

# GLOBAL JOURNAL

OF SCIENCE FRONTIER RESEARCH: B

## Chemistry

Aqueous Acidic Medium

Spectrophotometric Determination

**Highlights**

Ion in Acidic Medium

Modelling and Experimentation

Discovering Thoughts, Inventing Future

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CHEMISTRY

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## Kinetic Approach to the Mechanism of Reduction of (7-Amino-8-Methyl-Phenothiazin-3-Ylidene)-Dimethyl-Ammonium Chloride by Thiocyanate Ion in Acidic Medium

By Babatunde O. A & Nwaji M. U

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**Abstract-** The kinetics of reduction of (7-Amino-8-methyl-phenothiazin-3-ylidene)-Dimethyl-Ammonium Chloride (hereafter referred to as TB) by thiocyanate ion have been studied in acidic medium under the pseudo-first order condition of excess  $[\text{SCN}^-]$  at  $30 \pm 1^\circ\text{C}$ ,  $[\text{H}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$  and ionic strength,  $I = 0.50 \text{ mol dm}^{-3}$  (NaCl). The stoichiometry of the reaction was observed to be 1:1 mole ratio of TB to SCN ions. The redox reaction follows second order kinetics at constant hydrogen ion concentration and the rate also increases with increase in hydrogen ion concentration.

**Keywords:** kinetics, mechanism, oxidation, thiocyanate, (7-amino-8-methyl-phenothiazin-3-ylidene)-dimethyl- ammonium chloride.

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# Kinetic Approach to the Mechanism of Reduction of (7-Amino-8-Methyl-Phenothiazin-3-Ylidene)-Dimethyl-Ammonium Chloride by Thiocyanate Ion in Acidic Medium

Babatunde O. A<sup>α</sup> & Nwaji M. U<sup>σ</sup>

**Abstract-** The kinetics of reduction of (7-Amino-8-methyl-phenothiazin-3-ylidene)-Dimethyl-Ammonium Chloride (here after referred to as TB) by thiocyanate ion have been studied in acidic medium under the pseudo-first order condition of excess [SCN<sup>-</sup>] at 30 ± 1°C, [H<sup>+</sup>] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup> and ionic strength, I = 0.50 mol dm<sup>-3</sup> (NaCl). The stoichiometry of the reaction was observed to be 1:1 mole ratio of TB to SCN ions. The redox reaction follows second order kinetics at constant hydrogen ion concentration and the rate also increases with increase in hydrogen ion concentration. The overall reaction conforms to the rate law

$$-\frac{d[TB^+]}{dt} = (a + b [H^+])[TB^+][SCN^-]$$

where a = 2.8 x 10<sup>-2</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>, b = 1.20 x 10<sup>-1</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>

Variation of the ionic strength and dielectric constant of the medium altered the rate of the reaction, addition anions and cations (X = SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) to the reaction mixture decreased the rate of the reaction. Spectroscopic and kinetic investigation showed no sign of intermediate complex formation; free radical polymerisation test showed no free radicals. A plausible mechanism which accommodates all the experimental data was proposed.

**Keywords:** kinetics, mechanism, oxidation, thiocyanate, (7-amino-8-methyl-phenothiazin-3-ylidene)-dimethyl-ammonium chloride.

## I. INTRODUCTION

Thiocyanate has reducing properties that include the ability to protect cells against oxidizing agents [1]. Thiocyanate ion is known to be an important part in the biosynthesis of hypothiocyanite by a lactoperoxidase [2, 3, 4]. Thus the complete absence of thiocyanate [5] or reduction in concentration of thiocyanate, in the human body, (cystic fibrosis) is damaging to the human host defense system [6, 7, 8].

(7-amino-8-methyl-phenothiazin-3-ylidene) - dimethyl- ammonium chloride is a dye belonging to the phenothiazine class same class as methylene blue and methylene green. Phenothiazines are important compounds in medicine and industry [9, 10]. The dye

can be used to treat methaemoglobinaemia [11]. The use of toluidine blue in this respect has been attributed to its electron donor –acceptor property [12]. However despite these and numerous other uses of TB not much is known about the kinetic and mechanism information vital to the understanding of the chemical characteristics of this dye so that its full potentials can be harnessed for more informed use(s).

## II. EXPERIMENTAL

There agents used were of analytical grade and were used as supplied. Stock solutions of TB, potassium thiocyanate and sodium chloride (BDH) was used to maintain ionic strength constant at 0.5 mol dm<sup>-3</sup> and they were prepared by dissolving known quantities in distilled water; hydrochloric acid which was used to investigate the effect of [H<sup>+</sup>] on the rate of reaction. This was standardized titrimetrically using standard solution of sodium bicarbonate. The λ<sub>max</sub> = 600 nm was determined by measuring the absorbance of the solution of TB in the wavelength range 500 – 650nm.

## III. STOICHIOMETRY

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method by keeping the concentration of the dye constant at 1.0 x 10<sup>-5</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>, I = 0.50 mol dm<sup>-3</sup>, λ<sub>max</sub> = 600 nm, T = 30 ± 1°C while [SCN<sup>-</sup>] was varied from 1.0– 6.0 x 10<sup>-5</sup> mol dm<sup>-3</sup>. The absorbance of the reacting mixture was measured after the reaction had gone to completion over a period of 24 hours when the absorbance attained a steady absorbance value. A point of inflexion on the curve of absorbance versus [SCN<sup>-</sup>] plot indicates the mole ratio of the reactants [13].

## IV. KINETIC MEASUREMENTS

The kinetics of the reaction was monitored using a Corning colorimeter Model 252 at 30 ± 1°C, [H<sup>+</sup>] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup> and I = 0.50 mol dm<sup>-3</sup>. The progress of the reaction was monitored by following the decrease in absorbance of the dye at 600 nm. All kinetic

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runs were performed under pseudo-first order conditions with the concentration of the thiocyanate ions at least 20-fold greater than that of the dye. The pseudo-first order plots of the  $\log (A_t - A_\infty)$  versus time  $t$  were made (where  $A_t$  and  $A_\infty$  are the absorbance at time,  $t$  and the end of the reaction) and from the slope of the plots, the pseudo-first order rate constant ( $k_1$ ) was determined. The second order rate constant ( $k_2$ ) was obtained from the relation:

$$k_2 = \frac{k_1}{[\text{SCN}^-]}$$

a) *Effect of  $[H^+]$  on the Reaction Rate*

The effect of  $[H^+]$  on the rate of the reaction was studied in the range of  $0.5 \times 10^{-3} \leq [H^+] \leq 2.5 \times 10^{-3} \text{ mol dm}^{-3}$  while concentration of TB and SCN ion were kept constant at  $1.0 \times 10^{-5}$  and  $20 \times 10^{-5} \text{ mol dm}^{-3}$  respectively at  $30 \pm 1^\circ\text{C}$  and  $I = 0.50 \text{ mol dm}^{-3}$ .

b) *Effect of Ionic Strength*

The effect of ionic strength on the rate of the reaction was investigated in the range of  $0.3 - 1.2 \text{ mol dm}^{-3}$ , while the concentrations of other reactants were kept constant at  $30 \pm 1^\circ\text{C}$ . The results are presented in Table 1.

c) *Effect of Added Cation and Anion*

The effect of added cation and anion were investigated for  $[X] = 0.2 \times 10^{-5} - 1.0 \times 10^{-5} \text{ mol dm}^{-3}$  ( $X = \text{Ca}^{2+}, \text{Mg}^{2+}, \text{SO}_4^{2-}, \text{NO}_3^-$ ) and the concentration of all other reactants were kept constant at  $30 \pm 1^\circ\text{C}$  and the ionic strength was maintained constant at  $0.50 \text{ mol dm}^{-3}$ .

d) *Test for Intermediate Complex*

The electronic spectra of the reaction mixture were obtained after five minutes of the commencement of the reaction, over the wavelength range of  $500 - 650 \text{ nm}$ . This was compared with the spectra of the dye alone within the same range. Michaelis-Mentens plot of  $1/k_1$  versus  $1/[\text{SCN}^-]$  was also made (Fig. 2).

e) *Test for Free Radical*

Acrylamidesolution was added to the partially oxidized reaction mixture of TB and the SCN ions in a large excess of methanol and to each of the reactants separately.

## V. RESULTS AND DISCUSSION

a) *Stoichiometry and Product Analysis*

A stoichiometric study showed that one mole of the dye was consumed by one mole of the thiocyanate ion. This conforms to the equation:



Product analysis was carried out by reacting equimolar amount of the dye and the thiocyanate at  $[H^+] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$  and  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl) After the completion of the reaction a colourless solution was obtained and UV visible spectra of the product showed no absorption peak at  $\lambda_{\text{max}} 600 \text{ nm}$ . This indicates the

destruction of the quinoid structure that gives the dye colour.

Qualitative test for cyanide ion was carried out. Cyanide ion was identified by precipitating with  $\text{AgNO}_3$ .

b) *Kinetics*

The pseudo-first orders of  $\log (A_t - A_\infty)$  versus time,  $t$  for these reactions were linear to about 90% of the reaction (Fig 1). The linearity of these plots indicates that these reactions are first order with respect to  $[\text{TB}^+]$ . A plot of  $\log k_1$  versus  $\log [\text{SCN}^-]$  was linear with a slope of 1.2 showing that the reaction is also first order with respect to  $[\text{SCN}^-]$ (Fig 2). This is also supported by the constancy of  $k_2$  values. Thus the reaction is second order at constant  $[H^+]$  and the rate equation for the reaction is:

$$-\frac{d[\text{TB}^+]}{dt} = k_2[\text{TB}^+][\text{SCN}^-] \quad \text{-- 2}$$

where  $k_2 = 9.96 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

c) *Effect of Acid*

The rate constants of the reaction were found to increase with increase in  $[H^+]$  in the range of  $(0.5 - 2.5) \times 10^{-3} \text{ mol dm}^{-3}$ . Plot of  $k_2$  versus  $[H^+]$  was also linear with a positive intercept (Fig. 3) therefore the acid dependent rate constant is given by:

$$k_2 = a + b [H^+] \quad \text{-- 3}$$

where  $a = 2.8 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ,  $b = 1.20 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

From equation (3) it is evident that the reaction proceeds through acid dependent and acid independent reaction pathways. Similar acid dependence was observed in the reaction between toluidine blue and phenyl ascorbic acid [14].

d) *Effect of Ionic Strength*

The effect of ionic strength on the reaction was investigated by varying the ionic strength of the medium within the range  $0.3 - 1.2 \text{ mol dm}^{-3}$ . The rate of reaction was found to decrease with increase in ionic strength of the reaction medium (figure 5). The result implies that positive and negatively charged species are participating in the rate determining step.[15]. The trend portrayed by the variation of ionic strength was verified by investigating the effect of the changes in dielectric constant of the reaction medium. Decrease in dielectric constant of the medium enhanced the rate of the reaction.

e) *Effect of Added Species*

Addition of  $\text{Ca}^{2+}, \text{Mg}^{2+}, \text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ions decreases the rate of the reaction. The inhibitive effect of these ions could be due to the columbic forces of attraction which tend to pull the reacting partners apart there by retarding the rate of the reaction and this

happens where there is no formal bond between the oxidant and the reductant prior to the rate determining step which is characteristic of outer sphere mechanism.

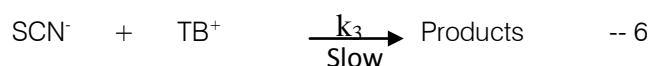
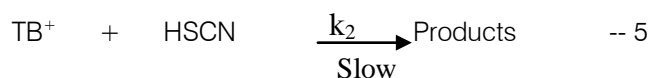
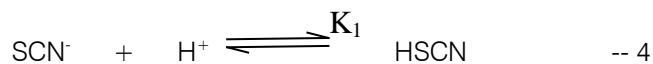
f) *FreeRadical Test*

The addition of acrylamide to the partially reacted mixture of the reactants followed by large excess of methanol did not lead to the formation of gelatinous precipitate. This suggests that free radicals might not likely be involved in this reaction[16].

g) *Intermediate Complex Formation*

The results of the spectroscopic studies indicated no shift from the absorption maxima of 600 nm characteristic of TB. This suggests the formation of an intermediate complex during the reactions is very unlikely. Michaelis-Mentens plots of  $1/k_1$  versus  $1/[\text{SCN}^-]$  gave a straight line which passed through the origin (Fig 5). This further suggests the absence of intermediate complex of significant stability thereby supporting the outer-sphere mechanism (Idris et al., 2005 and Benson, 1996) for this reaction.

On the basis of the above experimental results, the following plausible mechanism is hereby proposed:



The equations 5 and 6 are the rate determining steps

$$\text{Rate} = k_2 [\text{TB}^+] [\text{HSCN}] + k_3 [\text{TB}^+] [\text{SCN}^-] \quad \text{-- 7}$$

From equation 4

$$[\text{HSCN}] = K_1 [\text{SCN}^-] [\text{H}^+] \quad \text{-- 8}$$

Substitute equation 8 into equation 7

$$\text{Rate} = k_2 K_1 [\text{TB}^+] [\text{SCN}^-] [\text{H}^+] + k_3 [\text{TB}^+] [\text{SCN}^-] \quad \text{-- 9}$$

Rearranging equation 9

$$\text{Rate} = k_3 + k_2 K_1 [\text{H}^+] [\text{TB}^+] [\text{SCN}^-] \quad \text{-- 10}$$

Where  $k_3 = a$

$$k_2 K_1 = b$$

Equation 10 becomes

$$\text{Rate} = (a + b [\text{H}^+]) [\text{TB}^+] [\text{SCN}^-] \quad \text{-- 11}$$

Where  $a = 2.8 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $b = 1.20 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

the inhibition of the reaction rates, when the absorbance of the reaction mixture were measured as the reaction progresses the  $\lambda_{\text{max}}$  of TB remains at 600nm, this is an indication of the absence of intermediate complex formation which would be as a result of a chemical bond between the reactants, thereby tempering with the electronic transition of the TB, and hence a shift in the  $\lambda_{\text{max}}$  of  $\text{TB}^+$  or appearance of a new peak which was hitherto absent. Also Michaelis-Menten plot of  $1/k_1$  against  $1/[\text{SCN}^-]$  passed through the origin. These points greatly favour the outer sphere mechanistic pathway for this reaction.

