitric acid (the Sveikina reaction)

The reaction of iron(III)–thiocyanate complex with nitrite ion in nitric acid with iodide ion as catalyst has been employed for many years. It has been used for the determination of ultra-micro amounts of iodide by utilizing its catalytic effect on the color-fading of iron(III)-thiocyanate [5].

There are many literature on the kinetics and the net reaction is given below:

$$2SCN^- + 3NO_2^- + 3NO_3^- + 2H^+ \rightarrow 2CN^- + 2SO_4^{2-} + 6NO + H_2O \quad (3.1)$$

3.2.1 The effect of iodide concentration

The rate of reaction increases with the amount of iodide, as shown in Figure 3.4 (in the presence of 0.056 M of chloride ion in the solution) [3]. When iron(III), thiocyanate, nitric acid and nitrite concentration was kept constant but changing the iodide concentration, it was found that iodide concentration caused a change in the slope of the curve, as shown in Figure 3.5 [6].

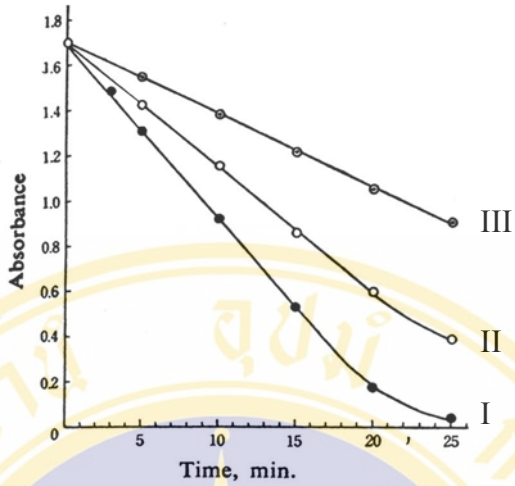


Figure 3.4 Dependence of Absorbance - Time relation on $[I^-]$ in the presence of $[Cl^-]$ = 0.056 M. Conditions: $[Fe^{3+}]$ = 0.062 M, $[SCN^-]$ = 2.5 x 10^{-3} M, $[HNO_3]$ = 3.5 M and at 60 ^oC. Monitoring wavelength, 460 nm. (I). $[I^-]$ = 0.070 x 10^{-6} M, (II). $[I^-]$ = 0.039 x 10^{-6} M and (III). $[I^-]$ = 0.00 M.

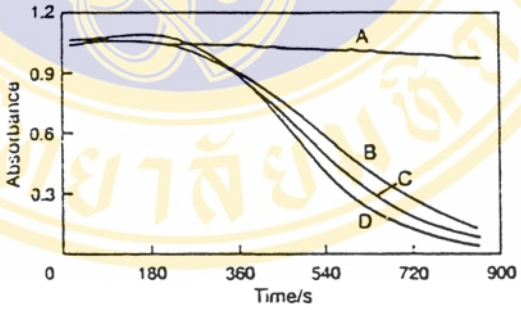


Figure 3.5 Dependence of Absorbance - Time relation on $[I^-]$. Conditions: $[Fe^{3+}]$ = 0.067 M, $[SCN^-]$ = 2.7 x 10^{-4} M, $[HNO_3]$ = 1.3 M, $[NO_2^-]$ = 4.6 x 10^{-6} M and at 24.0 ^oC. Monitoring wavelength, 458 nm. A. $[I^-]$ = 0.00 M, B. $[I^-]$ = 8.00 x 10^{-6} M, C. $[I^-]$ = 1.07 x 10^{-6} M and D. $[I^-]$ = 1.33 x 10^{-6} M.

3.2.2 The effect of nitrite concentration

It was found that [4], in the presence of nitrite ions, the color-fading of the iron(III)-thiocyanate complex was accelerated. The effect of the concentration of nitrite ions is shown in Figure 3.6 [5]. The results which shown in Figure 3.7 [6] was shown that the nitrite concentration not only effect on the rate but also the length of the induction period is also greatly affected.

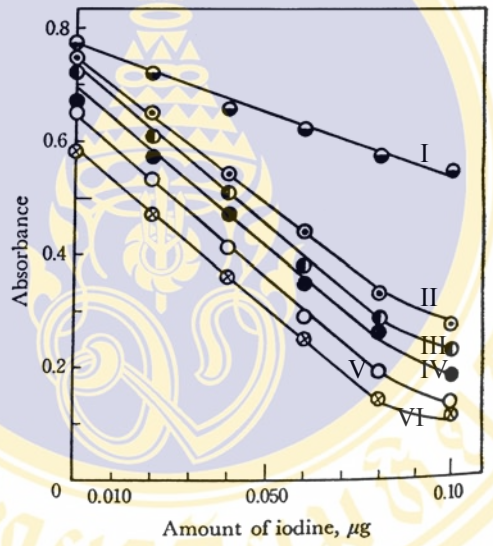


Figure 3.6 Dependence of Absorbance - Amount of iodine on $[NO_2^-]$. Conditions: $[Fe^{3+}]$ = 0.062 M, $[SCN^-]$ = 2.5 x 10^{-3} M, $[HNO_3]$ = 3.5 M and at 60 ^oC. Monitoring wavelength, 460 nm. (I). $[NO_2^-]$ = 0.025 x 10^{-3} M, (II). $[NO_2^-]$ = 0.125 x 10^{-3} M, (III). $[NO_2^-]$ = 0.250 x 10^{-3} M, (IV). $[NO_2^-]$ = 0.500 x 10^{-3} M, (V). $[NO_2^-]$ = 0.750 x 10^{-3} M and (VI). $[NO_2^-]$ = 1.0 x 10^{-3} M.

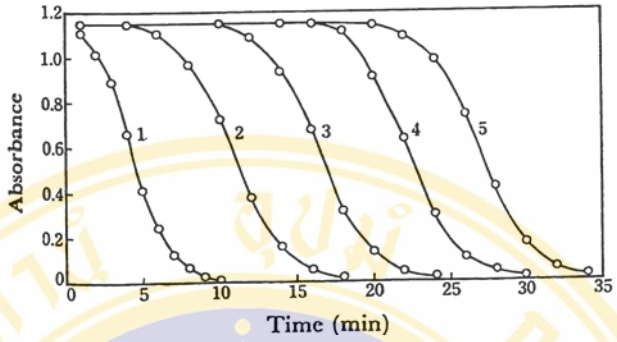


Figure 3.7 Dependence of Absorbance - Time on $[NO_2^-]$. Condition: $[Fe^{3+}]$ = 0.062 M , $[SCN^-]$ = 2.5 x 10^{-3} M, $[HNO_3]$ = 3.5 M and at 25 ^oC. Monitoring wavelength, 460 nm. 1. $[NO_2^-]$ = 0.2000 x 10^{-3} M, 2. $[NO_2^-]$ = 0.0200 x 10^{-3} M, 3. $[NO_2^-]$ = 0.0020 x 10^{-3} M, 4. $[NO_2^-]$ = 0.00002 x 10^{-3} M and 5. $[NO_2^-]$ = 0 M.

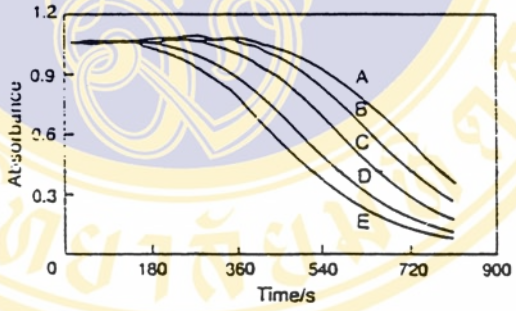


Figure 3.8 Dependence of Absorbance - Time relation on $[NO_2^-]$. Conditions: $[Fe^{3+}]$ = 0.067 M, $[SCN^-]$ = 2.7 x 10^{-4} M, $[HNO_3]$ = 1.3 M. $[I^-]$ = 1.1 x 10^{-4} M and at 25.0 ^oC. Monitoring wavelength, 458 nm. A. $[NO_2^-]$ = 5.8 x 10^{-6} M, B. $[NO_2^-]$ = 1.2 x 10^{-6} M, C. $[NO_2^-]$ = 2.3 x 10^{-6} M, D. $[NO_2^-]$ = 4.6 x 10^{-6} M and E. $[NO_2^-]$ = 9.3 x 10^{-6} M.

3.2.3 The effect of nitric acid concentration

At higher concentration of HNO_3, the induction period was shorter than at low HNO_3 concentration, and the reaction is more rapid. This effect was studied using HNO_3 as three reagent solutions 6.00, 7.00 and 8.00 M. The experimental results of different HNO_3 concentration as shown in Figure 3.9 [5]. The effect of HNO_3 concentration not only effect on the rate but also the length of the induction period is also greatly affected as shown in Figure 3.10 [6].

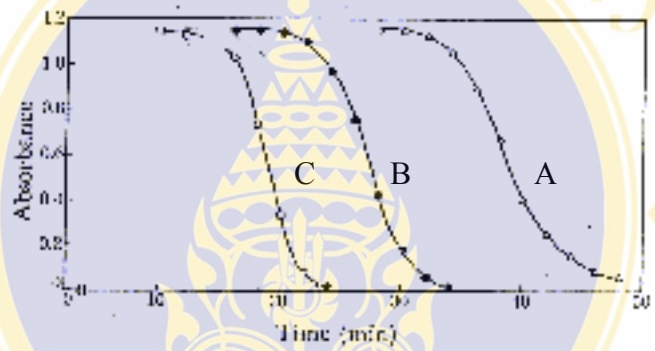


Figure 3.9 Dependence of Absorbance - Time relation on $[HNO_3]$. Conditions: $[Fe^{3+}]$ = 0.062 M, $[SCN^-]$ = 2.5 x 10^{-3} M, $[NO_2^-]$ = 3.5 x 10^{-3} M and at 25 ^oC. Monitoring wavelength, 460 nm. A. $[HNO_3]$ = 6.00 M, B. $[HNO_3]$ = 7.00 M, C.$[HNO_3]$ = 8.00 M.