## VI. CONCLUSION

The reaction is found to be second order overall at constant  $[\text{H}^+]$ . And the proposed reaction steps point to an outer sphere electron transfer process, considering the fact that addition of foreign ions led to

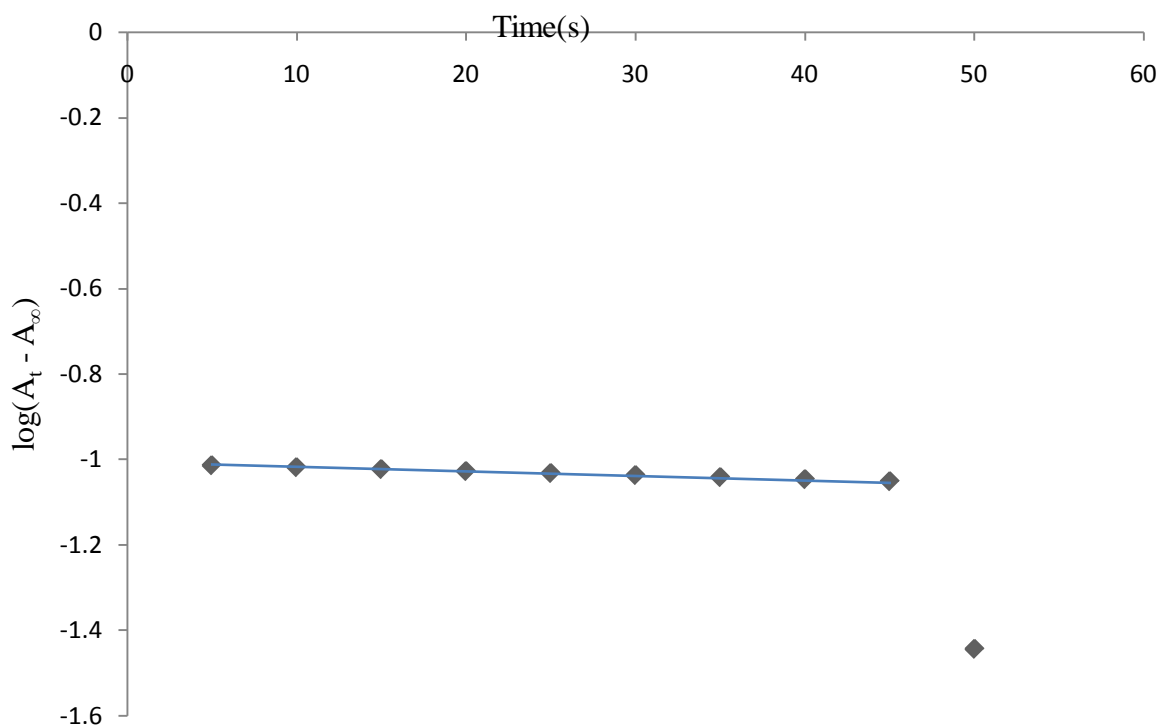


Figure 1 : Pseudo-first Order Plot for the Reduction of TB by SCN

Table 1 : Pseudo – first order and second order rate constants for TBreduction by SCN<sup>-</sup> in aqueous HCl medium at [TB<sup>+</sup>] = 1.0 x 10<sup>-5</sup> mol dm<sup>-3</sup>, T = 30 ± 1°C and , λ<sub>max</sub> = 600 nm

10 <sup>5</sup> [SCN <sup>-</sup> ] mol dm <sup>-3</sup>	I (NaCl) mol dm <sup>-3</sup>	10 <sup>3</sup> [H <sup>+</sup> ] mol dm <sup>-3</sup>	10 <sup>1</sup> k <sub>1</sub> s <sup>-1</sup>	10 <sup>3</sup> k <sub>2</sub> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
20	0.5	1.0	2.03	1.02
30	0.5	1.0	3.04	1.01
40	0.5	1.0	3.98	1.00
50	0.5	1.0	4.91	0.98
60	0.5	1.0	5.84	0.97
20	0.5	0.5	1.81	0.91
20	0.5	1.0	1.90	0.95
20	0.5	1.5	2.02	1.01
20	0.5	2.0	2.35	1.17
20	0.5	2.5	2.60	1.30
20	0.3	1.0	2.21	1.10
20	0.5	1.0	1.92	0.96
20	0.7	1.0	1.70	0.85
20	1.0	1.0	1.55	0.77
20	1.2	1.0	1.44	0.67

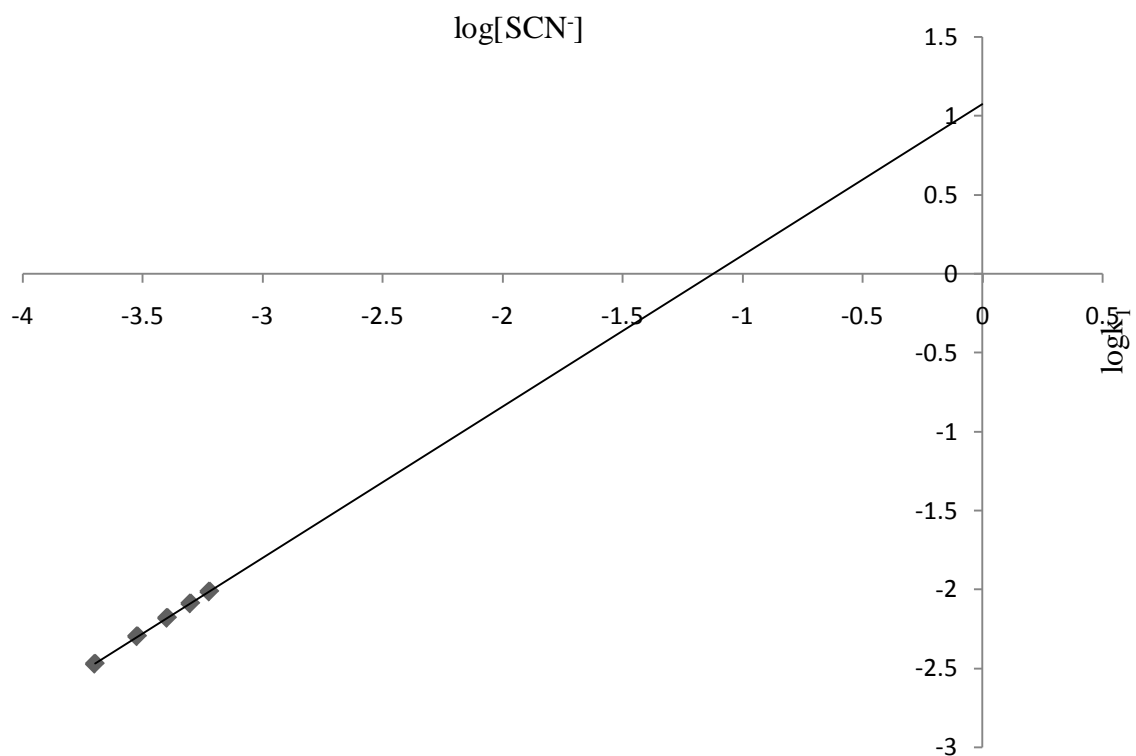


Figure 2 : Plot of  $\log k_1$  vs  $\log [\text{SCN}^-]$  for the Reduction of TB by  $\text{SCN}^-$

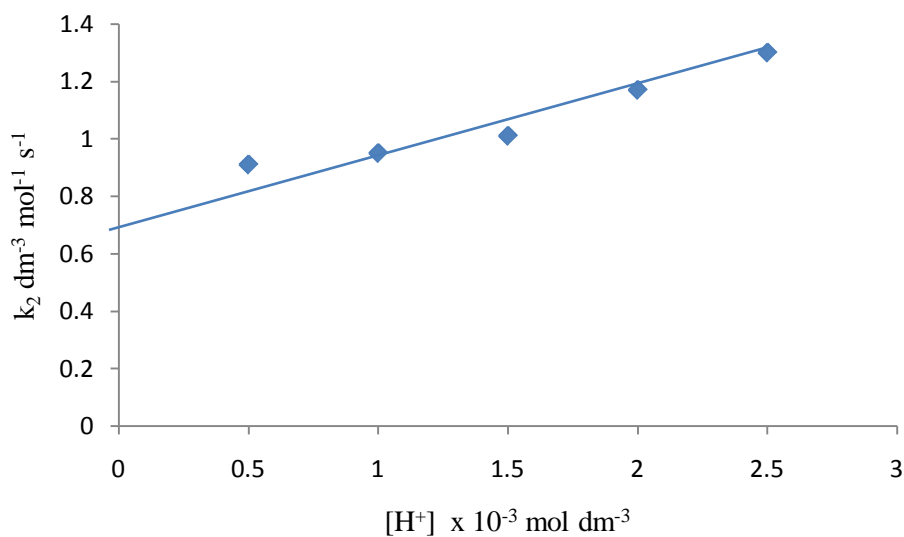


Figure 3 : Plot of  $k_2$  versus  $[\text{H}^+]$  of reduction of TB by  $\text{SCN}^-$

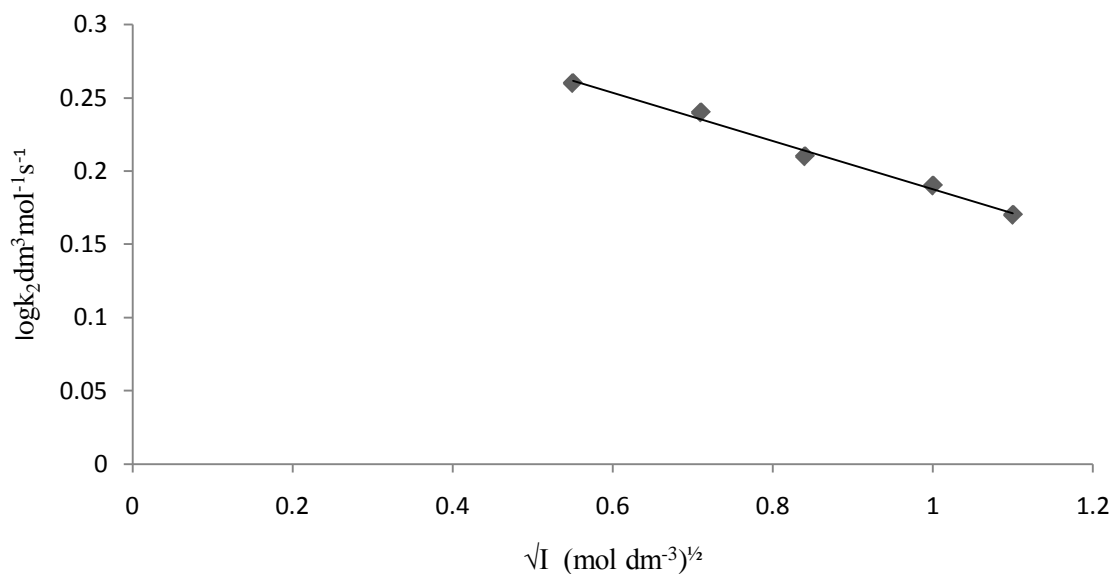


Figure 4 : plot of  $\log k_2$  versus  $\sqrt{I}$  for the reduction of  $TB^+$  by  $[SCN^-]$

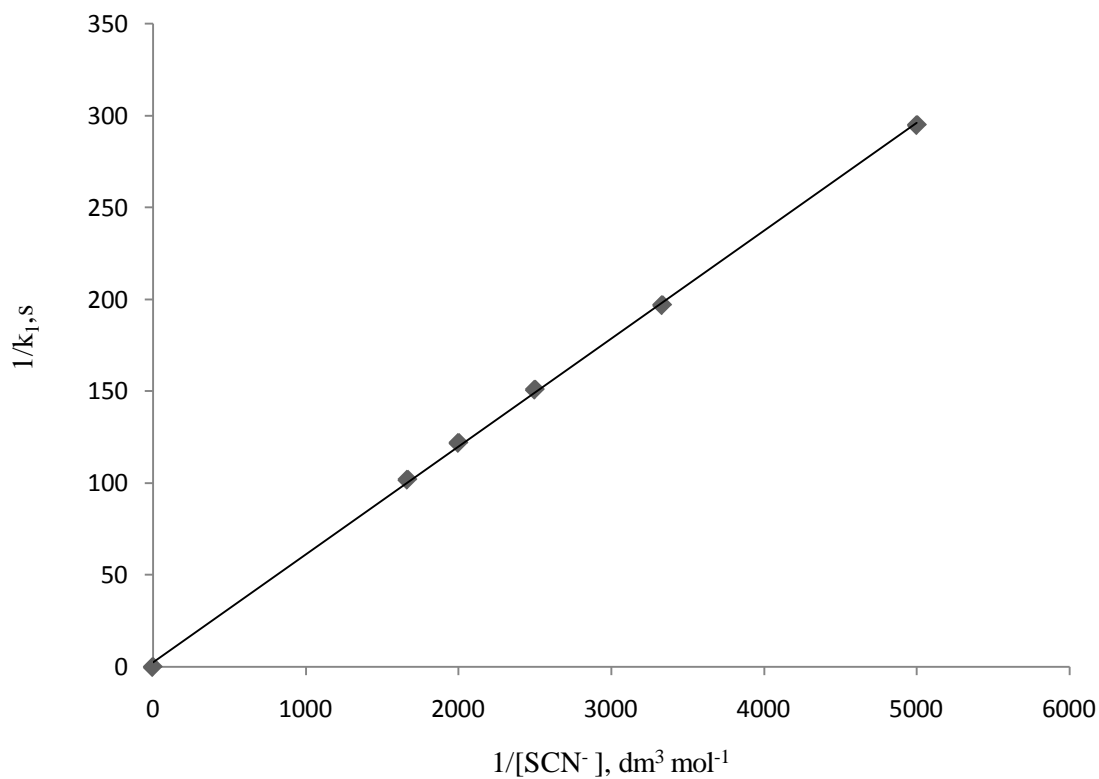


Figure 5 : Michaelis-Menten's plot for the reduction of TB by  $SCN^-$



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By Zuhair A-A Khammas, Shawkat K. Jawad & Ibtehaj R. Ali

*University of Baghdad, Iraq*

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**GJSFR-B Classification :** FOR Code: 030599



A NEW SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM VI AS  $\text{CrO}_4$  AFTER CLOUD-POINT EXTRACTION USING A LABORATORY-MADE ORGANIC REAGENT

*Strictly as per the compliance and regulations of :*



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**Keywords:** chromium oxyanion, new azo dye reagent, ion-association complex cloud-point extraction, spectrophotometry.

## 1. INTRODUCTION

Chromium (VI) is known to be a highly toxic metal and one of sources that drives to many cancer diseases namely, cancer of lung, oesophagus, and liver <sup>(1)</sup>. Due to sever toxicity of Cr (VI), WHO and USEPA have set the guideline for drinking water with upper limit of 50  $\mu\text{g L}^{-1}$  <sup>(2-4)</sup>, whereas the Agency for Toxic Substances and Diseases Registry (ATSDR) classifies Cr (VI) as the top eighteenth hazardous substance and the Minimal National Standards (MINAS) upper limit of Chromium in industrial wastewater is of 100  $\mu\text{g L}^{-1}$  <sup>(5)</sup>. Consequently, the determination of Cr (VI) in an industrial effluent is necessary to control the level of Cr

species in waste water, natural water, and drinking water. The determination of Cr (VI) in other environmental samples such as soils, plants and vegetables is also of prime importance to realize its concentration levels and extent of its impact on human health.

Trace amount of chromium determination in such complex matrices is a challenge and difficult analytical task, mostly due to the low concentration of metal in the samples, the existence of Cr (VI) as  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{CrO}_4^{2-}$  species in most environmental matrices beside the matrix interferences, which should be required sensitive instrumental techniques and often a pre-concentration step.