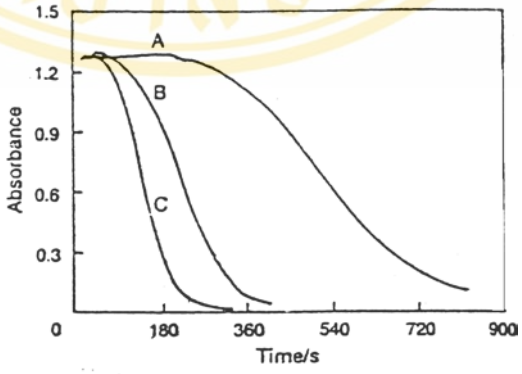


Figure 3.10 Dependence of Absorbance - Time relation on $[HNO_3]$. Conditions: $[Fe^{3+}]$ = 0.067 M, $[SCN^-]$ = 3.3 x 10^{-4} M, [NO_2^-] = 4.6 x 10^{-6} M and at 25.0 ^oC. Monitoring wavelength, 458 nm. A. $[HNO_3]$ = 1.3 M ,B. $[HNO_3]$ = 2.0 M and C. $[HNO_3]$ = 2.7 M.

3.2.4 The effect of iron(III) concentration

It was found [6] that the initial absorbance of the iron(III)-thiocyante complex of solution and the length of induction period increased with increasing Fe^{3+} concentration, whilst the reaction rate decreased, as shown in Figure 3.11.

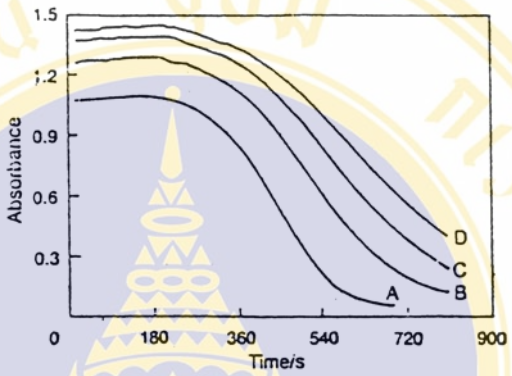


Figure 3.11 Dependence of Absorbance - Time relation on $[Fe^{3+}]$. Conditions: $[HNO_3]$ = 1.3 M, $[SCN^-]$ = 3.3 x 10^{-4} M, $[I^-]$ = 1.1 x 10^{-4} M, $[NO_2^-]$ = 2.3 x 10^{-6} M and at 25.0 ^oC. Monitoring wavelength, 458 nm. A. $[Fe^{3+}]$ = 0.033 M, B. $[Fe^{3+}]$ = 0.067 M, C. $[Fe^{3+}]$ = 0.100 M and D. $[Fe^{3+}]$ = 0.133 M.

3.2.5 The effect of thiocyanate concentration

It was found [6] that the effect of SCN^- concentration on the reaction rate was large, but the length of induction period remained almost unchanged as shown in Figure 3.12. The initial absorbance increased linearly with increasing SCN^- concentration.

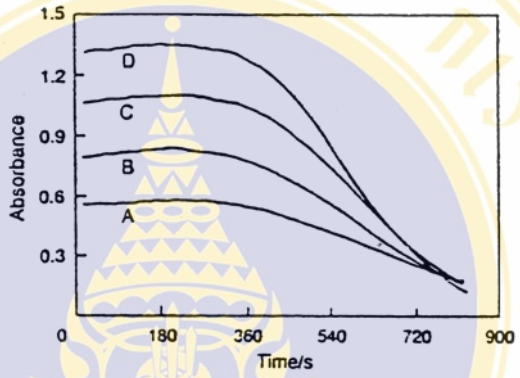


Figure 3.12 Dependence of Absorbance - Time relation on $[SCN^-]$. Conditions: $[HNO_3]$ = 1.3 M , $[Fe^{3+}]$ = 3.3 x 10^{-4} M, $[I^-]$ = 1.1 x 10^{-4} M, $[NO_2^-]$ = 2.3 x 10^{-6} M and at 25.0 ^oC. Monitoring wavelength, 458 nm. A. $[SCN^-]$ = 1.3 x 10^{-4} M , B. $[SCN^-]$ = 2.0 x 10^{-4} M, C. $[SCN^-]$ = 2.7 x 10^{-4} M and D. $[SCN^-]$ = 3.3 x 10^{-4} M.

3.2.6 The effect of temperature

On changing the temperature of the solution it was found [5] that the induction period decreased with increase in temperature, as shown in Figure 3.13 (in the absence and presence of nitrite ions). It can be seen from Figure 3.14 [6] that the reaction was accelerated and the induction period shortened with an increase in temperature.

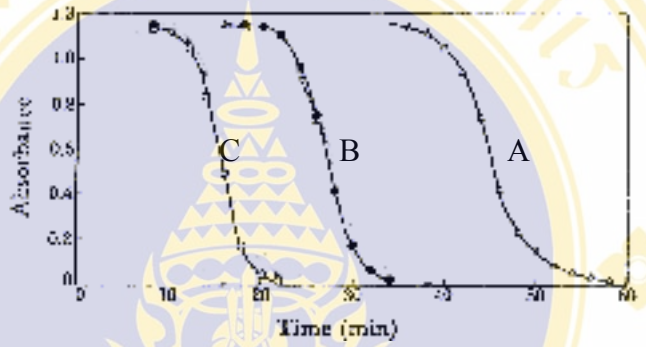


Figure 3.13 Dependence of Absorbance - Time relation on temperature. Condition: $[Fe^{3+}]$ = 0.062 M, $[SCN^-]$ = 2.5 x 10^{-3} M, $[NO_2^-]$ = 3.5 x 10^{-3} M and $[HNO_3]$ = 3.5 M. A. Temperature = 20 ^oC, B. Temperature = 25 ^oC and C. Temperature = 30 ^oC.

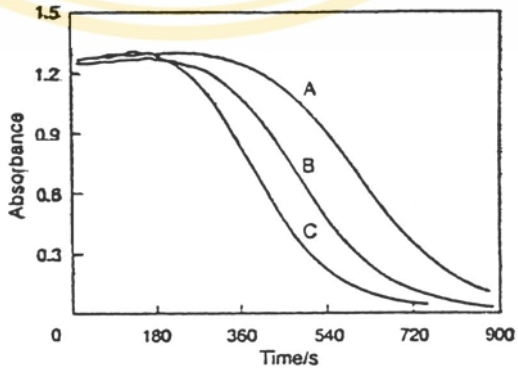


Figure 3.14 Dependence of Absorbance - Time relation on temperature. Conditions: $[Fe^{3+}]$ = 6.7 x 10^{-4} M, $[SCN^-]$ = 3.3 x 10^{-4} M, $[HNO_3]$ = 1.3 M, $[NO_2^-]$ = 2.3 x 10^{-6} M and $[I^-]$ 1.1 x 10^{-4} M. A. Temperature = 21.7 ^oC, B. Temperature = 24.6 ^oC. and C. Temperature = 27.5 ^oC.

3.3 The mechanism of reaction

Although the articles referred to in above section presented data on the effect of the various reactions (i.e. $[Fe^{3+}]$, $[SCN^-]$, $[NO_3^-]$, $[NO_2^-]$, $[H^+]$, $[I^-]$, temperature) on the kinetics, there were no discussion on the possible mechanism of the reaction, especially the rate of the iodide catalyst. In 1994, Zhong-liang Zhu and Zhi-cheng Gu [1] studied the reaction of the catalytic action of iodide on the color-fading reaction of iron(III)-thiocyanate complex. They described in detail the kinetics, and quantitative dependence of this reaction. They concluded that I^- does not act as a catalyst on the decomposition of iron(III)-thiocyanate complex. Although it accelerates reaction in the presence of NO_2^-, the true catalyst is the oxidation product of I^-. It was found that iodine can significantly accelerate the reaction without the presence of NO_2^-. They proposed that the true catalyst may be iodine. The oxidation of I^- to iodine is a slow reaction. NO_2^- can accelerate this reaction, which is why there is an induction period in the catalytic reaction and the length of the induction period depends on the NO_2^- concentration. However some steps of the reaction are still unclear.

3.4 Formation of ferric–thiocyanate complex

The reaction between $Fe(H_2O)_6^{3+}$ and SCN^- is well established and several reasonably concordant values of its association constant have been published [8-10]. The distribution of complex ions of iron-thiocyanate is shown in Figure 3.15. The association constant for ferric and one thiocyanate ion in aqueous solution is 116.4 ± 1.3 (see Appendix II).

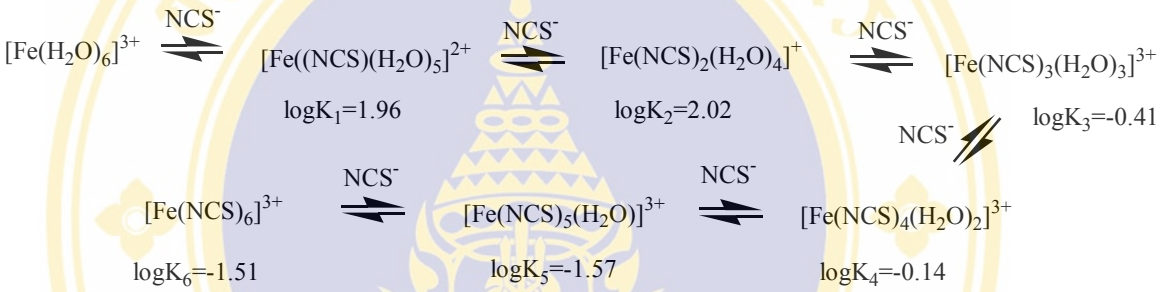


Figure 3.15 Distribution of complex ions of ions of iron–thiocyanate.

In 1958, John F. Below, JR., Robert E. Connick and Claude P. Coppel studied the kinetics of thiocyanate complex by using a newly designed rapid mixing device [11]. The equilibria in achieved within records.

CHAPTER IV
MATERIALS AND METHOD

4.1 Instruments : UV-VIS spectrophotometer

The kinetic studies were carried out using the following spectrophotometer:

4.1.1 PerkinElmer Lambda800 (U.S.A.) double beam UV/VIS spectrophotometer, with wavelength range 185-3300 nm, thermostatted by Polyscience (U.S.A) circulating water bath.

4.1.2 PerkinElmer Lambda 25 (U.S.A) double beam UV/VIS spectrophotometer with wavelength range 190-1100 nm, with PerkinElmer Peltier Temperature Programmer model PTP-1.

4.2 Chemicals

All chemicals used in this research were of analytical reagent grade, and were obtained from various source as indicated in Table 4.1.

Table 4.1 List of chemicals and suppliers.

Chemicals	Formula	Manufacturer
Ammonium iron(III)-sulphate	$FeNH_4(SO_4)_2.12H_2O$	Sigma-Aldrich
Sodium nitrite	$NaNO_2$	BDH (England)
Sodium nitrate	$NaNO_3$	APS (Australia)
Potassium thiocyanate	KSCN	E. Merck (Germany)
Sulphuric acid	H_2SO_4	E. Merck (Germany)
Potassium iodide	KI	E. Merck (Germany)

4.3 Preparation of solutions

The following sections include procedures for the preparation of solutions employed in this work. All solutions were prepared using deionized-distilled water obtained from a Barnstead, Nano pure, Ultra pure water system.

4.3.1 Ammonium iron(III) sulphate in sulphuric acid (0.2254 M in 1.785 M H_2SO_4)

5.434 g of $FeNH_4(SO_4)_2.12H_2O$ was dissolved with by heating in 6.35 ml of 7 M H_2SO_4 in a sonicated water bath. The solution was cooled to room temperature. Deionized water was then added to this solution to make the final volume of 25.0 ml.

For other concentrations of Fe(III) in various concentrations of H_2SO_4, the preparation procedure was similar to that described above. All of the stock Fe(III) solution was prepared over night.

4.3.2 Potassium thiocyanate

a) Primary stock concentration of 0.01 M

Solid potassium thiocyanate, 0.097 g, was dissolved in deionised–distilled water in a 100.0 ml volumetric flask.

b) Working thiocyanate solution

The stock solution was diluted in a volumetric flask with deionised–distilled water to give a thiocyanate concentration of 0.002 M.

4.3.3 Sodium Nitrate (5M)

21.248 g of $NaNO_3$ was dissolved in deionised – distilled water to a volume of 50.0 ml in a volumetric flask.

4.3.4 Sodium Nitrite (0.04M)

Solid $NaNO_2$, 0.2760 g, was dissolved in deionised – distilled water in a 100.0 ml volumetric flask.

4.3.5 Potassium iodide

a) Primary stock solution, 500 mg I/L

Solid potassium iodide, 0.065 g, was dissolved in deionised-distilled water in a 100.0 ml volumetric flask.

b) Working iodide solution.

10.0 ml of primary stock solution was diluted to 100.0 ml in a volumetric flask with deionized–distilled water to give a concentration 50 mg I/L. Then, 10 ml of 50 mg I/L stock was further diluted to 100.0 ml with deionised-distilled water to give a standard iodide concentration of 5 mg I/L. Finally, 1.00 ml of 5 mg I/L stock was diluted to 100.0 ml with deionised–distilled water to give a concentration of 0.5 mg I/L. This was used as the working standard solution for preparation of iodide for solution used in various kinetic studies.

4.4 Experimental Method

The reactants were divided into 2 solutions. Solution A contained iron(III), thiocyanate, sulphuric acid and nitrate. Solution B contained nitrite and iodide. Both A and B were prepared in 10.0 ml volumetric flasks.

The solution A was prepared by mixing iron(III) in 1.785 M sulphuric acid, thiocyanate and nitrate from stock solutions. Solution B was prepared by adding nitrite and iodide from stock solutions.

5.0 ml of solution B was pipetted and mixed rapidly with 5.0 ml of solution A. The absorbance at 458 nm was monitored with time.

4.5 Treatment of kinetic data

In this study, data were analysed using non-linear least squares regression (Enzfit, SigmaPlot, TableCurve 2D) and Microsoft Excel.

CHAPTER V
RESULTS AND DISCUSSION

5.1 The condition for pseudo-first order kinetics

A pseudo-first order reaction was obtained when the ratio between $[Fe^{3+}]$ and $[SCN^-]$ was sufficiently large because an excess of Fe^{3+} ensured that the $[SCN^-]$ exist mostly as $FeSCN^{2+}$. An exponential decay function was used to fit the experimental data, using non-linear least square programme:

$$y = y_0 + ae^{-kt} \quad (5.1)$$

where

y = absorbance at different time

t = time

y_0, a and k are the parameters obtained from the fitting equation

Figure 5.1 shows the experimental data for $[Fe^{3+}]$ = 64mM, $[SCN^-]$ = 128μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM, and the least square fit of the exponential function (SigmaPlot). The result of the fitting confirmed, that the reaction is pseudo-first order in iron(III)-thiocyanate complex. The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is 500.

Figure 5.2 shows the experimental data for $[Fe^{3+}]$ = 16 mM, $[SCN^-]$ = 800 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 1.98 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM, and the least square fit of the exponential function, with fitting by a non-linear least square programme (SigmaPlot). The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is now 40.

Figure 5.3 Absorbance against time at $[Fe^{3+}]$ = 16 mM, $[SCN^-]$ = 128 μM,$[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 1.98 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM, with fitting by a non-linear least square programme (SigmaPlot). The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is now 125.

Figure 5.4 shows the experimental data for $[Fe^{3+}]$ = 16 mM, $[SCN^-]$ = 200 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 1.98 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM, and the least square fit of the exponential function. The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is now 320.

Figure 5.5 shows the experimental data for $[Fe^{3+}]$ = 40 mM, $[SCN^-]$ = 40 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 1.98 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM, and the least square fit of the exponential function. The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is now 1000.

For the different ratio between $[Fe^{3+}]$ and $[SCN^-]$, the concentration of $FeSCN^{2+}$ in the solution can be calculated (see Table 1A – 1C in Appendix V for $[FeSCN^{2+}]$ in these study).

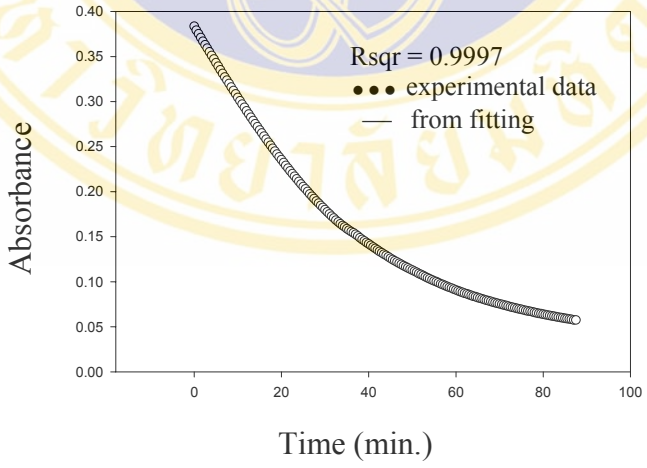


Figure 5.1 Absorbance against time at $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ =128 μM,$[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2.0 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM, with fitting by a non-linear least square programme (SigmaPlot). The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is 500.

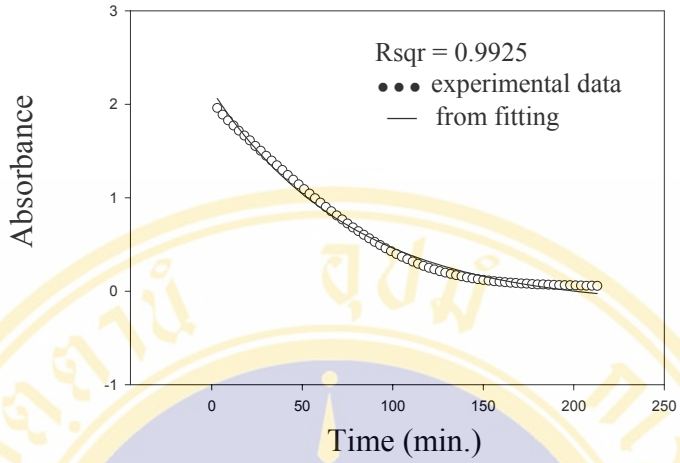


Figure 5.2 Absorbance against time at $[Fe^{3+}]$ = 16 mM, $[SCN^-]$ = 800 μM,$[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 1.98 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM, with fitting by a non-linear least square programme (SigmaPlot). The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is 40.

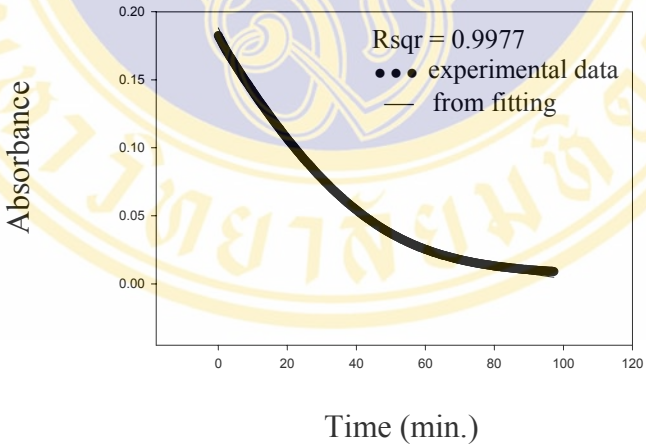


Figure 5.3 Absorbance against time at $[Fe^{3+}]$ = 16 mM, $[SCN^-]$ = 128 μM,$[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 1.98 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM, with fitting by a non-linear least square programme (SigmaPlot). The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is 125.

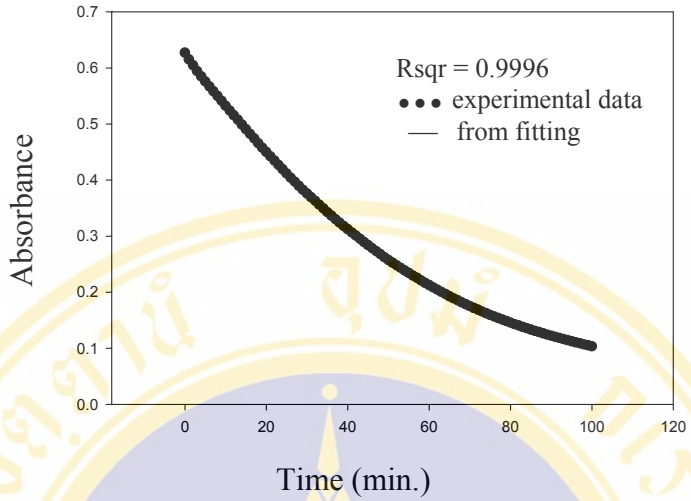


Figure 5.4 Absorbance against time at $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 200 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2.0 mM, $[H^+]$ =0.5 M, $[I^-]$ = 0.787 μM, with fitting by a non-linear least square programme (SigmaPlot). The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is 320.