Since its inception in 1985, cloud-point extraction (CPE) methodology has constituted an important theme in the analytical chemistry as promising procedure for the separation and preconcentration for the metal ions and organic compounds from the complex matrices samples. Nowadays, it has begun to take a large noteworthy position among the other modern separation methods in scientific research and applications fields on a high level due to its simplicity, rapidity, more precise and cheapness beside environmentally-friendly method. However, most applications of CPE dealt with extraction of metal ions after complexing with chelating agent forming chelate at a certain pH as a hydrophobic molecule which is easily extracted by nonionic surfactant. But, to the best of our knowledge, the separation and pre-concentration of inorganic anions such as metal halo anions ( $\text{MX}_4^-$ ) metal oxyanions ( $\text{MO}_4^-$ ) and metal cyanoanions  $[\text{M}(\text{CN})_6]^{3-}$ ,  $[\text{M}(\text{CN})_4]^{2-}$ ,  $[\text{M}(\text{CN})_2]^-$  or metal thiocyanate anion  $[\text{M}(\text{SCN})_4]^{2-}$  into surfactant by CPE in a single-step extraction compared to the most common metal chelate extraction is so scanty and scarcely nonexistence so far since the commencement of CPE. Nevertheless, there were only two attempts based on the above conception for the determination of Cd (II) as  $\text{CdI}_4^{2-}$  by CPE with flame atomic absorption spectrometry <sup>(6)</sup> and the reaction of CTAB with the heteropoly acid formed between  $\text{MoO}_4^{2-}$  and  $\alpha\text{-PO}_4^{2-}$  to give a high molecular weight complex, which was quantitatively extracted in a non-ionic

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surfactant for the preconcentration and determination of orthophosphates<sup>(7)</sup> beside our two papers recently published elsewhere<sup>(8-9)</sup> for the determination of Cd(II) and Mn(VI) as inorganic anions by CPE-Spectrophotometry.

In the present study, an attempt has been performed to establish a new procedure for the separation and extraction of Cr (VI) by CPE methodology and its detection spectrophotometrically for the first time. The method is based on the formation of ion-association hydrophobic complex between  $\text{Cr}_2\text{O}_7^{2-}$  and BTABN as a new synthesized reagent in acidic medium and subsequently extracted into the surfactant Triton X-100 at optimum conditions. The separated surfactant-rich phase is diluted with minimum amount of ethanol and Cr (VI) determined by UV-Vis spectrometry at  $\lambda_{\text{max}}$  of 475 nm. The proposed method was applied for the determination of Cr (VI) in different environmental matrices.

## II. MATERIALS AND METHODS

### a) Apparatus

A Shimadzu double beam UV-Vis Spectrophotometer model UV-1700 (Japan) working at wavelength of 190-1100 nm ( $\pm 0.3\text{nm}$  accuracy at D<sub>2</sub> peak 656.1 nm, 486.0 nm and  $\pm 0.1$  repeatability), spectral bandwidth of 1.0 nm (190 to 900 nm) equipped with 10-mm optical path cell was used for the scanning of absorption spectra of all reagents and complex throughout this study. While absorbance measurements in the optimization study and detection of metal was done with Single beam (UV-Vis) Spectrophotometer, TRIUP International Corp- TRUV. 74, S (Italy).

### b) Reagent and materials

All analytical grade reagents were used without further purification as received from different company. Doubly distilled water was used for diluting the standard, reagents and samples. The nonionic surfactant (Triton X-100) whose chemical structure is  $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4(\text{OC}_2\text{H}_4)_n$  with  $n$  equal to 9-10 and an average molecular weight of 625 g/mol, was purchased from Sigma (Sigma Ultra, >99.6%). (UK) and. Potassium dichromate (98.0%) 2-aminobenzothiazol (99%), NaOH (99%), HCl (37%),  $\text{NaNO}_2$  (99%) were purchased from BDH(UK), p-benzenenaphthol(98%) from Fluka (Germany) and diphenylcarbazine(>98%) from Chem. Supply Pty limited(Australia). The stock solution of Cr (VI) at 1000  $\mu\text{g mL}^{-1}$  was prepared by dissolving of  $0.2829 \pm 0.0010$  g of  $\text{K}_2\text{Cr}_2\text{O}_7$  in a minimum amount of water in 100 mL volumetric flask and completed to mark with water and mixed thoroughly. A stock solution of 2- [benzene thiazolyazo]- 4- benzenenaphthol (BTABN) reagent solution at concentration of  $1 \times 10^{-2}$  M was prepared by dissolving 0.3810 g in 0.5 mL of 1% Triton X-100 and minimum amount of water in 100 mL volumetric flask and diluted to mark with water. A 0.25% of

Diphenylcarbazine solution was prepared by dissolving 0.25 g of 1, 5-diphenylcarbazine ( $\text{C}_{13}\text{H}_{14}\text{N}_4\text{O}$ ) in 50 ml of acetone and quantitatively transferred to a 100 ml volumetric flask, diluted to the mark with water and mixed thoroughly. The solution was transferred to a brown bottle, cap tightly and keep in the refrigerator. The solution is stable for at least one month.

### c) Synthesis and Characterization of Reagents

A 2- [benzene thiazolyazo] - 4- benzenenaphthol reagent was prepared according to the procedure published elsewhere<sup>(10)</sup> by dissolving (1.5 g 0.01 mole) of 2-aminobenzthiazol in a mixture containing 4 mL of concentrated HCl and 25 mL distilled water. After cooling this solution to 0 °C, 1.4 g of sodium nitrite dissolved in 10 mL distilled water was added with maintaining the temperature at 0 °C. The mixture was set aside for 15 min for complete diazotization process. Thereafter, the diazonium solution was poured drop by drop into beaker containing (2.2 g, 0.01 mole) of p- benzenenaphthol and 1.2 g sodium hydroxide dissolved in 150 mL ethyl alcohol with keeping temperature at 0 °C. After complete addition, the contents was left for two hours, then 150 mL of cooled distilled water was added and the pH of the solution maintained at 6, a brown powder were precipitated and left for 24 h. The solid product was filtered off, washed with cold water, crystallized twice from hot absolute ethanol and dried over  $\text{CaCl}_2$ . Yield 77%; mp 127-128 °C; anal calcd for  $\text{C}_{23}\text{H}_{15}\text{N}_3\text{OS}$  (382.48 g mol<sup>-1</sup>); C, 72.23; H, 4.22; N, 10.98; S, 8.38; O, 4.18; found C, 72.65; H, 3.99; N, 11.50; S, 8.56; O, 5.32; IR(KBr)  $\nu_{\text{max}}/\text{cm}^{-1}$ , 3194.23(m, Ar-OH), 3063.06 C-H aromatic, 2920(w, C-H aliphatic), 1643(s, C=N), 1514.17(m, N=N), 1367.58(m, C=C), 1303.92(m, C-O), 1249.91(m, C-N), 1180.47(m, C-S) 949.01 (s,  $\delta$ , bend aromatic, C-H); <sup>1</sup>HNMR(DMSO-*d*<sub>6</sub>, 298 K,)  $\delta$ /ppm) 5.295 (m, 1H, OH), 8.515-8.492 (s, 2 H, benzthiazole phenyl), 7.575-7.559 (s, 2 H, benzthiazole phenyl), 7.495, 7.524, 7.865, 7.891 and 7.931 (s, 5H, p-phenoyl), 7.916 (s, H, phenol), 8.057, 8.485, 7.982, 7.931 (s, 4H, naphthol, phenyl). The chemical structure of 2- [benzene thiazolyazo]- 4- benzenenaphthol abbreviated as BTABN is shown in Figure 1. This reagent does not dissolved in water, but it dissolve in the organic solvents such ethanol, ethanol, chloroform, Acetone, DMF etc. However, to avoid for dissolving this reagent in organic solvents, it was prepared in 0.5% Triton X-100 before use.

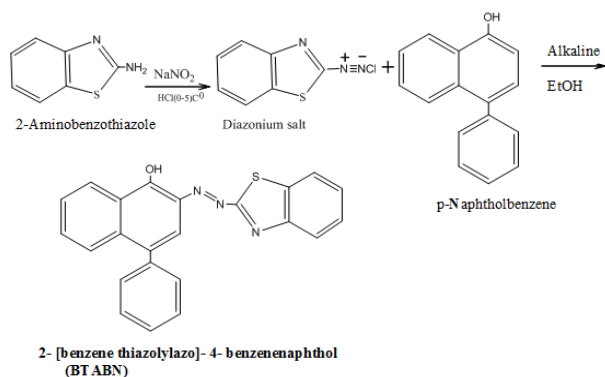


Figure 1 : Synthetic path of BTABN reagent

d) General Procedure for CPE

To an aliquot of 10 mL of a solution containing known amount of Cr (VI) as  $\text{Cr}_2\text{O}_7^{2-}$  standard or sample solution in 0.1M HCl,  $5 \times 10^{-4}$  M of BTABN reagent solution, 0.4 mL of 1% Triton X-100 were mixed and allowed to stand for stand for 25 min in a thermostated bath at 80 °C to form cloud solution. Separation of the two phases were occurred immediately where the surfactant-rich phase became a highly viscous (without need of centrifugation and cooling) and settled down at the bottom of the tube making the aqueous phase easily discarded by simply inverting the tube. Later, the surfactant-rich phase in the tube was dissolved in minimum amount of ethanol and the absorbance of the resulting solution was measured at  $\lambda_{\text{max}}$  of 475 nm in a 1-cm cell against a reagent blank prepared in similar manner without analyte. The remaining quantity of Cr (VI) as  $\text{Cr}_2\text{O}_7^{2-}$  in surfactant-poor phase (i.e. aqueous phase) was determined spectrophotometrically at  $\lambda_{\text{max}}$  of 540 nm by using the diphenylcarbazide method<sup>(11)</sup> for the purpose of determining the distribution ratio (D) and extraction efficiency (%E).

e) Preparation of Samples

A duplicate sample (soils, plants and vegetables) solution was prepared by transferring approximately 5 g of dried sample into a 250 mL conical flask and adding 10 mL of  $\text{HNO}_3$ . The contents of the flask were heated on an electric hotplate until the volume was reduced to 2-3 mL. After cooling, a further of 10 mL of concentrated  $\text{HNO}_3$ , 5 mL of concentration  $\text{H}_2\text{SO}_4$  and 4mL  $\text{H}_2\text{O}_2$  were added and the content reheated to boiling until the volume became 2-3 mL, then 10 mL of water were added until colorless solution was obtained indicating of the oxidation of organic matter. The content was cooled and transferred into 100 mL volumetric flask and diluted to the mark with distilled water. An aliquot of 5 mL of sample solution was diluted into 25 mL conical flask and treated with 1 mL of 20% potassium sodium tartarate solution with continuous shaking and then filtered. The filtrate was transferred into 10 mL volumetric flask and diluted to the mark with water. The metal ions content was determined according to the recommended CPE procedure. The

blank solution was prepared in the similar manner without analyte.

f) Statistical analysis

All mathematical and statistical computations were made using Excel 2007 (Microsoft Office) and Minitab version 14 (Minitab Inc., State College, PA, USA).

### III. RESULTS AND DISCUSSION

a) Absorption Spectra

The absorption spectra of chromium as  $\text{Cr}_2\text{O}_7^{2-}$  oxyanions with organic reagent of 2-[benzene thiazolylazo]-4-benzenenaphthol (BTABN) in acidic medium was recorded in the presence of surfactant against a reagent blank prepared under the identical conditions according to general CPE procedure. Figure 3 shows the overlaid spectra of (a) BTABN reagent and (b) its complex with  $\text{Cr}_2\text{O}_7^{2-}$  oxyanion after CPE procedure. It has been evident that the oxyanion  $\text{Cr}_2\text{O}_7^{2-}$  can form an ion-association complex with BTABN reagent in acidic medium as  $[\text{HBTABN}]^+ [\text{HCr}_2\text{O}_7]^-$  due to the appearance of another distinct absorption maximum at  $\lambda_{\text{max}}$  of 475 nm with molar absorptivity ( $\epsilon$ ) of  $5.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  while the BTABN reagent alone gave the absorption maxima at  $\lambda_{\text{max}}$  of 452 nm as depicted in the spectra (a) and (b) of Figure 2

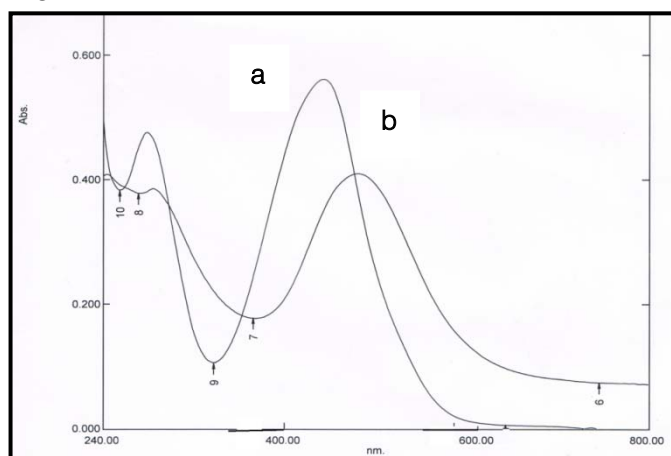


Figure 2 : Absorption spectra of (a)  $5 \times 10^{-4}$  M of (BTABN) 10 mL of  $20 \mu\text{g Cr}_2\text{O}_7^{2-}$ , 0.1 M HCl, ( $5 \times 10^{-4}$  M) (BTABN) reagent and 0.5mL (1 % Triton X-100)].

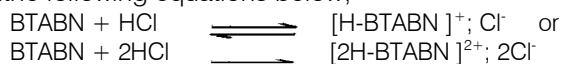
b) Optimization of CPE procedure

Several factors affect the CPE procedure for Cr (VI) extraction such as, HCl concentration, Triton X-100 amount, BTABN concentration, heating time and equilibrium temperature by using classical optimization was investigated.