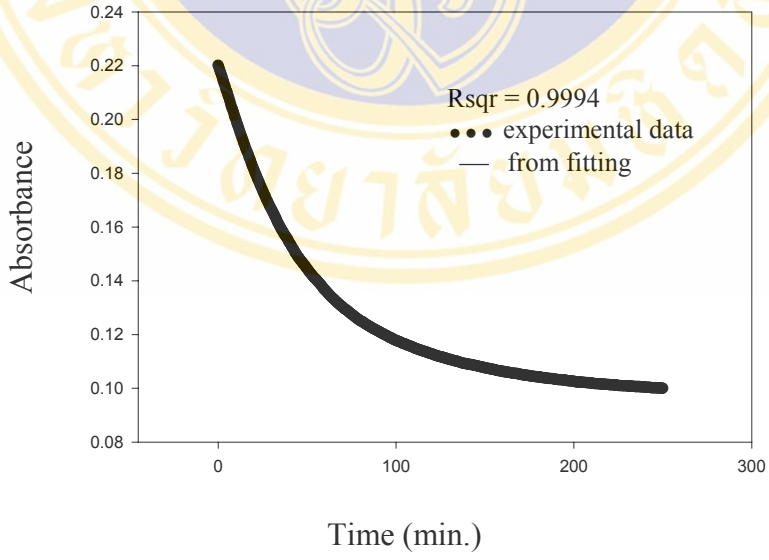


Figure 5.5 Absorbance against time at $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 40 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2.0 mM, $[H^+]$ =0.5 M, $[I^-]$ = 0.787 μM, with fitting by a non-linear least square programme (SigmaPlot). The ratio of $[Fe^{3+}]$ to $[SCN^-]$ is 1000.

5.2 Variation of the observed pseudo-first order rate constant with thiocyanate, iron(III), nitrate, nitrite, acid and iodide concentration

5.2.1 Effect of thiocyanate concentration

The experimental concentrations employed in this kinetic study were

[Fe(III)]	:	64 mM
[SCN^-]	:	20.0 - 180 μM
[NO_3^-]	:	0.50 M
[NO_2^-]	:	2.0 mM
[H^+]	:	0.5 M
[I^-]	:	0.787 μM
Temperature	:	30.0 ^oC
Monitoring wavelength	:	458 nm

Figure 5.5 shows the change of the rate constant as a function of [SCN^-] at constant [Fe(III)], [NO_3^-], [NO_2^-], [H^+] and [I^-] (see Table 1D in Appendix VI for the values of the rate constants at various [SCN^-]). The rate constant decreased with increasing thiocyanate concentration.

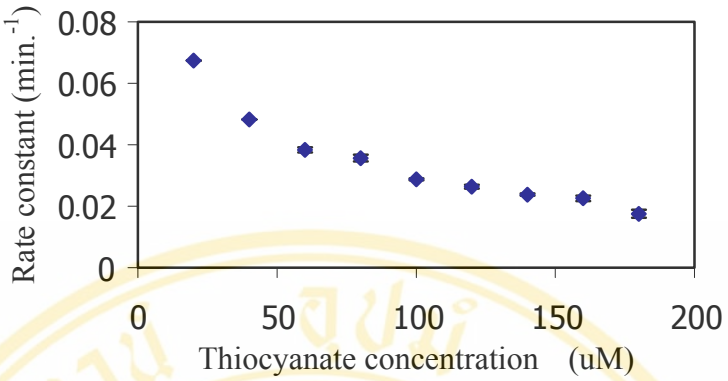


Figure 5.6 The variation of rate constant at various thiocyanate concentration. Conditions; $[Fe^{3}]$ = 64 mM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30 ^oC.

5.2.2 Effect of iron(III) concentration

The experimental concentrations employed in this kinetic study were

[Fe(III)] : 16 - 128 mM
[SCN^-] : 40 μM and 128 μM
[NO_3^-] : 0.5 M
[NO_2^-] : 2 mM
[H^+] : 0.5 M
[I^-] : 0.787 μM
Temperature : 30.0 ^oC
Monitoring wavelength : 458nm

Figure 5.7 shows the change of the rate constant as a function of [Fe(III)] at constant [SCN^-], [NO_3^-], [NO_2^-], [H^+] and [I^-] (see Table 1E in Appendix VI for the values of the rate constants at various [Fe^{3+}]). The rate constant is constant with [Fe(III)].

Figure 5.8 shows the variation of rate constant as a function of [Fe^{3+}] at constant [SCN^-] = 40μM, [NO_3^-] = 0.5M, [NO_2^-] = 2mM, [H^+] = 0.5M, [I^-] = 0.787 μM and temperature at 30^{o}C. (see Table 1B in Appendix V for the values of the rate constant at various [Fe^{3+}]). The rate constant is also constant with [Fe(III)].

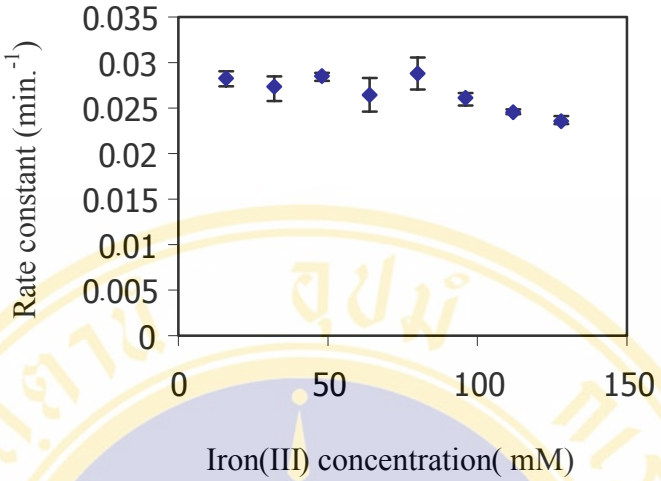


Figure 5.7 The variation of rate constant as a function of iron(III) concentration. Conditions; $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30°C.

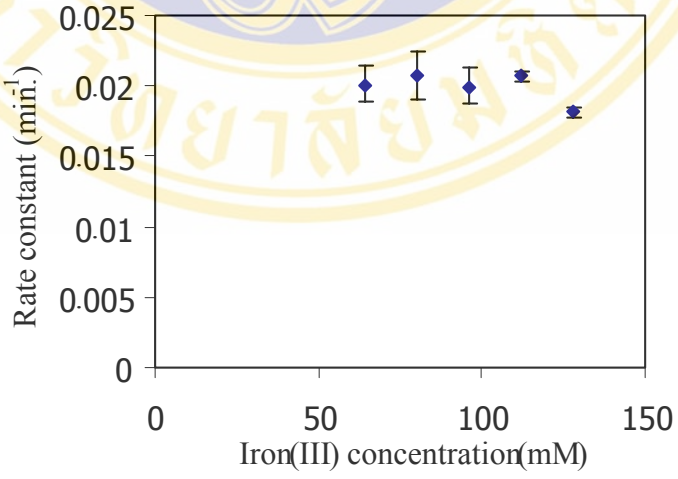


Figure 5.8 The variation of rate constant as a function of iron(III) concentration. Conditions; $[SCN^-]$ = 40 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30°C.

In this study, the iron(III) stock solution was prepared over night. It is found that different preparation of iron(III) stock solution gave difference in rate constant, in the range of 10 – 20 %. But the rate constant from each stock solution gave the same rate law if the reaction was studied by the iron(III) stock solution prepared and used in the same day, as shown in Figure 5.9 to Figure 5.13.

Figure 5.9 shows the rate constant as a function of [Fe(III)] at constant [SCN^-], [NO_3^-], [NO_2^-], [H^+] and [I^-] with different iron(III) stock solution (see Table 1E in Appendix VI for the values of the rate constants).

Figure 5.10 shows the rate constant as a function of [SCN^-] at constant [Fe(III)] , [NO_3^-], [NO_2^-], [H^+] and [I^-] with different iron(III) stock solution (see Table 1D in Appendix VI for the values of the rate constants).

Figure 5.11 shows the rate constant as a function of [NO_3^-] at constant [SCN^-], [Fe(III)], [NO_2^-], [H^+] and [I^-] at different iron(III) stock solution (see Table 1G in Appendix VI for the values of the rate constants).

Figure 5.12 shows the rate constant as a function of [NO_2^-] at constant [SCN^-], [Fe(III)], [NO_3^-], [H^+] and [I^-] at different iron(III) stock solution (see Table 1H in Appendix VI for the values of the rate constants).

Figure 5.13 shows the rate constant as a function of [H^+] at constant [SCN^-], [Fe(III)], [NO_3^-], [NO_2^-] and [H^+] at different iron(III) stock solution (see Table 1I in Appendix VI for the values of the rate constants).

Figure 5.14 shows the rate constant as a function of [I^-] at constant [SCN^-], [Fe(III)], [NO_3^-], [NO_2^-] and [H^+] at different iron(III) stock solution (see Table 1J in Appendix VI for the values of the rate constants).

When the same iron(III) stock solution was used in the same day the error for the rate constant is 3.0 – 5.0 %, as shown in Figure 5.15. If the iron(III) stock solution was used 2 days after preparing, the rate constant gave larger error, as shown in Figure 5.16 for the over night and 1 day after preparing the stock solution.