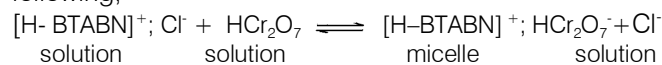
c) Effect of HCl

The separation of oxyanions such as  $\text{Cr}_2\text{O}_7^{2-}$  by CPE method involves the formation of ion-association complexes between  $\text{Cr}_2\text{O}_7^{2-}$  oxyanion and the

protonated BTABN reagent in the presence of HCl, to get sufficient hydrophobicity that can be extracted into micelle medium thus obtaining desired enrichment. It is known that the HCl in aqueous medium will contribute most probably in converting  $\text{Cr}_2\text{O}_7^{2-}$  ions into  $\text{HCr}_2\text{O}_7^-$  species and the reagent BTABN into ion pair complex  $(\text{H-BTABN})^+$ ;  $\text{Cl}^-$ . Consequently, the effect of HCl concentration was studied by measuring the absorbance of 10 mL solution containing 20  $\mu\text{g}$   $\text{Cr}_2\text{O}_7^{2-}$ ,  $1 \times 10^{-4}$  MBTABN and 0.5 mL of 1 % Triton X-100 and subjected to general CPE procedure. The results are depicted in the Figures 3. The results revealed that 0.1M of HCl was the optimum concentration giving highest percent extraction, indicating better thermodynamic equilibria can be reached and more stable ion pair complex extracted in micelles. Thus, the major effect of HCl was the formation of ion pair complexes as shown in the following equations below;



Thereafter, an exchange of small anions  $\text{Cl}^-$  with large anions of  $\text{Cr}_2\text{O}_7^{2-}$  may occur in micelles as the following;



or

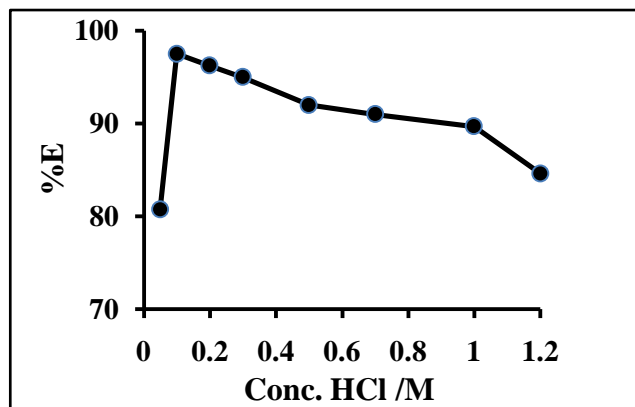
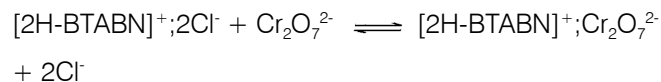


Figure 3 : Effect of HCl on extractability of Cr(VI)

Below 0.1M of HCl, it appeared that no favourable thermodynamic equilibria were reached leading to low extraction efficiency of complex. While at higher than 0.1M of HCl, there is a difficulty of exchange of  $\text{Cr}_2\text{O}_7^{2-}$  as well as the smaller anion  $\text{Cl}^-$  to large cation  $[\text{H-BTABN}]^+$  thereby led to increase their dissociation equilibrium. This behaviour led to decrease ion pair complex formation with  $\text{Cr}_2\text{O}_7^{2-}$  and obvious depress the extraction efficiency (%E) as shown in Figure 3.

#### d) Effect of BTABN concentration

The extraction according to CPE methodology depends on the major step of complexation between organic reagent and Cr (VI) as  $\text{Cr}_2\text{O}_7^{2-}$  which can be transferred to surfactant after formation cloud point phase. Therefore, the effect of BTABN concentration was carried out by taking 10 mL solution containing 20  $\mu\text{g}$  Cr (VI) as  $\text{Cr}_2\text{O}_7^{2-}$  or 0.1 M HCl, 0.5 mL of 0.1% Triton X100 plus various concentrations ( $1 \times 10^{-6}$ - $1 \times 10^{-3}$  M) of BTABN and subjected to the general CPE procedure. The results are shown in Figures 4.

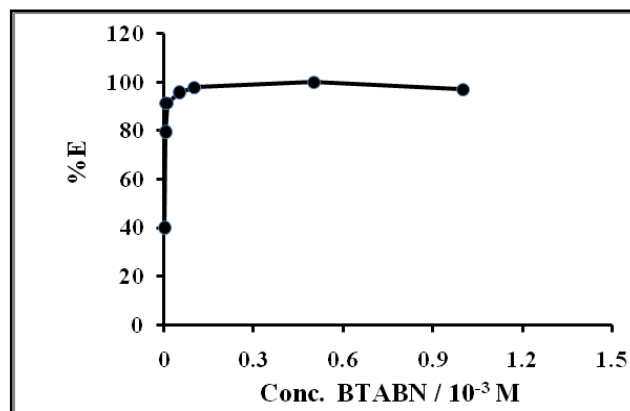


Figure 4 : Effect of BTABN concentration

It was appeared that the magnitude of the extraction efficiency increased sharply by increasing BTABN concentration and reached a plateau up to  $1 \times 10^{-4}$  M. Therefore, a concentration of  $5 \times 10^{-4}$  M was chosen as optimal. This may be gave thermodynamic equilibria favourable for the complexation because the rate of formation of ion pair complex for the extracted element Cr(VI) is probably much faster than back forward reaction at optimum concentration thereby a high extraction efficiency obtained. But at concentration of less than  $1 \times 10^{-4}$  M., the rate of back reaction was predominated leading to the dissociation of ion pair complex and decreased in extraction efficiency.

#### e) Effect of TX-100 Amount

It is known that the amount of surfactant used in CPE process for the separation for any analyte is a critical factor and its success depends on obtaining a maximum extraction efficiency and minimum phase volume ratio so that to increase the preconcentration factor <sup>(12)</sup>. The effect of Triton X-100 amount was conducted by taking 10 mL solution containing 20  $\mu\text{g}$   $\text{Cr}_2\text{O}_7^{2-}$ ,  $5 \times 10^{-4}$  M (BTABN), 0.1 M HCl varying volumes of 0.1-2.5 mL of 1% Triton X-100 and the solutions subjected to general CPE procedure The results are seen in Figure 5. It was shown that the maximal extraction efficiency was achieved for ion-association complex extracted when the volume of 1% (w/v) Triton X-100 was of 0.4 mL. Thereafter the %E was decreased because of the increment in the overall analyte volumes

and viscosity of surfactant-rich phase, or most probably due to incomplete dehydration of cloud point layer may be occur thereby the two phases cannot be formed leading to poor sensitivity and subsequently decreased in extraction efficiency. At volume less than 0.4 mL of 1% Triton X-100, on the other hand, a decrease in extraction efficiency of Cr (VI) has taken place due to insufficient extraction of ion pair complex formed. Accordingly, Triton X-100 concentration of 0.04% (i.e. 0.4 mL of 1% TX-100) was employed for the rest of this work.

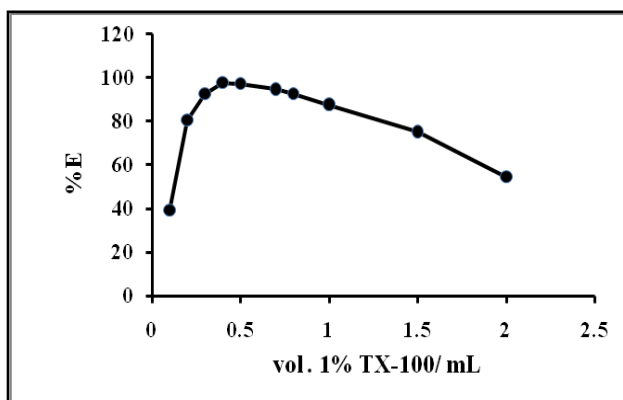


Figure 5 : Effect of Triton X-100 amount

f) Effect of Equilibrium Temperature and Incubation Time

The equilibration temperature and incubation (heating) time are very crucial and important parameters in CPE process for complete reaction to achieve easy phase separation and the preconcentration as efficient as possible. Therefore, the effect of temperature and time on the extraction of Cr (VI) was performed individually for solution containing 10 mL of 20  $\mu\text{g}$  of  $\text{Cr}_2\text{O}_7^{2-}$  by varying the temperature between 70-80  $^{\circ}\text{C}$  at 25 min and time between 5 and 40 min at 80  $^{\circ}\text{C}$ , keeping other variables at optimal. A preliminary experiment has indicated that at temperature below 70  $^{\circ}\text{C}$ , no concrete phase separation (i.e. two phases cannot be formed) was observed due to very low number of micelles leading to difficulty in distinguishing the two phases thereby the ion-pair association complex cannot be well separated. However, the results have shown that at temperature of 80  $^{\circ}\text{C}$  and time of 25 min gave a maximum extraction efficiency of 98.56%. But, at higher temperatures than 80  $^{\circ}\text{C}$  such problem has caused the instability of complex due to thermal decomposition of ion-association complex and as well as increase diffusion of micelles in aqueous solution which lead to increase in surfactant-rich phase volume resulting in decreasing the extraction efficiency.

g) Thermodynamic Study

It is useful to study the mechanism of phase separation by CPE which is still ambiguous and not yet intensively investigated. Therefore, in this study we were determined some thermodynamic data for  $[\text{H-}$

$\text{BTABN}]^+;\text{HCr}_2\text{O}_7^-$  system using Triton X-100 as a mediated extracting agent in order to understand a probable mechanism above the cloud point temperature (CPT). Depending on different operation temperatures and the distribution of target species between two phases via calculating the distribution ratios (D), the equilibrium extraction constants ( $K_{\text{ex}}$ ) can be calculated. Table 1 summarize the variation of equilibrium extraction constants with temperature during CPE of the above ion-association complex system.

Table 1 : Variation of equilibrium constant with temperature during CPE for the extraction Cr (VI) as  $\text{Cr}_2\text{O}_7^{2-}$  with (BTABN).

T $^{\circ}\text{C}$	70	75	78	80
T $^{\circ}\text{K}$	343	348	351	353
1/T	2.915	2.8735	2.849	2.8329
$K_{\text{ex}} \times 10^9$	1.9263	2.200	2.858	3.606

These thermodynamic equilibrium constants ( $K_{\text{ex}}$ ) is actually represents all equilibrium constants that affect the separation process such as aggregation micelles constant with increasing temperature, complex transference constant from aqueous phase to surfactant phase, association constant of the complex and distribution constant of the surface between aqueous phase and surfactant (micelles) phase. From the results in Table 1, a plot of logarithm values of  $K_{\text{ex}}$  versus inverse temperature in Kelvin gave a straight line and from its slope, the enthalpy of extraction ( $\Delta H_{\text{ex}}$ ) can be calculated for CPE method as shown in Figure 6. While the values of entropy ( $\Delta S_{\text{ex}}$ ) and Gibb free energy ( $\Delta G_{\text{ex}}$ ) of this extraction process are determined from following thermodynamic relationships [ $\Delta G_{\text{ex}} = -RT \ln K_{\text{ex}}$ ] and [ $\Delta G_{\text{ex}} = \Delta H_{\text{ex}} - T\Delta S_{\text{ex}}$ ] respectively. Once ( $\Delta H_{\text{ex}}$ ) and ( $\Delta G_{\text{ex}}$ ) are obtained, the  $\Delta S_{\text{ex}}$  is calculated from second relationship and the results are summarized in Table 2.

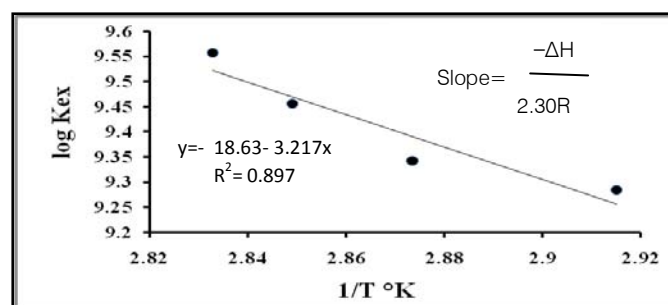


Figure 6 : Extraction constant  $K_{\text{ex}}$  as a function of equilibrium temperature for ion pair complex of  $\text{Cr}_2\text{O}_7^{2-}$  with (BTABN)



**Table 2 :** Thermodynamic parameters for the extraction of  $\text{Cr}_2\text{O}_7^{2-}$  ion-pair complex by CPE

$T^\circ$ (°K)	$\Delta H_{\text{ex}}$ (KJ mol <sup>-1</sup> )	$-\Delta G_{\text{ex}}$ (KJ mol <sup>-1</sup> )	$\Delta S_{\text{ex}}$ (J mol <sup>-1</sup> )
343	0.0544	60.9662	177.8151
348		62.2393	178.9186
351		63.5393	181.0932
353		64.5831	183.0192

It can be seen from Table 2, the enthalpy change ( $\Delta H_{\text{ex}}$ ) is quite low and equal to 0.0544 KJ mol<sup>-1</sup>, indicating that the endothermic reaction for the solubilisation process of ion pair ( $\text{H-BTABN}^+$ ;  $\text{HCr}_2\text{O}_7^-$ ) complex is controlled by positive value of  $\Delta H_{\text{ex}}$  which reflects a high efficiency of the extraction process of the complex that achieved thermodynamically into the surfactant-rich phase. This is explicates that a strong electrostatic association exists between Cr (VI) anion with cationic reagent beside the contribution of the complex itself in driving water molecules out of surfactant phase in which more of micelles are aggregated enabling the precise extraction of complex especially in extracting of trace amounts. Accordingly, the extraction of ion-pair complex is easy and thermodynamically favourable and due to the positive value of  $\Delta H_{\text{ex}}$ , the dehydration of micelles (i.e. decrease the value of  $\Delta H_{\text{solv}}$  and increase  $\Delta H_{\text{hyd}}$ ) is achieved resulting in increasing the phase-volume ratio thus extraction efficiency enhancement<sup>(13)</sup>.

$$\Delta H_{\text{ex.}} = \Delta H_{\text{solv.}} - \Delta H_{\text{hyd.}}$$

The variation of  $\Delta G_{\text{ex}}$  with temperature at optimum conditions of the extraction system (Table 2) was revealed that  $\Delta G_{\text{ex}}$  increase with temperature and found to be negative, showing the extraction process is a spontaneous phenomenon because the complex transference and surfactant phase formation are synchronized processes occurs at the same time. Thus the more negative value of  $\Delta G_{\text{ex}}$ , the large spontaneous process is. Accordingly, the spontaneity of ion pair complex extraction is governed by the negative value of  $\Delta G_{\text{ex}}$ <sup>(14)</sup>. The entropy ( $\Delta S_{\text{ex}}$ ), on the other hand, was increased with increasing temperature and be positive values which shows a good affinity of ion-pair complex towards surfactant micelles and proves that the solubilisation of ion-association complex molecules are organized in more random fashion during extraction process (i.e. entropic in region).

#### h) Selection of Diluents

Since the surfactant-rich phase obtained after the cloud point preconcentration is a highly viscous layer containing analyte to be determined, it generally needs a little amount of solvent for transferring the solution into detection system. The effect of various organic solvents such as amyl alcohol, methanol, chloroform, acetone and ethanol, on the absorption

behaviour of complex in the presence of surfactant was investigated. The results are summarized in Table 3.

**Table 3 :** Effect of organic solvent on absorbance

solvent	$\lambda_{\text{max}}$	Absorbance	Molar absorptivity (L mol <sup>-1</sup> cm <sup>-1</sup> )
Amyl alcohol	443	1.037	$2.69 \times 10^4$
Methanol	433	1.002	$2.60 \times 10^4$
Chloroform	colloid	-	-
Acetone	445	0.140	$3.636 \times 10^3$
Ethanol	475	0.855	$2.221 \times 10^4$

It can be seen that all solvents gave a good solubility of complex in micelles phase, except chloroform which form a colloidal solution that is inconvenient for measuring the solution in the detection system used thus it can be ruled out, while the acetone gave poor sensitivity. Therefore, we chose ethanol as a diluent for many reasons because (1) it gave adequate sensitivity (i.e. good molar absorptivity), (2) non toxic and (3) better for reducing the viscosity and facilitating the sample transference into a quartz cell.

#### i) Selection of surfactant type

In CPE, the type of surfactant plays a significant role in the separation and extraction process. Therefore, the experiments were conducted according to general CPE procedure via using different non-ionic surfactants such as, Tween-80 and Tween-20, Triton x-114 and one anionic surfactant like sodium dodecyl sulphate (SDS). Table 4 shows the behaviour of each surfactant on the extractability of ( $\text{H-BTABN}^+$ ;  $\text{HCr}_2\text{O}_7^-$ ) ion-pair complex. The results have been revealed that both Triton X-100 and Triton X-114 gave much better extraction efficiency than the rest surfactants. While the surfactants such as, Tween-20, Tween-80 have shown that the formation of the separated surfactant-rich phase needs very high cloud point temperature which might be led to dissociation of ion pair complex and hence a poor extraction efficiency obtained as shown in Table 4. SDS, on the other hand, as anionic surfactant which contain sulphate ion in its structure seems indeed incompatible for solubilisation of hydrophobic ion-pair complex under study. Accordingly, Triton X-100 was chosen throughout this study despite Triton X-114 has too lower cloud temperature and gave easy phase separation than Triton X-100, but relatively less extraction efficiency obtained because of low solubility of Triton X114 in aqueous phase<sup>(15)</sup>.

**Table 4 :** Effect of surfactant type on CPE for the extraction  $\text{Cr}_2\text{O}_7^{2-}$  with BTABN.

Surfactant	Tw-20	Tw-80	SDS	TX-114	TX-100
$\lambda_{\text{max}}$	473	475	472	472	475
Abs,	0.221	0.181	0.230	0.445	0.855
D	2.33	0.67	1.22	55.40	68.50
%E	69.96	39.97	54.99	98.22	98.56

*j) Interference effect*

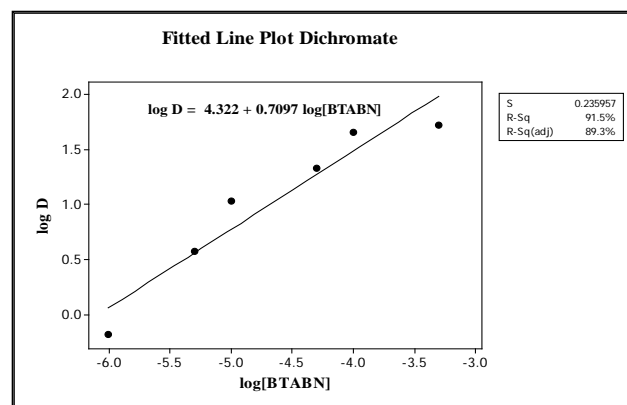
The effect of some diverse ions that may be expected being in environmental samples on the determination of Cr (VI) was studied following the general CPE procedure. It is agreed that an extraneous ion deemed to interfere seriously when it gives a relative error percent more than  $\pm 10\%$ . The selectivity of CPE for Cr(VI) ion as  $\text{Cr}_2\text{O}_7^{2-}$  was conducted by studying the effect of some salts containing, for example, both cations ( $\text{Na}^+$  and  $\text{K}^+$ ) and metal anions ( $\text{I}^-$ ,  $\text{WO}_4^{2-}$  and  $\text{Mo}_7\text{O}_{24}^{4-}$ ) in addition to picrate,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{NO}_3^-$  ions on the extraction efficiency of  $\text{Cr}_2\text{O}_7^{2-}$  by CPE at the concentration of Interferent/ Cr(VI) ratio of 13 fold. The results are presented in Table 5. It can be seen that most of interferences have no appreciable effect on the Cr(VI) extractability expect  $\text{I}^-$  and  $\text{MoO}_4^{2-}$  ions which have exceeded the allowable limits of interferences for Cr(VI). Therefore, these anions should be removed first, if present, by using suitable masking agents before determination of Cr (VI) in any samples.

**Table 5 :** Interferences effect of some salts on extractability of  $\text{Cr}_2\text{O}_7^{2-}$  with BTABN (percent extraction = 98.56%).

Interferent	Percent extraction (%E) found	%E <sub>rel</sub>
KClO <sub>4</sub>	92.21	-6.4
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	96.68	-1.9
Picric acid	92.63	-6.0
NaI	83.09	-15.6
(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub>	74.83	-24.0
Na <sub>2</sub> WO <sub>4</sub>	97.48	-1.1
Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	95.28	-3.4

*k) Stiochiometry of the Extracted Complex*

It is reported that the analysis of the dependence  $\log D = f(\log C_{\text{REAGENT}})$  permits the determination of the stiochiometry in the extracted complex<sup>(16)</sup>. Consequently, the slope in the Figure 7 for  $\log D = f(\log C_{\text{BTABN}})$  coordinates is nearly equal to less than one (i.e. 0.71), indicating the ion pair complex with ratio 1:1 is extracted into the surfactant-rich phase. Thus the most probable composition of the complex extracted in the forms of  $[\text{H-BTABN}]^+; \text{HCrO}_4^-$ .



**Figure 7 :**  $\log D = f(\log C_{\text{BTABN}})$

*l) Analytical Figures of Merit*

Under the optimized conditions established by CPE procedure, a series of standard Cr (VI) solutions ranging from 0.1-2.0  $\mu\text{g mL}^{-1}$  were taken and subjected to the general CPE and the Cr (VI) was determined spectrophotometry at  $\lambda_{\text{max}}$  of 475 nm in order to test the linearity of the method. The analytical figures of merit are presented in Table 6. The statistical evaluation of calibration curve has shown that a strong correlation between absorbance and Cr (VI) concentration may exist ( $R^2=100\%$ ). The analysis of variance (ANOVA), On the other hand, also proved the linear regression equations  $[y = (0.428 \pm 0.003534) x - (0.0016 \pm 0.00389)]$  was statistically valid. This because of the ratio ( $MS_{\text{reg}}/MS_{\text{error}}$ ) for 1 and 6 degree of freedom (DOF), larger than critical values ( $F_{16} = 5.987$  at 95% CI), indicating that the prediction based on the regression is satisfactory (Table 7).

The limit of detection ( $\text{LOD} = 0.017 \mu\text{g mL}^{-1}$ ) and limit of quantitation ( $\text{LOQ} = 0.0568 \mu\text{g mL}^{-1}$ ) obtained for Cr (VI) with the prepared ligand (BTABN) by developed CPE-Spectrophotometry were based on the standard deviation of the response and the slope of the calibration curve using the following equations;  $\text{LOD} = 3 \sigma_B/s$ ;  $\text{LOQ} = 10 \sigma_B/s$ , where ( $\sigma_B$ ) is the standard deviation of the calibration line and ( $s$ ) its slope.

Concerning the detection limit, our findings was generally in harmony with that obtained by Madhuchandr et al<sup>(17)</sup> and Suvardhan et al<sup>(18)</sup> who used the combined CPE-ETAAS and FAAS, respectively. But, it was worse than that obtained by Li et al<sup>(19)</sup> and Shemirani et al<sup>(20)</sup> who employed the sophisticated instrumentation such as EV-ICP OES and FAAS combined with CPE respectively. However, by considering 5 g of the analyzed sample in 100 mL and  $17 \mu\text{g L}^{-1}$ , the detection limit was of  $0.34 \mu\text{g g}^{-1}$ , thus the adopted method was applied for the determination of Cr (VI) in various environmental samples in order to test its applicability and reliability.

**Table 6 :** Figures of merit for the determination of  $\text{Cr}_2\text{O}_7^{2-}$  by the proposed method

Parameter	value
$\lambda_{\text{max}}$ (nm)	475
Regression equation	$y = 0.428x - 0.0016$
Correlation coefficient(r)	0.9999
Coefficient of determination ( $R^2$ )	100%
C.L. for the slope ( $b \pm \text{tsb}$ ) at 95%	$0.428 \pm 0.003534$
C.L. for the intercept ( $a \pm \text{tsa}$ ) at 95%	$-0.0016 \pm 0.00389$
Concentration range ( $\mu\text{g mL}^{-1}$ )	
Limit of Detection ( $\mu\text{g mL}^{-1}$ )	0.1-2.0
Limit of Quantitation ( $\mu\text{g mL}^{-1}$ )	0.0170
Sandell's sensitivity ( $\mu\text{g cm}^{-2}/0.001\text{A.U}$ )	$1.16 \times 10^{-7}$
Molar absorptivity ( $\text{L.mol}^{-1}.\text{cm}^{-1}$ )	$4.47 \times 10^4$
Composition of complex (M: L)*	1:1
RSD% (n=7) at $2 \mu\text{g mL}^{-1}$	0.31
Preconcentration factor**	250
Enrichment factor***	270

\*obtained by slope analysis method \*\* calculated as the ratio of the original sample volume to that of extracted volume \*\*\*Calculated as the ratio of slope of calibration curve obtained by CPE to that obtained without preconcentration

**Table 7 :** Analysis of Variance of regression line of Cr (VI)

Source	DOF	SS	MS	F	P
Regression	1	0.5195	0.51954	87824	0.00
Error	6	0.00004	0.00001		
Total	7	0.51958			

DOF=degrees of freedom, SS: sum of squares, MS: mean of squares, F (Fisher F-test). P: probability at 0.05

#### m) Determination of Cr (VI) in Real Samples

The developed method was applied for the Cr (VI) detection in various environmental and botanical samples and the results were statistically compared with standard flame atomic absorption spectrometry (FAAS) that had done in our laboratory under the conditions outlined by company's manual. The method involved the determination of Cr(VI) in two types of soils collected near the roadside streets, most of near of the rivers (agriculture street), water collected from different point of Al-Forat river and water purification projects, plant and vegetables from local market used for human consumption, and wastewater from Leather Tanning Company in Al-Zuafraina/ Baghdad. The results are presented from Table 8 to Table 12. All statistical results performed by the paired t- test<sup>(21)</sup> for comparison of means between the proposed and standard FAAS methods for all samples (Tables 8 to 12) have shown that all p values [P(T<t) two tailed] based on the 5% critical values (t -two tailed) were more than the |t|

calculated values indicating acceptance of null hypothesis ( $H_0$ ) which specified that there appears insufficient evidence to suggest the accuracy of the established CPE- Spectrophotometry differs with that of standard AAS method(i.e. there is a good agreement between the results obtained by the two methods).

From the environmental point of view, the means and concentration range of Cr(VI) were entirely different depending on the site of collection in both non agriculture and agriculture soils and found to be of 5.18(4.88-7.20) and 1.57(0.72-3.44) as  $\mu\text{g g}^{-1}$  respectively. This indicated that the extent of chromium pollution of soil in some places selected in the Al-Najaf city was slightly high, but appears naturally more significant than in non-agriculture soil due to its location in the vicinity to the roadsides which might be contaminated by congestion of the traffic. In fact, there is no guideline level for Cr (VI) in agricultural soils approved by Iraqi body. However, the international and/or national guidelines regarding Cr (VI) in soil are not firmly established so far and varied from country to the other; for example, the quality guideline for Cr (VI) in Canadian soils is of  $0.4 \mu\text{g g}^{-1}$ <sup>(22)</sup> while the permissible limit for Cr in Dutch standards is  $100 \mu\text{g g}^{-1}$ <sup>(23)</sup>. In Poland, it is accepted that the natural content of chromium in the surface layer (0-15 cm depth) of sandy soil is  $2.0-30.0 \mu\text{g g}^{-1}$  and in dusty and loamy soil is of  $14.8 - 81.0 \mu\text{g g}^{-1}$ <sup>(24)</sup>. In conclusion, the concentrations of Cr (VI) were found to be low in agriculture soil of Al-Najaf city, which is below the plant toxicity threshold value of  $5 \mu\text{g g}^{-1}$ <sup>(25)</sup>.

The Cr (VI) levels in water (river and water projects) samples of the Al-Najaf city were also determined by the proposed method. The results have revealed that the average concentration of Cr (VI) in water sample was of  $1.01 \mu\text{g g}^{-1}$  with concentration range of 0.24 to  $2.72 \mu\text{g g}^{-1}$ . Unfortunately, most limits, guidelines and criteria for water are based on total chromium levels. Thus the standards based on total chromium do not recognize the significant differences between the health and environmental impacts of Cr (VI). However, the dissolved Cr(VI) content in freshwater and marine water according to UK environmental quality standard are of 0.0043 and  $0.0006 \mu\text{g g}^{-1}$  respectively, indicating that all water samples analyzed were mostly above the maximum permitted concentration for protection of aquatic life and drinking<sup>(26)</sup>.

The results have shown, on the other hand, that the concentration of Cr(VI) in some plant and vegetables with mean value of  $1.283 \mu\text{g g}^{-1}$  and ranged from 0.40 to  $2.65 \mu\text{g g}^{-1}$ . The results in Table 12 shows the Cr (VI) content in different sites of the General Company of Leather (Tanning site) in Al-Zuafrania / Baghdad, before, after removal of chromium by chemical process and in leather piece too. It can be seen that the content of Cr (VI) after chemical treatment of wastewater ( $0.8 \pm 0.055 \mu\text{g g}^{-1}$ ) in Tanning site of the

company is still high in accordance to the Agency for Toxic Substances and Diseases Registry (ATSDR) which classified Cr (VI) as the top eighteenth hazardous substance and assessed that the Minimal National Standards (MINAS) upper limit of Chromium in industrial wastewater is  $100 \mu\text{g L}^{-1}$  (27).

**Table 8 :** Cr (VI) content ( $\mu\text{g g}^{-1}$ ) in the non-agriculture soil samples with statistical paired t-test at 95% confidence level

Sample	Proposed method	AAS method	Paired t test
1	5.69±0.168	5.09±0.364	$\bar{X}_d = 0.0160$ $S_d = 0.035777$ $t_{\text{cal}(n=5)} = 1.0$ $t_{\text{crit. at 95\%}} = 2.78$ P-value=0.374
2	5.84±0.161	4.98±0.136	
3	7.20±0.451	6.90±0.368	
4	4.88±0.205	5.33±0.311	
5	5.44±0.417	5.21±0.224	

1) Al-Muthana street near street; 2) Al-Ashreen street; 3) Al-Mufeed street; 4) Al-Rawan street; 5) Al-Muthana street far-off street.

**Table 9 :** Cr (VI) content ( $\mu\text{g g}^{-1}$ ) in the agriculture soil samples with statistical paired t-test at 95% confidence level

Sample	Proposed method	AAS method	Paired t -test
1	2.24±0.209	2.10±0.523	$\bar{X}_d = 0.115714$ $S_d = 0.144897$ $t_{\text{cal}(n=8)} = 2.11$ $t_{\text{crit. at 95\%}} = 2.36$ P-value=0.079
2	1.00±0.903	0.97±0.341	
3	0.80±0.168	0.77±0.624	
4	1.20±0.569	1.10±0.335	
5	BDL*	BDL*	
6	1.60±0.611	1.55±0.258	
7	0.72±0.187	0.69±0.038	
8	3.44±0.420	3.01±0.492	

\*BDL = below detectable limit; 1) Near Kufa river; 2) Al-Huria; 3) Al-shamia; 4) Shamia; 5) Abarat; 6) Abasia; 7) Heara; 8) Al-Mashkab.

**Table 10 :** Cr (VI) content ( $\mu\text{g g}^{-1}$ ) in water samples with statistical paired t-test at 95% confidence level

Sample	Proposed method	AAS method	Paired t -test
1	0.73±0.581	0.65±0.444	$\bar{X}_d = 0.236000$ $S_d = 0.455006$ $t_{\text{cal}(n=5)} = 1.19$ $t_{\text{crit. at 95\%}} = 2.78$ P=0.301
2	0.56±0.127	0.52±0.627	
3	0.80±0.519	0.81±0.253	
4	2.72±0.492	1.69±0.085	
5	0.24±0.620	0.20±0.710	
6	BDL*	BDL*	
7	BDL*	BDL*	

\*BDL = below detectable limit; 1) Old kufa bridge; 2) River(water project); 3) Al- Abasia river; 4) Kary saad; 5) Meesan; 6) Alamam Ali bridge; 7) New project water.