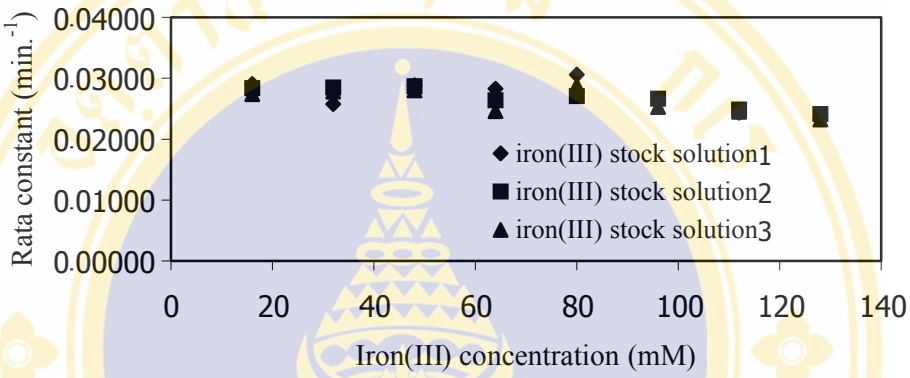


Figure 5.9 The variation of rate constant as a function of iron(III) concentration at different iron(III) stock solution . Conditions; $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30 ^oC.

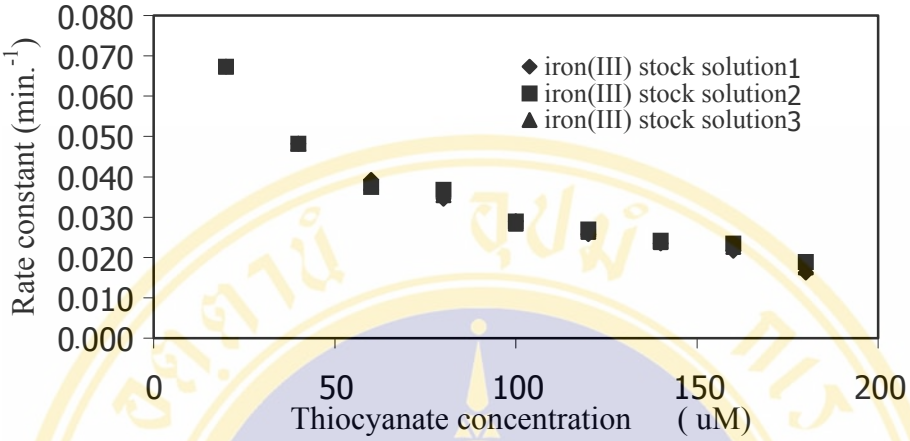


Figure 5.10 The variation of rate constant as a function of thiocyanate concentration at different iron(III) stock solution . Conditions; $[Fe^{3+}]$ = 64 mM,$[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30 ^oC.

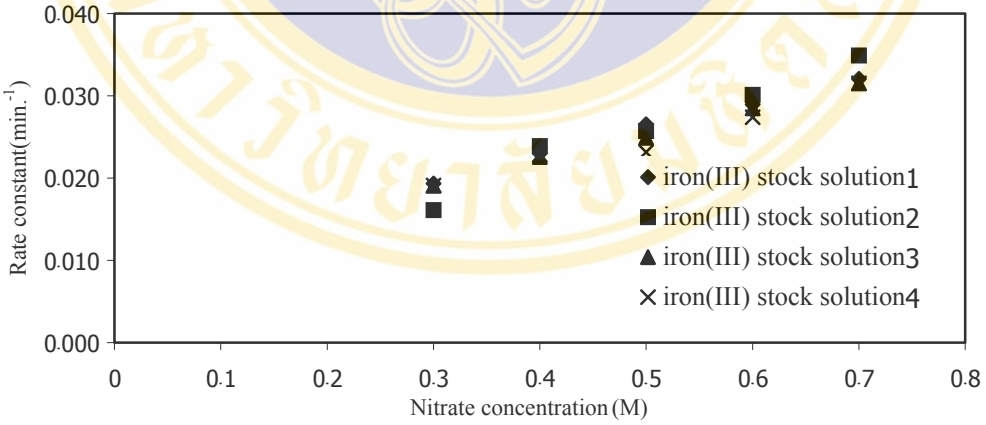


Figure 5.11 The variation of rate constant as a function of nitrate concentration at different iron(III) stock solution . Conditions; $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30 ^oC.

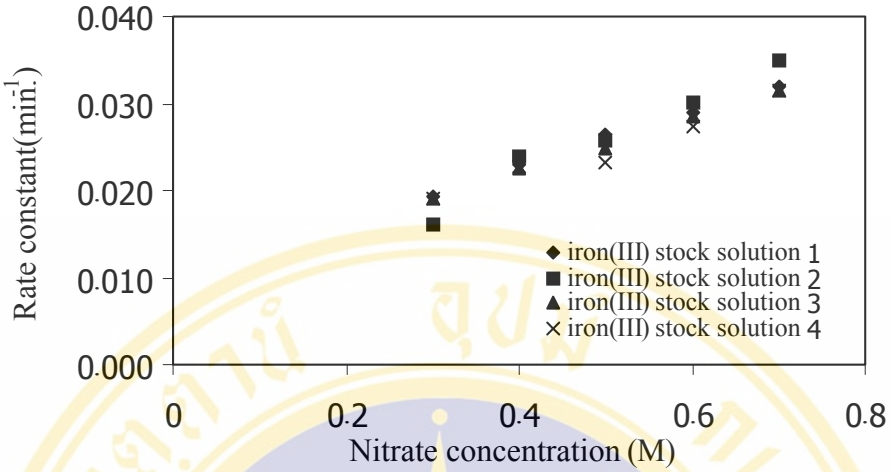


Figure 5.12 The variation of rate constant as a function of nitrite concentration at different iron(III) stock solution . Conditions; $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30 ^oC.

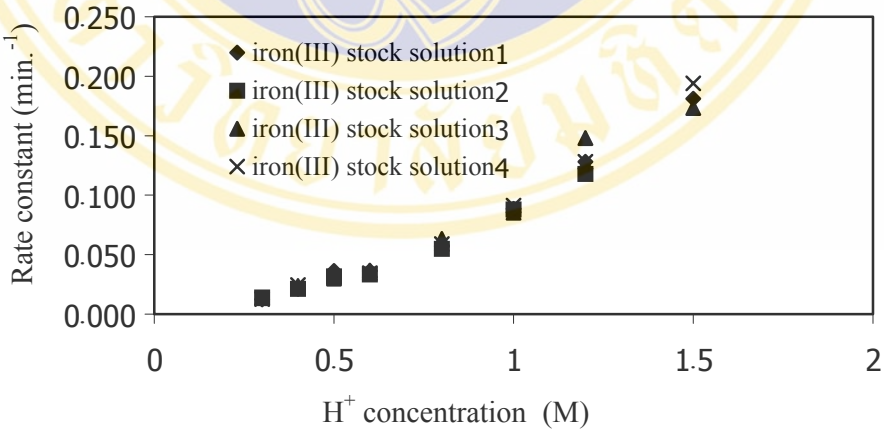


Figure 5.13 The variation of rate constant as a function of H^+ concentration at different iron(III) stock solution. Conditions; $[Fe^{3+}]$ = 64mM, $[SCN^-]$ = 128μM, $[NO_3^-]$ = 0.5M, $[NO_2^-]$ = 2mM, $[H^+]$. 0.5M and temperature at 30 ^oC.

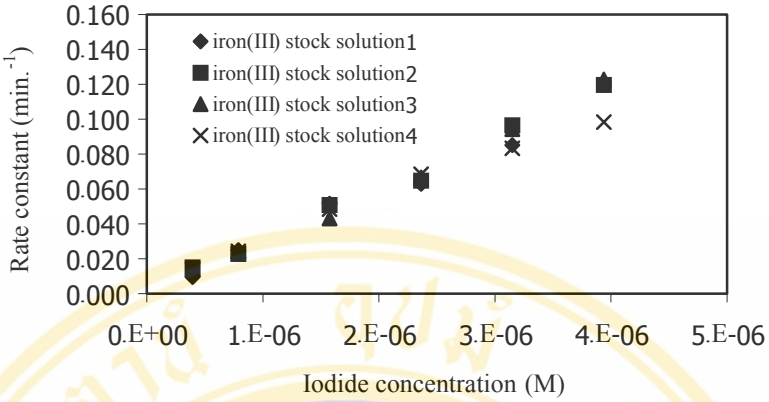


Figure 5.14 The variation of rate constant as a function of iodide concentration at different iron(III) stock solution . Conditions; $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$. 0.5 M and temperature at 30 ^oC.

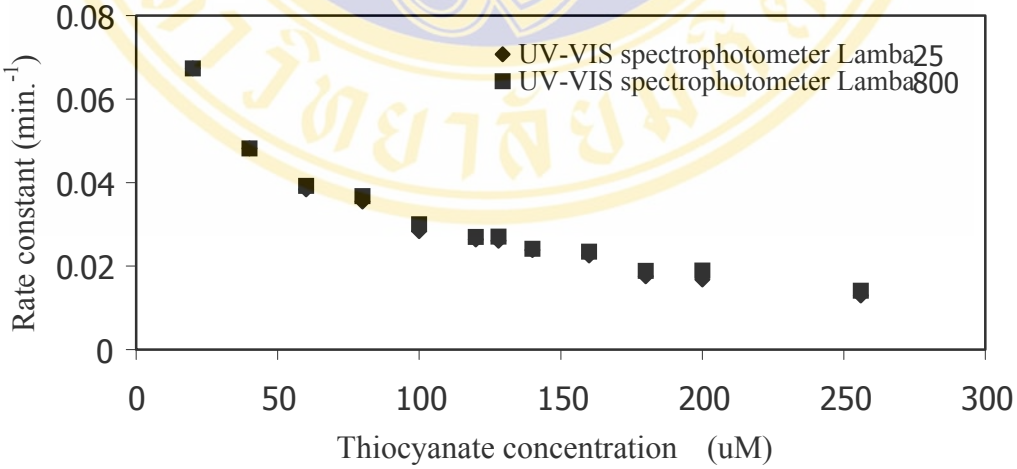


Figure 5.15 The variation of rate constant as a function of thiocyanate concentration with the same iron(III) stock solution . Conditions; $[Fe^{3+}]$ = 64 mM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$. 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30 ^oC.