**Table 11 :** Cr (VI) content ( $\mu\text{g g}^{-1}$ ) in plants and vegetable samples with statistical paired t-test at 95% confidence level.

Sample	Proposed method	AAS method	Paired t -test
1	BDL	BDL	$\bar{X}_d = 0.323333$ $S_d = 0.456216$ $t_{\text{cal}(n=3)} = 1.23$ $t_{\text{crit. at 95\%}} = 4.30$ P-value=0.344
2	2.65±0.400	1.8±0.059	
3	BDL	BDL	
4	BDL	BDL	
5	BDL	BDL	
6	0.40±0.625	0.35±0.026	
7	0.80±0.183	0.73±0.53	
8	BDL	BDL	

\*BDL = below detectable limit; 1) Solanum melongena; 2) Potato; 3) Tomato; 4) Aplum gravealens; 5) Iraqi dates; 6) Cucumbers; 7) Capsicum sp; 8) Vicitoria regia.

**Table 12 :** Cr (VI) ( $\mu\text{g g}^{-1}$ ) content in wastewater of leather tanning plant and saffron Sheep leather and statistical paired t-test at 95% confidence level

Sample	Proposed method	AAS method	Paired t -test
1	7600±0.6	7598.5±0.82	$\bar{X}_d = 0.992500$ $S_d = 0.710557$ $t_{\text{cal}(n=4)} = 2.79$ $t_{\text{crit. at 95\%}} = 3.18$ P-value=0.068
2	3360±0.2	3358.4±0.17	
3	500.0±0.3	499.2±0.26	
4	0.8±0.05	0.730±0.17	

1) Before chemical treatment; 2) Tanned leather piece; 3) Outside after saturated leather ; 4) After chemical treatment.

#### IV. CONCLUSIONS

In this work, a new essay for the extraction and detection of Cr (VI) as  $\text{Cr}_2\text{O}_7^{2-}$  was examined using a new synthesised organic reagent, for the first time, in an attempt to extent the analytical capability of CPE technique in conjugation with spectrophotometry for inorganic anions analysis. The results we have attained are promised that enough to continue ahead to carry out further works that concerning the development more sensitive methods in this field. Though there has been a marked improvement in most analytical figures of merits, the thermodynamic study is still needs much work to investigate the effect of other parameters such as the variation of surfactant amount added and the concentration of the reacting species abreast with temperature for the formation an ion-association complex to fully understand the mechanism of solubilisation of this type of molecules in micelles. However, it should be borne in mind that the implementation of inorganic anion analysis by CPE is not as straightforward as anticipated as with metal ions

in the form of chelates due to the limitations such as interfering species, surfactant type and electrolytic salts which can expect be solved in future works. These limitations have been alleviated to some extent by careful optimization of the chemical variables in this study. However, the proposed procedure permits to increase the popularity of UV-Vis spectrophotometric technique after CPE beside the solvent-free extraction for metal anions from complex matrices which proved to be fairly simple, sensitive, precise and accurate thereby it might be considered as an alternative for atomic spectrometric techniques.

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## Kinetic Approach to the Reduction of Toluidine Blue by Dithionate Ion in Aqueous Acidic Medium

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**Keywords:** kinetics, reduction, toluidine blue dye, dithionate.

**GJSFR-B Classification :** FOR Code: 250000



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# Kinetic Approach to the Reduction of Toluidine Blue by Dithionate Ion in Aqueous Acidic Medium

Babatunde O.A <sup>α</sup> & Ajayi J.O <sup>σ</sup>

**Abstract-** The kinetics of redox reduction of Toluidine blue (hereafter referred to as TB<sup>+</sup>) by dithionate ion have been studied in acidic medium under pseudo-first order condition of excess [S<sub>2</sub>O<sub>6</sub><sup>2-</sup>] at 31 ± 1°C, [H<sup>+</sup>] = 1 × 10<sup>-2</sup> mol dm<sup>-3</sup>, ionic strength (I) = 0.5 mol dm<sup>-3</sup> (NaCl) and λ max 600 nm. The redox reaction displays a 1:1 stoichiometry and the reaction was found to be first order and 3/2 order in the oxidant and the reductant respectively. The reaction is also catalyzed by hydrogen ion with the empirical rate law as:

$$-d[\text{TB}^+] = (a + b [\text{H}^+])[\text{TB}^+][\text{S}_2\text{O}_6^{2-}]^{3/2}$$

dt

Where a = 0.52 × 10<sup>-1</sup> dm<sup>3</sup> mol<sup>-1</sup>s<sup>-1</sup>, b = 7.2 dm<sup>6</sup> mol<sup>-2</sup>s<sup>-1</sup>

The rate of reaction decreases with increase in ionic strength while it increases with increase in dielectric constant of the reaction mixture. Added anions and cations catalyzed the reaction. The result of kinetic studies, spectroscopic investigations and Michealis-Mentens plot did not suggest the formation of intermediate complex. Outer - sphere mechanism is therefore postulated for this reaction.

**Keywords:** kinetics, reduction, toluidine blue dye, dithionate.

## I. INTRODUCTION

Toluidine blue dye (3-amino-7-(dimethylamino)-2-methyl phenothiazine chloride) is a coloured dye which is a phenothiazine that is mainly used as biological stains most especially in medical laboratory [1]. It has many uses, among the uses of this dye are: to detect oral cancer or pre-cancer, confirm the cells in rape victims [2, 3, 4, 5], as breast localization marker [6]. It also has antimicrobial property [7, 8]. Recently toluidine blue is used to study pneumocystis carinii pneumonia (pcp), a frequent and potentially life – threatening complication of the acquired immune deficiency syndrome (AIDS) [9,10]. It is also useful in chemistry as a redox indicator for many redox reactions such as Nitrite ion, Dithionite ion [11, 12] and Bromate ion [13] which has earlier been reported. As a dye, it is also very useful in the textile industry [14].

Dithionate is an important ion in inorganic chemistry [15, 16]. Strong oxidants oxidize dithionate to sulphate and strong reducing agents reduce them to sulphite and dithionite [17, 18].

In this paper, we report on the kinetics of reduction of TB<sup>+</sup> and dithionate ion with the aim of providing relevant data to help gain a deep insight into the nature and reaction of both reactants so as to enhance the applicability of this dye in biological sciences, medicine, and industry.

## II. EXPERIMENTAL

### a) Materials

Stock solutions of TB<sup>+</sup> were prepared by dissolving known quantities in distilled water and the observed λ max = 600nm which agrees with literature value. Sodium dithionate (BDH), sodium chloride (BDH) and other reagents were used as supplied.

### b) Stoichiometric studies

The stoichiometry of the reaction was determined by spectrophotometric titration using the mole ratio method [19] and keeping the concentration of the dye constant at 1 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1 × 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.5 mol dm<sup>-3</sup>, λ max = 600nm, T = 31 ± 1°C and varying the concentration of S<sub>2</sub>O<sub>6</sub><sup>2-</sup> from (1 – 6) × 10<sup>-3</sup> mol dm<sup>-3</sup>. The absorbance of the reacting mixture was obtained after the reaction had gone to completion by the steady readings recorded after 24 hours. The stoichiometry was then evaluated from the plot of absorbance against different concentrations of S<sub>2</sub>O<sub>6</sub><sup>2-</sup>.

### c) Kinetic Measurements

The kinetics of the reaction was monitored under various conditions by following decrease in the absorbance of TB<sup>+</sup> at λ max = 600 nm on a colorimeter 252. All measurements were made under pseudo - first order conditions with [S<sub>2</sub>O<sub>6</sub><sup>2-</sup>] in large excess over [TB<sup>+</sup>]. The pseudo-first order plots of log(A<sub>t</sub> / A<sub>∞</sub>) versus time were made, where A<sub>t</sub> and A<sub>∞</sub> are the absorbance at time (t) and at the end of the reaction respectively. From the slope of the plots, the pseudo-first order rate constants (k<sub>o</sub>) were determined and second order rate constant

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( $k_2$ ) were obtained from  $k_0$  as  $k_0 / [S_2O_6^{2-}]$ . The results were presented in table 1.

d) *Effect of  $[H^+]$*

The effect of  $[H^+]$  on the rate of reaction was studied within the range of  $(0.5 - 3.0) \times 10^{-2} \text{ mol dm}^{-3}$  while  $[TB^+]$  and  $[S_2O_6^{2-}]$  were kept constant at  $T = 31 \pm 1^\circ\text{C}$ ,  $\lambda_{\text{max}} = 600 \text{ nm}$  and  $I = 0.5 \text{ mol dm}^{-3}$  (NaCl). The results are presented in Table 1.

e) *Effect of ionic strength*

The effect of ionic strength on the rate of reaction was investigated in the range of  $(0.5 - 2.4) \text{ mol dm}^{-3}$  (NaCl) while the concentration of other reactants were kept constant at  $31 \pm 1^\circ\text{C}$ . The result are presented in table 1.

f) *Effect of Dielectric Constant*

The effect of medium dielectric constant, D, on the rate of reaction was investigated by adding  $0.1 - 0.6 \text{ cm}^3$  (accounting for 2 - 12%) of 10% mixture of water and acetone to the mixture, while keeping all other parameters constant.

g) *Test for added ion*

The effect of added cation and anion were investigated for  $X = (0.5 - 2.0) \times 10^{-3} \text{ mol dm}^{-3}$  where  $X = \text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  while the concentration of other reagents were kept constant.

h) *Test for intermediate complex formation*

The spectrophotometric test was carried out by comparing the electronic spectra of the reaction mixture and that of  $TB^+$  alone within 400 - 700 nm. Michealis - Mentens plot of  $1/k_0$  versus  $1/[S_2O_6^{2-}]$  was made Fig. 3.

i) *Test for free Radical*

The detection of free radicals in the reaction mixture was by Acrylamide polymerization studies.

j) *Product Analysis*

This was carried out by reacting equimolar amount of the dye and dithionate at  $31 \pm 1^\circ\text{C}$ ,  $[H^+] = 1 \times 10^{-2} \text{ mol dm}^{-3}$  and  $I = 0.5 \text{ mol dm}^{-3}$ . After the completion of the reaction a colorless solution was obtained. This indicates the destruction of the quinoid (chromophore) group.  $\text{BaCl}_2$  solution and HCl was then used to test for the inorganic product of the reaction.

### III. RESULTS AND DISCUSSION

a) *Stoichiometry*

A stoichiometric study showed that one mole of the dye was consumed by one mole of the dithionate ion given the equation of reaction shown below:  
 $TB^+ + S_2O_6^{2-} \rightarrow \text{Products} \dots 1$

The stoichiometry agrees with the consumption ratio obtained for dithionate and Triaminotolydiphenyl

The stoichiometry agrees with the consumption ratio obtained for dithionate and Triaminotolydiphenyl methane chloride [20].

b) *Kinetics*

The pseudo-first order plot of  $\log(A_t - A_\infty)$  versus time for the reaction were linear to greater than 80% of the reaction indicating that the reaction is first order with respect to  $[TB^+]$ . A plot of  $\log k_0$  (pseudo - first order rate constant) versus  $\log [S_2O_6^{2-}]$  were linear with a slope of 1.5 showing that the reaction is 3/2 order with respect to  $[S_2O_6^{2-}]$  ( Fig.1 ). The second order rate constants  $k_2$  were calculated as  $k_0 / [S_2O_6^{2-}]$  and the reading were found to be fairly constant, the results are presented in Table 1. Thus the overall order of the reaction is 5/2 at constant  $[H^+]$  and the rate equation for the reaction is:

$$- \frac{d[TB^+]}{dt} = k_2 [TB^+] [S_2O_6^{2-}]^{3/2} \dots 2$$

where  $k_2 = 1.19 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Similar fractional order has been reported for redox reaction of  $TB^+$  with dithionite ion, stannous ion and phenylhydrazine (pz) [12, 21, 23] respectively.

c) *Effect of  $[H^+]$*

The value of the reaction rate constant of the reaction increases with increasing  $[H^+]$  (Table 1). The plot of  $k_2$  versus  $[H^+]$  was linear with an intercept on  $k_2$  axis. The acid dependence rate constant is therefore given as:

$$k_2 = (a + b [H^+]) \dots 3$$

Based on the above observations, the rate equation for the reaction can then be written as:

$$- \frac{d[TB^+]}{dt} = (a + b [H^+]) [TB^+] [S_2O_6^{2-}]^{3/2} \dots 4$$

Where  $a = 0.52 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $b = 7.2 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

From equation 4 it is evident that the reaction proceeds through two pathways i.e acid dependent and acid independent reaction pathways. Similar trend has been reported in the reaction of  $TB^+$  with ascorbic acid by [24].

The positive  $[H^+]$  dependence on the rate of oxidation of dithionate has been explained in terms of its protonation to form  $\text{HS}_2\text{O}_6$  which subsequently reacts with the substrate in a slow step to give the product [25].

d) *Effect of ionic strength*

The rate of reduction of  $TB^+$  by  $S_2O_6^{2-}$  decreases with increasing ionic strength ( Table 1 ), this suggest that activated complex is formed from two ions of unlike charges. A plot of  $k_2$  versus  $\sqrt{I}$  gave a slope of 0.07 (Fig.3). This suggests that some other interactions

must be taking place to account for this non-integral value of the slope for the product species at the transition state.

e) *Effect of Dielectric Constant*

The rate of the reaction increases with increase in dielectric constant Table 2. This suggests that both positively and negatively charged species are participating in the rate determining step.

f) *Effect of added species*

Addition of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $NO_3^-$  and  $SO_4^{2-}$  ions to the reaction mixture catalyzes the rate of reaction Table 3. The enhancing effects suggest that there is interference of these ions in the transition state, which shows that an outer-sphere mechanism might be in operation [26, 27].

g) *Free radical test*

Acrylamide, a radical scavenger was added to the partially reacted mixture in the presence of excess of methanol, there was no formation of gelatinous precipitate - an indicator of the absence of free radical in the reaction.

h) *Test for intermediate complex*

Spectroscopic results indicate no significant shift from the absorption maxima of 600nm which is characteristic of Toluidine blue dye. This suggests that the formation of an intermediate complex during the reaction is very unlikely [28].

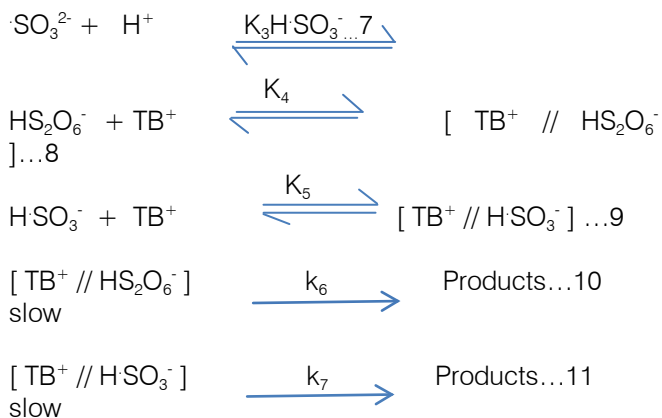
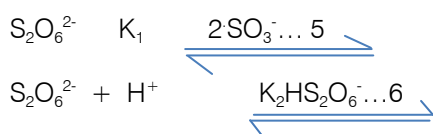
Michealis-Menten's plots of  $1/k_o$  versus  $1/[S_2O_6^{2-}]$  gave a straight line which passes through the origin fig. 4. This further suggests the absence of formation of intermediate complex thereby supporting the outer-sphere mechanism for this reaction Babatunde [19].