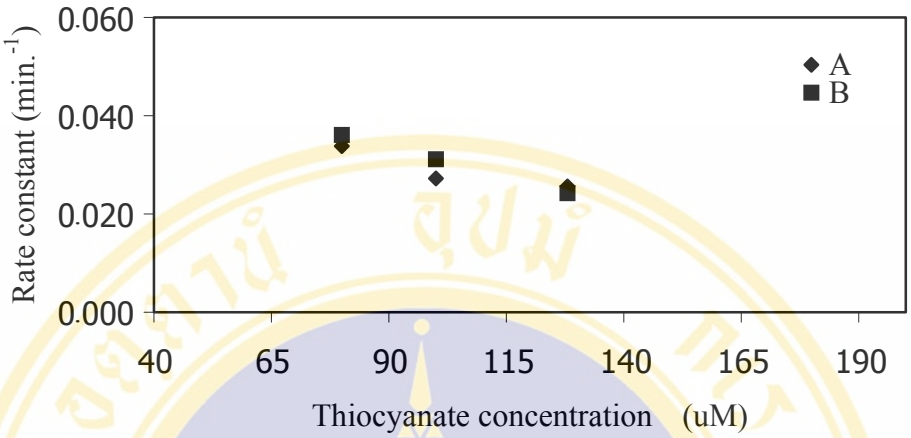


Figure 5.16 The variation of rate constant as a function of thiocyanate concentration. Conditions; $[Fe^{3+}]$ = 64 mM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30 ^oC. A. over night iron(III) stock solution and B. 1 day after preparing iron(III) stock solution.

5.2.3 Effect of nitrate concentration

The experimental concentrations employed in this kinetic study were

[Fe(III)] : 64 mM
[SCN^-] : 128 μM
[NO_3^-] : 0.3 – 0.7 M
[NO_2^-] : 2.0 mM
[H^+] : 0.5 M
[I^-] : 0.787 μM
Temperature : 30.0 °C
Monitoring wavelength: 458 nm

Figure 5.17 shows the change of the rate constant as a function of [NO_3^-] at constant [Fe(III)], [SCN^-], [NO_2^-], [H^+] and [I^-] (see Table 1G in Appendix VI for the values of the rate constants at various [NO_3^-]). There is a linear relationship between the rates and [NO_3^-] . The data could be fitted to the following equation:

$$k_1 = A[NO_3^-] \quad (5.2)$$

where

A = 0.0339

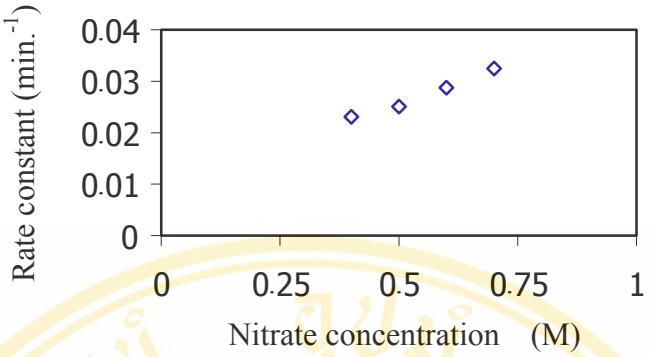


Figure 5.17 The variation of rate constant as a function of nitrate concentration. Conditions; $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30 ^oC.

5.2.4 Effect of nitrite concentration

The experimental concentrations employed in this kinetic study were

[Fe(III)] : 64 mM
[SCN^-] : 128 μM
[NO_3^-] : 0.5 M
[NO_2^-] : 1.0 - 7.0 mM
[H^+] : 0.5 M
[I^-] : 0.787 μM
Temperature : 30.0 °C
Monitoring wavelength : 458 nm

Figure 5.18 is the graph of the rate constant as a function of [NO_2^-] at fixed [Fe^{3+}], [SCN^-], [NO_3^-], [H^+] and [I^-] (see Table 1H in Appendix VI for the values of the rate constants at various [NO_2^-]). A second order polynomial function was observed between the observation rate constant and [NO_2^-]. The data were fitted to the equation:

$$k_2 = B_1 + B_2[NO_2^-]^2 \quad (5.3)$$

where

$B_1 = 0.0172$

$B_2 = 0.0026$

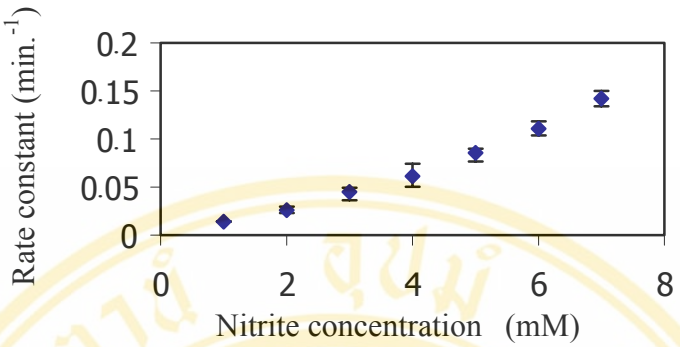


Figure 5.18 The variation of rate constant as a function of nitrite concentration. Conditions; $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and temperature at 30°C.

5.2.5. Effect of acid concentration

The experimental concentrations employed in this kinetic study were

[Fe(III)] : 64 mM
[SCN^-] : 128 μM
[NO_3^-] : 0.5 M
[NO_2^-] : 2.0 mM
[H^+] : 0.3 – 1.2 M
[I^-] : 0.787 μM
Temperature : 30.0 °C
Monitoring wavelength : 458 nm

Figure 5.19 is the graph of rate constant as a function [H^+] at fixed [Fe^{3+}], [SCN^-], [NO_3^-], [NO_2^-] and [I^-] (see Table 1I in Appendix VI for the values of the rate constants at various [H^+]). A quadratic relationship was found between the observed rate constant and [H^+]. The data were fitted to

$$k_3 = C[H^+]^2 \quad (5.4)$$

where

$$C = 0.0826$$

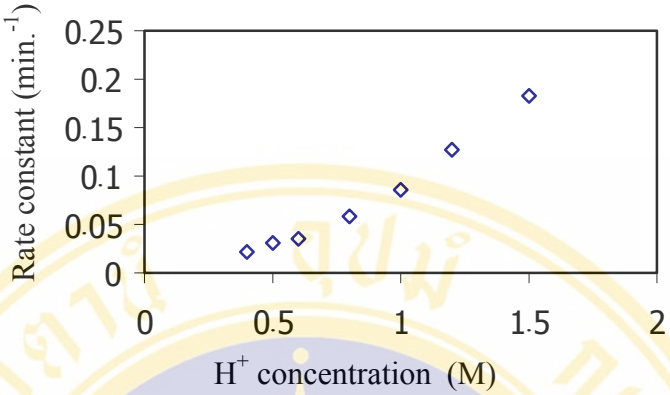


Figure 5.19 The variation of rate constant as a function of H^+ concentration. Conditions; $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[I^-]$ = 0.787 μM and temperature at 30 ^oC.

5.2.6 Effect of iodide concentration

The experimental concentrations employed in this kinetic study were

[Fe(III)] : 64 mM
[SCN^-] : 128 μM
[NO_3^-] : 0.5 M
[NO_2^-] : 2.0 mM
[H^+] : 0.5 M
[I^-] : 0.394 – 4.724 μM
Temperature : 30.0 ^oC
Monitoring wavelength : 458 nm

Figure 5.20 is the graph of rate constant as a function [I^-] at fixed [Fe^{3+}], [SCN^-], [NO_3^-], [NO_2^-] and [H^+] (see Table 1J in Appendix VI for the values of the rate constants at various [I^-]). A linear relationship was established between the rate constant and [I^-], as shown Figure 5.20. The data were fitted to

$$k_4 = D[I^-] \quad (5.5)$$

where

D = 28382

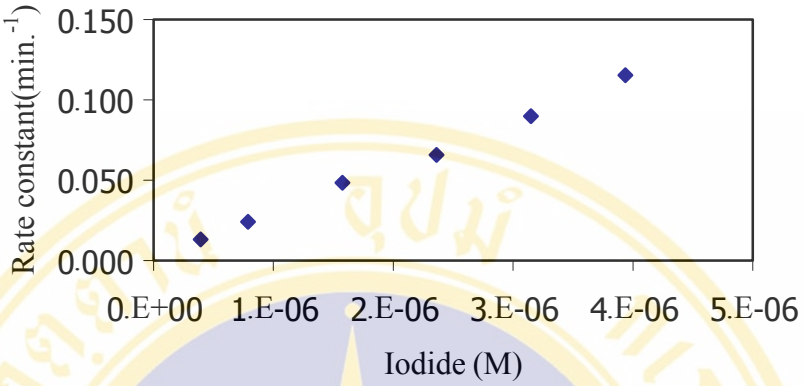


Figure 5.20 The variation of rate constant as a function of iodide concentration. Conditions; $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_2^-]$ = 2 mM, $[NO_3^-]$ = 0.5 M, $[H^+]$ = 0.5 M and temperature at 30 ^oC.

5.3 Discussion

The kinetic data of the iodide catalysed reaction between nitrite, nitrate, sulphuric acid and iron(III)-thiocyanate was a pseudo-first order reaction. The observed rate constant varied with $[NO_3^-]$, $[NO_2^-]$, $[H^+]$ and $[I^-]$ as follow:

1. At fixed SCN^-, NO_3^-, NO_2^-, H^+ and I^- concentrations, the rate constant is constant with Fe(III) concentrations, as shown in Figure 5.7.

2. At fixed Fe(III), NO_3^-, NO_2^-, H^+ and I^- concentrations, the rate constant decreased with increasing SCN^- concentrations, as shown in Figure 5.6.

3. At fixed Fe(III), SCN^-, NO_2^-, H^+ and I^- concentrations, the rate reaction is a linear function of NO_3^- concentrations, as shown in Figure 5.14.

4. At fixed Fe(III), SCN^-, NO_3^-, H^+ and I^- concentrations, the second order of polynomial function was established between the observation rate of reaction and NO_2^- concentrations, as shown in Figure 5.15.

5. At fixed Fe(III), SCN^-, NO_3^-, NO_2^-,and I^- concentrations, a quadratic relationship was established between the observation rate and H^+ concentrations, as shown in Figure 5.16.

6. At fixed Fe(III), SCN^-, NO_3^-, NO_2^- and H^+ concentrations, the rate reaction is a linear function of I^- concentrations, as shown in Figure 5.17.

From the above kinetic results, for varying $[NO_3^-]$, $[NO_2^-]$, $[H^+]$ and $[I^-]$ but keeping, $[Fe^{3+}]$ = 64mM and $[SCN^-]$ = 128μM at constant temperature of 30.0°C, the following relationship was found.

$$k_1 = A[NO_3^-] \quad (5.6)$$

$$k_2 = B_1 + B_2[NO_2^-]^2 \quad (5.7)$$

$$k_3 = C[H^+]^2 \quad (5.8)$$

$$k_4 = D[I^-] \quad (5.9)$$

From above relationship the rate law of the reaction can be written as

$$k_{observed} = k_5[NO_3^-][I^-][H^+]^2 (1 + k_6[NO_2^-]^2) \quad (5.10)$$

From above equation, the rate of reaction is directly proportional to the total iodide concentration, and can thus be employed to determine trace amount of iodide.

In studying the kinetics of this reaction, there are contain details that have to be taken into consideration:

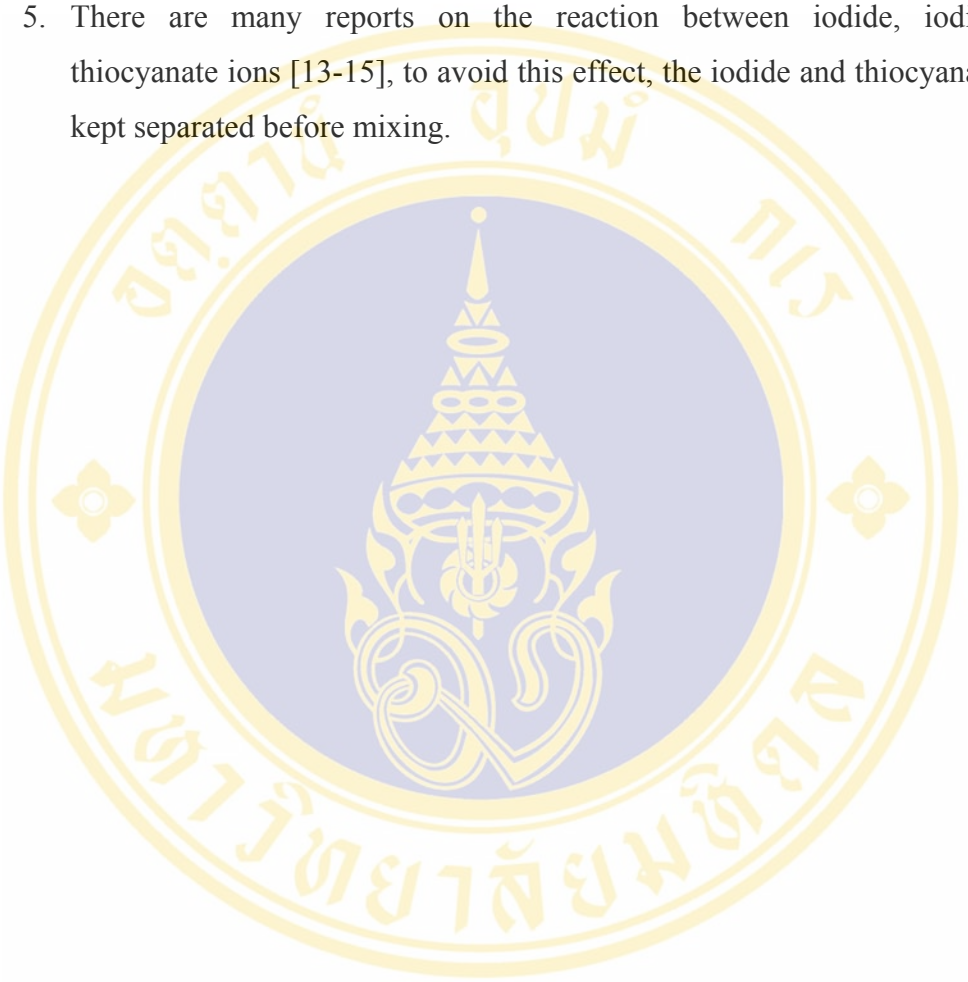
1. In this study, the iron(III) stock solutions were prepared by dissolving ammonium iron(III)-sulphate in sulphuric acid to avoid the trace amount of nitrite from nitric acid [5], and the nitrate ion is only from sodium nitrate.

2. To avoid the oxidation-reduction between Fe^{3+} and I^- [8] before mixing which can rapidly, produce iodine and iron(II), the iron(III) ion were separated from iodide ion.

3. To avoid the reaction between iodide and nitrite giving iodine in acidic medium [12], the nitrite and iodide were mixed in neutral aqueous medium.

4. The chemistry of the nitrite and nitrate give many species of nitrogen compound [8]. To avoid this effect, nitrate and nitrite ion were kept separated before mixing.

5. There are many reports on the reaction between iodide, iodine and thiocyanate ions [13-15], to avoid this effect, the iodide and thiocyanate were kept separated before mixing.



CHAPTER VI
CONCLUSION

The kinetics of the iodide catalysed reaction between nitrite, nitrate, acid with iron(III)-thiocyanate complexes was study by UV-VIS spectrophotometer technique . By varying the $[NO_3^-]$, $[NO_2^-]$, $[H^+]$ and $[I^-]$ but keep $[Fe^{3+}]$ = 64mM and $[SCN^-]$ = 128μM at temperature constant at 30.0°C, the following rate law was observed.

$$k_{observed} = k'[NO_3^-][I^-][H^+]^2 (1 + k''[NO_2^-]^2)$$

From the above rate law, it can be concluded that

1. The $FeSCN^{2+}$ concentration is the absorbance which is observed throughout the kinetic study.
2. The dependence on $[NO_3^-]$ concentration is first order throughout the concentration range of study ($[NO_3^-]$ = 0.2-0.7M).
3. The dependence on $[NO_2^-]$ concentration is a second order polynomial throughout the concentration range of study ($[NO_2^-]$ = 1.0-7.0mM).
4. The dependence on $[H^+]$ concentration is second order throughout the concentration range of study ($[H^+]$ = 0.25-1.2M).
5. The dependence on $[I^-]$ concentration is first order throughout the concentration range of study ($[I^-]$ =1.968 – 4.724μM).

For a fixed concentration of the reactants, the rate is first order in $[FeSCN^{2+}]$ and the reaction is also first order in total $[Fe^{3+}]$. There is the linear relationship between the observed pseudo-first order rate constant with the iodide concentration, which can be used for determining low concentration of iodide, i.e. use of catalytic reaction for analysis.

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APPENDIX

APPENDICES

Appendix I

The rate law and the mechanism of the oxidation of metal thiocyanate by nitric and nitrous acid by Stedman and Whincup.

The mechanism of the oxidation of metal thiocyanate by nitric and nitrous acid was proposed

$$H^+ + SCN^- \overset{\text{fast}}{\rightleftharpoons} HNCS \qquad K_1 \qquad (1A)$$

$$H^+ + HNO_2^- + NO_3^- \rightleftharpoons N_2O_4 + H_2O \qquad K_2 \qquad (2A)$$

$$N_2O_4 + HNCS \rightarrow HOSCN + N_2O_3 \qquad (3A)$$

$$N_2O_3 + H_2O \overset{\text{fast}}{\rightleftharpoons} 2HNO_2 \qquad (4A)$$

The net reaction is

$$SCN^- + HNO_2 + NO_3^- + 2H^+ \rightarrow OHSCN + 2HNO_2 \qquad (5A)$$

The variation of rate constant with thiocyanate concentration was two distinct parts.

At low concentrations of thiocyanate rate constant increases approximately linearly with thiocyanate concentration which is called “thiocyanate-dependent”, whereas at higher concentrations it is almost independent of thiocyanate and it is called the “thiocyanate-independent” region respectively.

At sufficiently high value of $[H^+][SCN^-]$ the concentration of unionized isothiocyanic acid is sufficiently high to trap all of the dinitrogen tetroxide formed in the form in the forward reaction of (2), so that none is hydrolysed back to nitric and nitrous acids. The rate of formation of nitrite is then the rate of formation of dinitrogen tetroxide $v = k_3'[H^+][HNO_2][NO_3^-]$, as is observed for high thiocyanate concentrations. The rate law of reaction observed are $v = k'[H^+][HNO_2][NO_3^-]$ at high concentrations of thiocyanate

At low thiocyanate concentrations most of the dinitrogen tetroxide is hydrolysed and reaction (2) is effectively on equilibrium, with $K_2 = [N_2O_4] / [H^+][HNO_2][NO_3^-]$. The rate of reaction is then determined by the rate of step (3) and the rate is

$$V = k_4[N_2O_4][HNCS] \quad (6A)$$

$$= k_5[N_2O_4][H^+][SCN^-] \quad (7A)$$

$$= k_5K_3K_2[H^+]^2[HNO_2][NO_3^-][SCN^-] \quad (8A)$$

where K_3 is the classical ionization constant of isothiocyanic acid.

$$v = k''[H^+]^2[HNO_2][NO_3^-][SCN^-] \quad (9A)$$

where $k'' = k_5K_3K_2$

Appendix II

The kinetic of the formation of ferric–thiocyanate complexes

The mechanism of the formation of ferric–thiocyanate complexes was proposed that it is pseudo-first order reaction in iron(III)-thiocyanate complexes which is studied by John FB with co-workers and G. Peintler with co-workers. The principle equilibria between ferric and thiocyanate ions in aqueous solution are

$$Fe^{3+} + SCN^- \underset{k_1}{\overset{k_1'}{\rightleftharpoons}} FeSCN^{2+} \qquad (10A)$$

Using the relationship $Q_1 = k_1/k_1'$, it follows that

$$d[FeSCN^{2+}]/dt = k_1[Fe^{3+}][SCN^-] - k_1/Q_1[FeSCN^{2+}] \qquad (11A)$$

Assuming $[Fe^{3+}]$ to be essentially constant during an experiment, expressing $[SCN^-]$ in terms of $[FeSCN^{2+}]$ and $[Fe^{3+}]$ and defining $[FeSCN^{2+}]_0$ and $[FeSCN^{2+}]_\infty$ as the concentrations of complex at the start of the reaction and after attainment of the final equilibrium value, respectively, the remove rate may be integrated, yielding

$$-kt = \frac{2.303}{[Fe^{3+}] + 1/Q_1} \log \frac{[FeSCN^{2+}]_\infty - [FeSCN^{2+}]}{[FeSCN^{2+}]_\infty - [FeSCN^{2+}]_0} \qquad (12A)$$

A plot of $\log\{[[FeSCN^{2+}]_\infty - [[FeSCN^{2+}]\}$ versus time yielded a straight line, thus confirming the assumption of first–order independence on SCN^- concentration.