#### IV. PRODUCT ANALYSIS

After the completion of the reaction, a colourless solution was obtained. The UV visible spectra of the product showed no absorption peak at  $\lambda_{max}$  of 600 nm. This indicates the destruction of the quinoid (chromophore) group. In addition  $BaCl_2$  solution was added to the complete reaction mixture of  $TB^+ / S_2O_6^{2-}$  followed by dilute HCl; a white precipitate was obtained which was insoluble in excess dilute HCl indicating the presence of  $SO_4^{2-}$  ions.

a) *Reaction mechanism*

The mechanism proposed below accommodates all the experimental findings for the reaction of Toluidine blue dye with dithionite ion.



Equations 10 and 11 are the rate determining steps.

$$\text{Rate} = k_6 [TB^+ // HS_2O_6^-] + k_7 [TB^+ // HSO_3^-] \dots 12$$

From equation 8

$$[TB^+ // HS_2O_6^-] = K_4 [HS_2O_6^-] [TB^+] \dots 13$$

And from equation 6

$$[HS_2O_6^{2-}] = K_2 [S_2O_6^{2-}] [H^+] \dots 14$$

From equation 9

$$[TB^+ // HSO_3^-] = K_5 [HSO_3^-] [TB^+] \dots 15$$

From equation 7

$$[HSO_3^-] = K_3 [SO_3^{2-}] [H^+] \dots 16$$

From equation 5

$$[SO_3^{2-}] = K_1^{1/2} [S_2O_6^{2-}]^{1/2} \dots 17$$

$$\text{Rate} = K_2 K_4 k_6 [S_2O_6^{2-}] [TB^+] [H^+] + K_1^{1/2} K_3 K_5 k_7 [S_2O_6^{2-}] [TB^+] [H^+] \dots 18$$

Rearrange equation

$$(K_2 K_4 k_6 + K_1^{1/2} K_3 K_5 k_7) [H^+] [TB^+] [S_2O_6^{2-}]^{3/2} \dots 19$$

$$(a + b [H^+])^2 [TB^+] [S_2O_6^{2-}]^{3/2}$$

$$\text{Where } a = 0.52 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}, b = 7.2 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

#### V. CONCLUSION

Redox reaction of toluidine blue dye with Dithionite ion showed a stoichiometry of 1:1 and the reaction involve two independent pathways, one directly dependent on  $[H^+]$  and the other indirectly independent on  $[H^+]$ .

The evidence for the formation of intermediate complex was neither detected nor identified by the spectroscopic method suggesting an outer-sphere mechanism [28].

*Table 1*: Pseudo-first order and second order rate constants for the reduction of TB<sup>+</sup> by dithionate ions in aqueous acidic medium at [TB<sup>+</sup>] = 1 × 10<sup>-3</sup> mol dm<sup>-3</sup>, λ max = 600 nm, T = 31 ± 1°C.

[S <sub>2</sub> O <sub>6</sub> <sup>2-</sup> ] × 10 <sup>-3</sup> × 10 <sup>-2</sup> mol dm <sup>-3</sup>	[H <sup>+</sup> ] mol dm <sup>-3</sup> mol dm <sup>-3</sup>	I(NaCl) × 10 <sup>-3</sup>	k <sub>0</sub> k <sub>2</sub> × 10 <sup>-1</sup>	s <sup>-1</sup> dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
20	1.0	0.5	2.0	1.00
30	1.0	0.5	3.7	1.26
40	1.0	0.5	4.40	1.11
50	1.0	0.5	6.15	1.23
60	1.0	0.5	8.00	1.33
30	0.5	0.5	3.02	1.01
30	1.0	0.5	3.68	1.23
30	1.5	0.5	5.64	1.88
30	2.0	0.5	6.92	2.31
30	2.5	0.5	7.35	2.45
30	3.0	0.5	8.42	2.81
30	1.0	0.5	3.68	1.23
30	1.0	1.0	3.53	1.18
30	1.0	1.6	3.41	1.14
30	1.0	2.0	3.35	1.12
30	1.0	2.5	3.291.10	

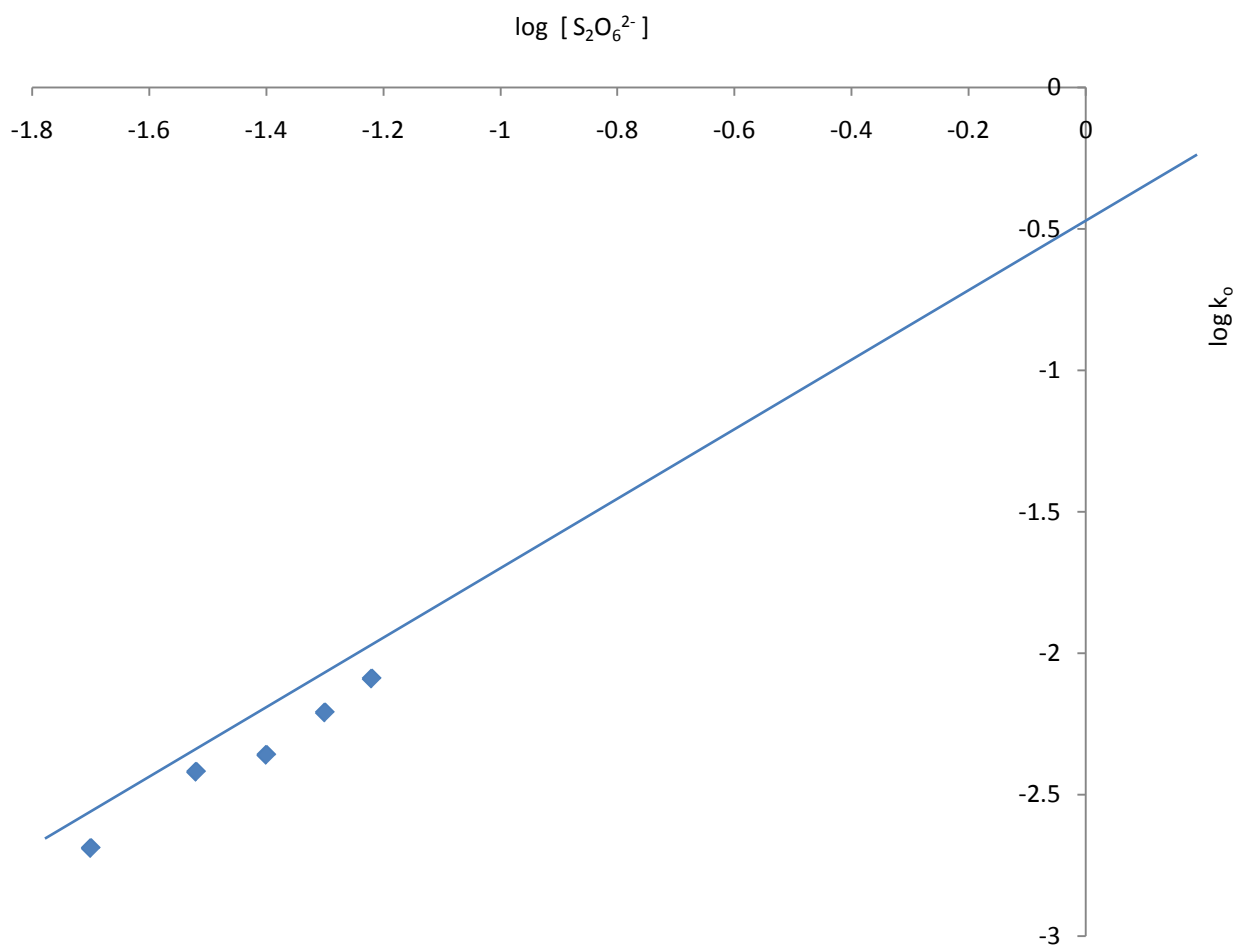
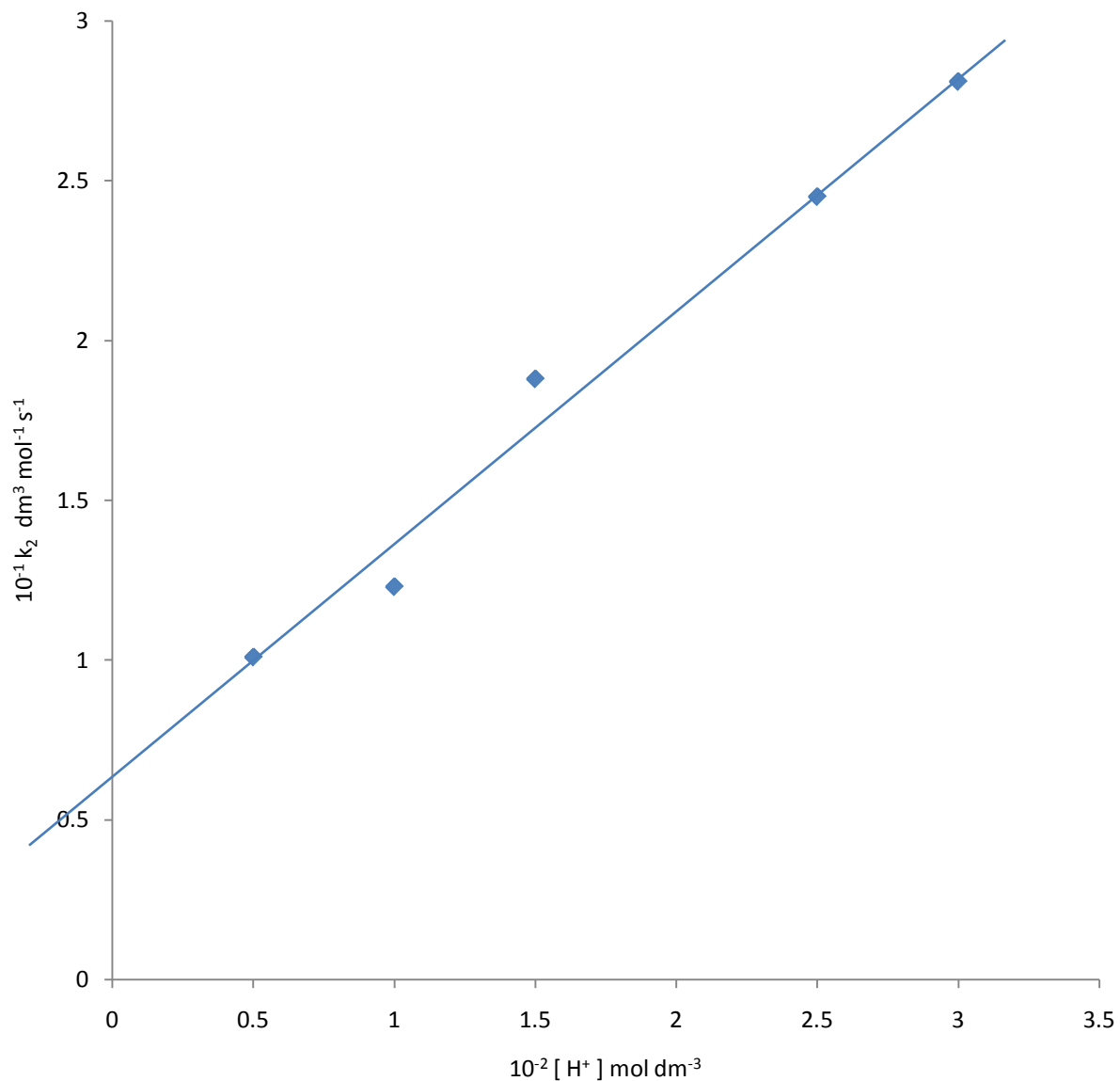


Fig.1 : Pseudo – first order plot of log k<sub>0</sub> versus log [S<sub>2</sub>O<sub>6</sub><sup>2-</sup>] for reduction of TB<sup>+</sup> by S<sub>2</sub>O<sub>6</sub><sup>2-</sup> at [TB<sup>+</sup>] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1 x 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.5 mol dm<sup>-3</sup>, λ<sub>max</sub> = 600 nm, T = 31 ± 1°C.



*Fig. 2:* Pseudo – first order plot of  $k_2$  versus  $[\text{H}^+]$  for the reduction of dithionite ion at  $[\text{S}_2\text{O}_6^{2-}] = 30 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{TB}^+] = 1 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ ,  $\lambda_{\text{max}} = 600 \text{ nm}$ ,  $T = 31 \pm 1^\circ\text{C}$ .