Appendix III

Rate law for the purpose mechanism of the iodide catalysed reaction between iron(III)-thiocyanate complex ion by nitrate and nitrite in sulphuric acid

In this study, the rate law was calculated from the relationship between rate constant with each [Fe(III)], $[NO_3^-]$, $[NO_2^-]$, $[H^+]$ and $[I^-]$ concentratrion which listed below

$$k_1 = A[NO_3^-] \quad (13A)$$

$$k_2 = B_1 + B_2[NO_2^-]^2 \quad (14A)$$

$$k_3 = C[H^+]^2 \quad (15A)$$

$$k_4 = D[I^-] \quad (16A)$$

Whereas k is constant with iron(III) and thiocyanate concentration. All equation are fit by using a linear least-squares (Microsoft Excel) and a non-linear least squares fitting program (Enzfit, SigmaPlot and TableCurve 2D). From above equation, $k_{observed}$ can be calculated and is shown below

$$k_{observed} = k_5[NO_3^-][I^-][H^+]^2 (1 + k_6 [NO_2^-]^2) \quad (17A)$$

Appendix IV

Determination of the rate reaction

In this study, the rate of reaction was calculated from the slope of the plot of the absorbance with time using a non-linear least-squares fitting program (Enzfit and SigmaPlot) . Each reported value of rates was the averanged values of the three kinetic measurements. The rate of reaction was calculated in terms of absorbance/min. The fitting equation is

$$y = y_0 + ae^{-kt} \quad (18A)$$

where

y = absorbance at different time

t = time

y_0, a and k are the parameters obtained from the fitting equation

Whereas y_0 is the color of the iron(III) remained in the solution when the reaction was complete, a is the amplitude of the color of the solution at the beginning of the reaction and k is the rate reaction.

Appendix V

Table 1A The calculated data of exist $FeSCN^{2+}$ in the solution at variation concentration of Fe^{3+} for $[SCN^-] = 128$ μM, $[NO_3^-] = 0.5$ M, $[NO_2^-] = 2$ mM, $[H^+] = 0.5$ M, $[I^-] = 0.787$ μM.

$[Fe^{3+}]$total(mM)	$[FeSCN^{2+}]$(μM)	$\%FeSCN^{2+}(\pm 0.1)$	$[Fe^{3+}]/ [SCN^-]$
16	0.083	65.2	125
32	0.100	78.8	250
48	0.109	84.9	375
64	0.113	88.2	500
80	0.116	90.4	625
96	0.118	91.8	750
112	0.119	92.9	875
128	0.120	93.7	1000

Table 1B The calculated data of exist $FeSCN^{2+}$ in the solution at variation concentration of Fe^{3+} for $[SCN^-] = 40$ μM, $[NO_3^-] = 0.5$ M, $[NO_2^-] = 2$ mM, $[H^+] = 0.5$ M, $[I^-] = 0.787$ μM.

$[Fe^{3+}]$ total(mM)	$[FeSCN^{2+}]$(μM)	$\%FeSCN^{2+}(\pm 0.1)$	$[Fe^{3+}]/ [SCN^-]$
16	0.026	20.3	400
32	0.031	24.6	800
48	0.034	26.4	1200
64	0.035	27.6	1600
80	0.036	28.3	2000
96	0.037	29.0	2400
112	0.037	29.0	2800
128	0.037	29.0	3200

Table 1C The calculated data of exist $FeSCN^{2+}$ in the solution at variation concentration of SCN^- for $[Fe^{3+}] = 64$ mM, $[NO_3^-] = 0.5$ M, $[NO_2^-] = 2$ mM, $[H^+] = 0.5$ M, $[I^-] = 0.787$ μM.

$[SCN^-]$ total(μM)	$[FeSCN^{2+}]$(μM)	$\%FeSCN^{2+}$(± 0.1)	$[Fe^{3+}]/[SCN^-]$
20	0.018	88.2	3200
40	0.035	88.2	1600
60	0.053	88.2	1067
80	0.071	88.2	800
100	0.088	88.2	640
128	0.113	88.1	500
140	0.123	88.1	457
160	0.141	88.1	400
180	0.159	88.1	356
200	0.176	88.1	320
256	0.226	88.1	250

Appendix VI

Kinetic data for the study of the iodide catalysed reaction between iron(III)-thiocyanate complex ion by nitrate and nitrite in sulphuric acid

Table 1D Kinetic data for the study of rate constant with SCN^- concentration for $[Fe^{3+}]$ = 64 mM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and at temperature 30 ^oC.

$[SCN^-](\mu M)$	Rate constant (1^{st})	Rate constant (2^{nd})	Rate constant (3^{rd})	Average rate constant
20	0.067	0.067	0.067	0.067
40	0.048	0.048	0.048	0.048
60	0.039	0.038	0.038	0.038
80	0.035	0.037	0.035	0.036
100	0.029	0.029	0.028	0.029
120	0.026	0.027	0.026	0.026
140	0.023	0.024	0.024	0.024
160	0.022	0.023	0.023	0.023
180	0.016	0.019	0.018	0.018

Table 1E Kinetic data for the study of rate constant with Fe^{3+} concentration for $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and at temperature 30 ^oC.

$[Fe^{3+}](mM)$	Rate constant (1^{st})	Rate constant (2^{nd})	Rate constant (3^{rd})	Average rate constant
16	0.0291	0.0284	0.0274	0.0283
32	0.0258	0.0285	0.0278	0.0273
48	0.0289	0.0287	0.0280	0.0285
64	0.0283	0.0264	0.0246	0.0264
80	0.0306	0.0271	0.0288	0.0288
96	0.0264	0.0267	0.0253	0.0261
112	0.0243	0.0249	0.0245	0.0246
128	0.0234	0.0241	0.0232	0.0236

Table 1F Kinetic data for the study of rate constant with NO_3^- concentration for $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and at temperature 30 ^oC.

$[NO_3^-](M)$	Rate constant (1^{st})	Rate constant (2^{nd})	Rate constant (3^{rd})	Rate constant (4^{th})	Average rate constant
0.3	0.019	0.016	0.019	0.019	0.018
0.4	0.023	0.024	0.023	0.023	0.023
0.5	0.027	0.026	0.025	0.023	0.025
0.6	0.029	0.030	0.029	0.027	0.029
0.7	0.032	0.035	0.032	0.032	0.033

Table 1G Kinetic data for the study of rate constant with NO_2^- concentration for $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[H^+]$ = 0.5 M, $[I^-]$ = 0.787 μM and at temperature 30 ^oC.

NO_2^-(mM)	Rate constant (1^{st})	Rate constant (2^{nd})	Rate constant (3^{rd})	Rate constant (4^{th})	Average rate constant
1.0	0.014	0.014	0.014	0.014	0.014
2.0	0.025	0.030	0.023	0.027	0.026
3.0	0.046	0.049	0.036	0.049	0.045
4.0	0.062	0.074	0.057	0.052	0.062
5.0	0.089	0.090	0.077	0.087	0.086
6.0	0.110	0.111	0.104	0.118	0.111
7.0	0.146	0.150	0.134	0.138	0.142

Table 1H Kinetic data for the study of rate constant with H^+ concentration for $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM and $[I^-]$ = 0.787 μM and at temperature 30 ^oC.

H^+(M)	Rate constant (1^{st})	Rate constant (2^{nd})	Rate constant (3^{rd})	Rate constant (4^{th})	Average rate constant
0.3	0.012	0.014	0.013	0.013	0.013
0.4	0.021	0.021	0.024	0.025	0.021
0.5	0.036	0.032	0.030	0.031	0.031
0.6	0.036	0.034	0.037	0.034	0.035
0.8	0.057	0.055	0.063	0.059	0.058
1.0	0.089	0.088	0.085	0.091	0.086
1.2	0.128	0.118	0.148	0.128	0.127

Table 1I Kinetic data for the study of rate constant with I^- concentration for $[Fe^{3+}]$ = 64 mM, $[SCN^-]$ = 128 μM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM and $[H^+]$ = 0.5 M and at temperature 30 ^oC.

I^-(μM)	Rate constant (1^{st})	Rate constant (2^{nd})	Rate constant (3^{rd})	Rate constant (4^{th})	Average rate constant
3.94	0.019	0.015	0.014	0.014	0.013
7.87	0.025	0.023	0.025	0.024	0.024
15.7	0.052	0.051	0.043	0.048	0.049
23.6	0.063	0.065	0.067	0.068	0.066
31.5	0.085	0.097	0.094	0.083	0.090
39.4	0.121	0.120	0.123	0.098	0.115

Table 1J Kinetic data for the study of rate constant with SCN^- concentration for $[Fe^{3+}]$ = 64 mM, $[NO_3^-]$ = 0.5 M, $[NO_2^-]$ = 2 mM, $[H^+]$ = 0.5 M and $[I^-]$ = 0.787 μM and at temperature 30 ^oC.

$[SCN^-]$ (μM)	Rate constant 1*	Rate constant 2*	$[SCN^-]$ (μM)	Rate constant 1*	Rate constant 2*
20	0.067	0.067	128	0.026	0.027
40	0.048	0.048	140	0.024	0.024
60	0.038	0.039	160	0.023	0.024
80	0.036	0.037	180	0.018	0.019
100	0.028	0.030	200	0.017	0.019
120	0.026	0.027	256	0.013	0.014

1* = following the absorbance by using UV-VIS spectrophotometer Lambda25

2* = following the absorbance by using UV-VIS spectrophotometer Lambda800

BIOGRAPHY

NAME	Miss Kittiya Wongkhan
DATE OF BIRTH	August 06 , 1977
PLACE OF BIRTH	Sisaket, Thailand
INSTITUTIONS ATTENDED	Ubon Ratchatani University, 1995-1999: Bachelor of Science (Chemistry)
RESEARCH GRANTS	University Development Committee (UDC)(2001-2003) The Postgraduate Education and Research Program in Chemistry (PERCH) (2000-2003)