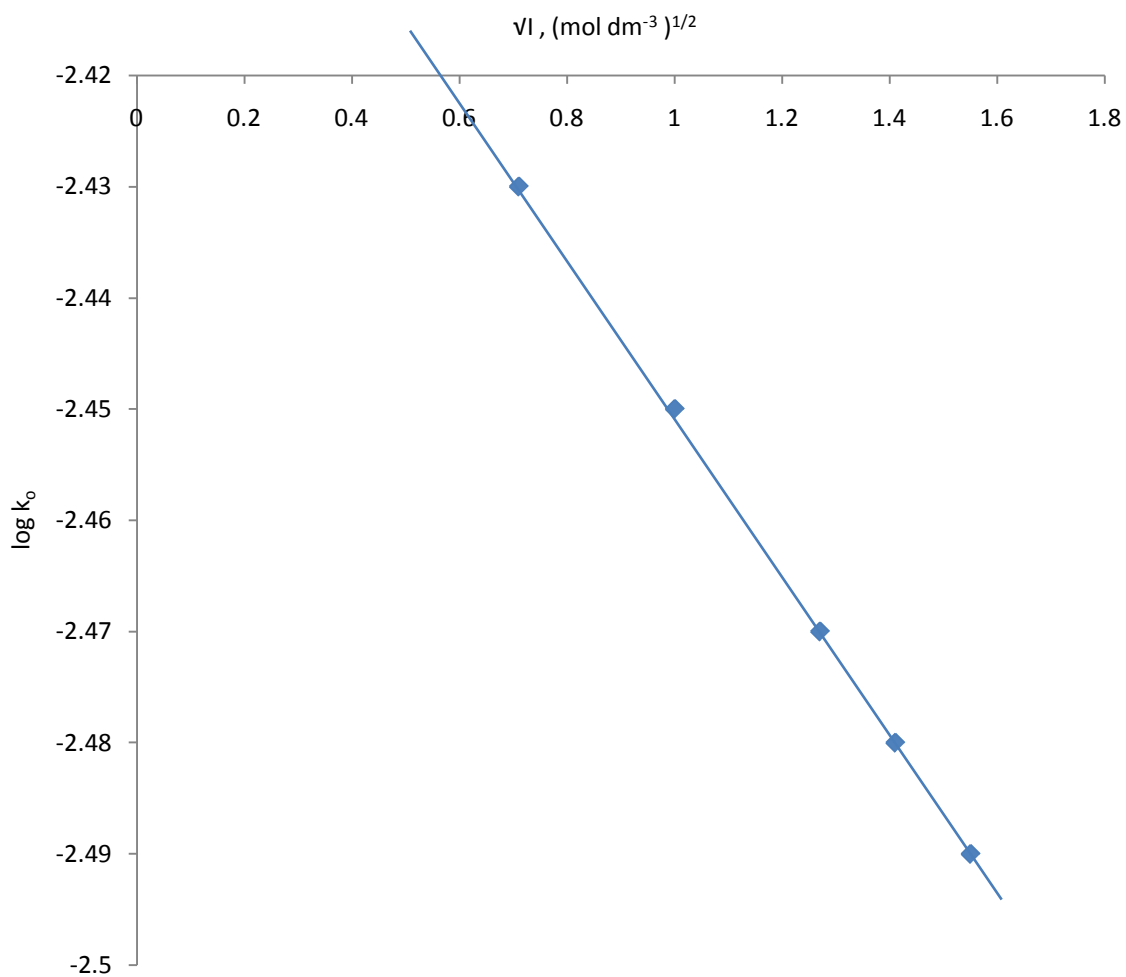
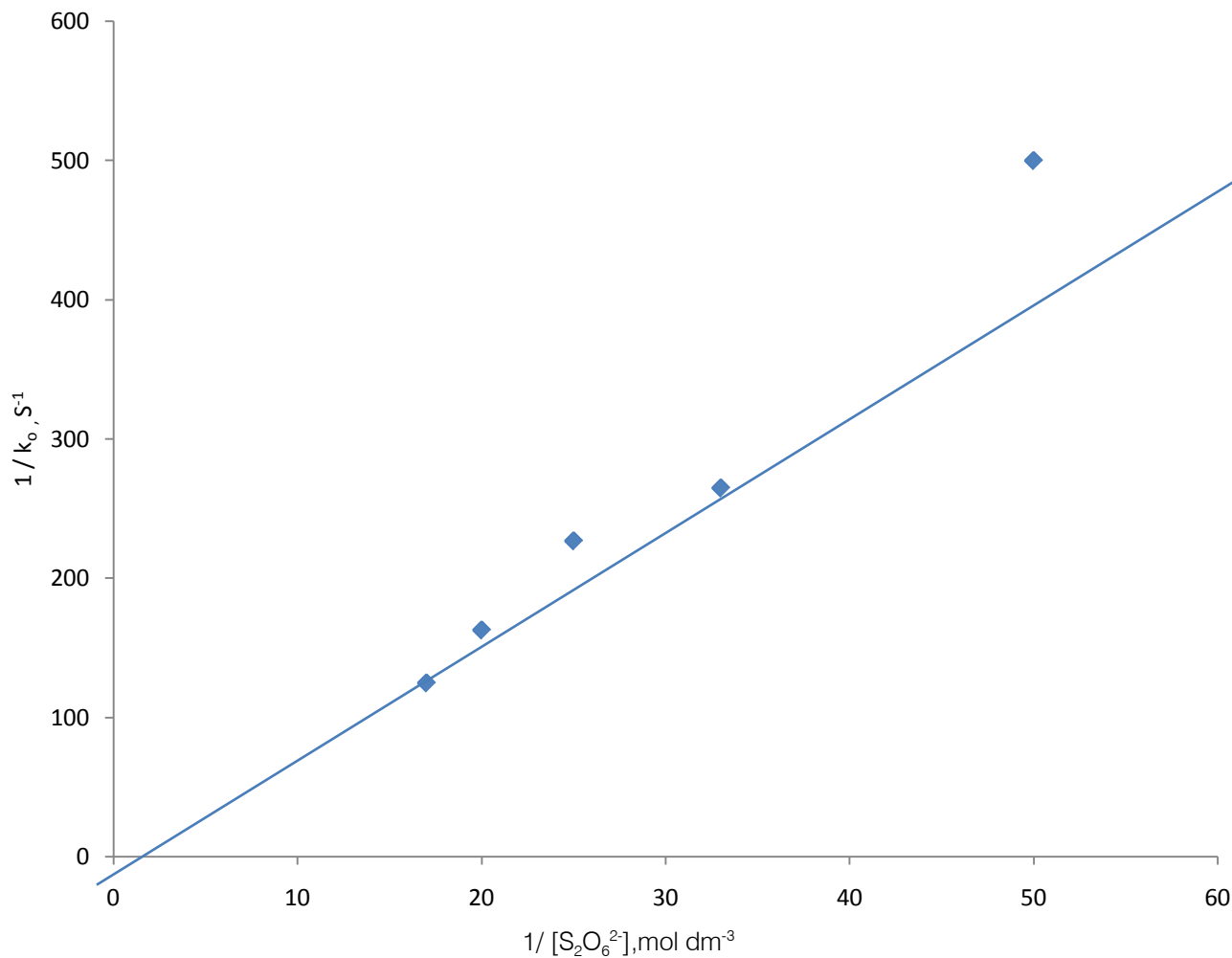


Fig.3 : Plot of  $\log k_0$  versus  $\sqrt{I}$  for the reduction of  $\text{TB}^+$  by dithionate ion.





*Fig. 4 :* Michealis – Menten's plot for the reduction of  $TB^+$  with  $S_2O_6^{2-}$  ion at  $[TB^+] = 1 \times 10^{-3} \text{mol dm}^{-3}$ ,  $[S_2O_6^{2-}] = 30 \times 10^{-3} \text{mol dm}^{-3}$ ,  $[H^+] = 1 \times 10^{-2} \text{mol dm}^{-3}$ ,  $I = 0.5 \text{mol dm}^{-3}(\text{NaCl})$ ,  $\lambda_{\text{max}} = 600 \text{nm}$ ,  $T = 31 \pm 1^\circ\text{C}$ .

*Table 2 :* Pseudo – first order and second order rate constants for the effect of change in dielectric constant of the medium on the toluidine blue oxidation by dithionate ion at  $[TB^+] = 1 \times 10^{-3} \text{mol dm}^{-3}$ ,  $[H^+] = 1 \times 10^{-2} \text{mol dm}^{-3}$ ,  $[S_2O_6^{2-}] = 30 \times 10^{-3} \text{mol dm}^{-3}$ ,  $I = 0.5 \text{mol dm}^{-3}(\text{NaCl})$ ,  $\lambda_{\text{max}} = 600 \text{nm}$ ,  $T = 31 \pm 1^\circ\text{C}$ .

D $\text{s}^{-1} \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$k_o$ $\times 10^{-2}$	$k_2$ $\times 10^{-1}$
0.2	0.893.00	
0.3	1.51	5.00
0.4	1.73	5.77
0.5	1.88	6.25
0.6	2.05	6.83



**Table 3** : Pseudo-first order and second order rate constants for the effect of added

ions on the reaction of TB<sup>+</sup> with dithionate ions at [TB<sup>+</sup>] = 1 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [S<sub>2</sub>O<sub>6</sub><sup>2-</sup>] = 30 x 10<sup>-3</sup> mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1 x 10<sup>-2</sup> mol dm<sup>-3</sup>, I = 0.5 mol dm<sup>-3</sup>(NaCl), λ<sub>max</sub> = 600 nm, T = 31 ± 1°C.

X	10 <sup>-3</sup> [X], mol dm <sup>-3</sup>	10 <sup>-2</sup> k <sub>o</sub> s <sup>-1</sup>	k <sub>2</sub> , dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
SO <sub>4</sub> <sup>2-</sup>	0.5	1.50	0.50
	1.0	1.52	0.51
	1.5	1.55	0.52
	2.0	1.60	0.53
	2.5	1.63	0.54
	3.0	1.66	0.55
NO <sub>3</sub> <sup>-</sup>	0.5	1.79	0.59
	1.0	1.82	0.61
	1.5	1.86	0.62
	2.0	1.89	0.63
	2.5	1.92	0.64
	3.0	1.93	0.63
Mg <sup>2+</sup>	0.5	3.64	1.21
	1.0	3.42	1.14
	1.5	3.34	1.11
	2.0	3.29	1.10
	2.5	3.19	1.06
	3.0	3.16	1.05
Ca <sup>2+</sup>	0.5	1.15	0.38
	1.0	1.17	0.39
	1.5	1.19	0.40
	2.0	1.20	0.40
	2.5	1.23	0.41
	3.0	1.24	0.41

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**Keywords:** *packaging material, diffusion, modelisation, finite difference method.*

**GJSFR-B Classification :** *FOR Code: 259999p*



ETHANOL DIFFUSION IN POLYETHYLENE VINYL ACETATE MODELLING AND EXPERIMENTATION

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# Ethanol Diffusion in Polyethylene Vinyl Acetate: Modelling and Experimentation

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**Abstract-** When a polymer is contacted with a liquid food, the transfer of materials can take place. So the study method is used to find a new method to understand the packaging behavior during contact with a food by combining experimentation with modeling. The numerical model takes into account all the experimental studies. Diffusivity of liquid simulator was determined and the analytical and numerical model has been developed which aims to provide better information on the concentration of liquid simulator inside the package (PEVA).

**Keywords:** packaging material, diffusion, modelisation, finite difference method.

## I. INTRODUCTION

Polymeric materials have become an indispensable part of food packaging. In recent years the plastic takes an important place in food packaging as well as pharmaceuticals and cosmetics packaging.

When a polymer is put in contact with a liquid, some matter transfers may take place. Generally, the process of the liquid transport within the polymer is controlled by transient diffusion. This contact can both contaminate our product and change the mechanical properties of the plastic packaging.

## II. THEORETICAL AND EXPERIMENTAL PART

The study the liquid diffusion into a polymer simulator, is based on the following simplifying assumptions:

- The distribution is in accordance with Fick's laws.
- The diffusion coefficient is independent of concentration.
- The diffusion in the sphere is three-way.
- The polymer was spherical in shape with a constant radius, as the amount of ethanol is very small.
- The chemical does not evaporate on surface.

### a) Analytical processing

When the diffusion is radial, Fick's second law expressing the diffusion equation under transient conditions is in the general form.

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$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left[ D \cdot r^2 \cdot \frac{\partial C}{\partial r} \right] \text{ (eq1)}$$

Where C is the concentration at time t and at a distance r from the center of the sphere.

When the diffusivity D is constant, the diffusion equation takes the form of:

$$\frac{\partial C}{\partial t} = D \cdot \left[ \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r} \right] \text{ (eq2)}$$

Analytical solutions can be obtained when the diffusivity is constant. Problems with a concentration-dependent diffusivity need numerical methods.

By putting:

$$U = C \cdot r \text{ (eq3)}$$

Equation (2) becomes:

$$\frac{\partial U}{\partial t} = D \cdot \frac{\partial^2 U}{\partial r^2} \text{ (eq4)}$$

Equation (4) is similar to the equation obtained for diffusion in one dimension through the plane sheet.

*Case study:* The initial distribution in the sphere is constant: C<sub>i</sub>.

### b) Mathematical model

The total amount of diffusing substance going into or leaving the sphere is given by integrating Fick's first law according to time.

$$M_t = - \int_0^t D \cdot \left( \frac{\partial C}{\partial r} \right)_{r=R} \cdot dt \text{ (eq5)}$$

By considering:  $\sum_1^{\infty} \frac{1}{n^2} = \frac{\pi^2}{6}$

$$\text{And: } M_{\infty} = \frac{4}{3} \pi R^3 \cdot C_0$$

We can obtain:

$$\frac{M_{\infty} - M_t}{M_{\infty}} = \frac{6}{\pi^2} \cdot \sum_1^{\infty} \frac{1}{n^2} \cdot \exp\left(-\frac{n^2 \pi^2}{R^2} Dt\right) \text{ (eq6)}$$

Another expression of the solution of the equation of diffusion in the sphere (equation 5) is given by:

$$\frac{C_{r,t} - C_i}{C_0 - C_i} = \frac{R}{r} \cdot \sum_0^{\infty} \left\{ \operatorname{erfc} \frac{(2n+1)R+r}{2(Dt)^{0.5}} - \operatorname{erfc} \frac{(2n+1)R-r}{2(Dt)^{0.5}} \right\} \quad (eq7)$$

The kinetics for the matter transported is:

$$\frac{M_t}{M_{\infty}} = 6 \left( \frac{Dt}{R^2} \right)^{0.5} \left\{ \pi^{-0.5} + 2 \sum_1^{\infty} i \operatorname{erfc} \frac{nR}{(Dt)^{0.5}} \right\} - 3 \frac{Dt}{R^2} \quad (eq8)$$

Case of short times. Equation (8) is very useful for short times because it can be reduced to:

$$\frac{M_t}{M_{\infty}} = \frac{6}{R} \left( \frac{Dt}{\pi} \right)^{0.5} \quad (eq9)$$

c) Numerical model - Finite difference method-

Analytical solutions can be obtained when the diffusivity is constant. Problems with a concentration-dependent diffusivity need numerical methods. In this case, the problem must be solved by using the numerical Finite difference method.

Case study: The amount of the remaining ethanol within the sphere.

$$M_t = 4\pi \int_0^R r^2 \cdot C_{r,t} \cdot dr \quad (eq10)$$

This expression can be rewritten using finite difference method.

$$M_t = 4\pi(\Delta r)^3 \left[ \frac{C_0}{24} + \sum_1^2 n^2 C_n + \frac{9}{8}(n-1)^2 C_{n-1} + \frac{3}{8} n^2 \cdot C_n \right] \quad (eq11)$$

d) Experimental procedure

The material used is polyethylene vinyl acetate (also known as PEVA) is the copolymer of ethylene and vinyl acetate. And our product simulator used is ethanol or ethyl alcohol is an alcohol of the structural formula CH<sub>3</sub>-CH<sub>2</sub>-OH. It is a colorless, volatil, flammable and miscible with water in all proportions liquid. Contacting: The contacting sample of polyethylene vinyl acetate is

carried out with ethanol at 25°C. During the contact, we measured the specific mass of the sphere each time to study the evolution of the mass sphere.

### III. RESULTS AND DISCUSSIONS

The percentage of ethanol mass variation inside our plastic sphere (fig.1) is given by the following equation:

$$\Delta m = \frac{m_t - m_0}{m_0} \times 100 \quad (eq12)$$

Effect of The diffusion coefficient is given by this relation:

$$D = \pi \left( \frac{\alpha \cdot R}{6} \right)^2 \frac{1}{60^2} \quad (eq13)$$

En cm<sup>2</sup>/s:

$$D = 1,390 \cdot 10^{-6} \text{ cm}^2/\text{s}$$

Figure 2 shows the variation of the amount of ethanol in the PEVA with time, we note that the ethanol in polyethylene vinyl acetate mass increases with the contact time. Until equilibrium reached.

Figure 3 show the amount of ethanol in the material according to simulation time for each solution (analytical, numerical and experience). We notice from this figure that three solutions gives the same variation in the amount of ethanol absorbed as a function of time. So we concluded that the model is validated.

Figure 4 show the profile of the concentration of ethanol after every 10 min.

- The ethanol concentration within the sphere is low, however the surfaces.
- This concentration profile is aimed to give good information on ethanol inside PEVA, ie for each point in our sample we can easily determine its concentration.

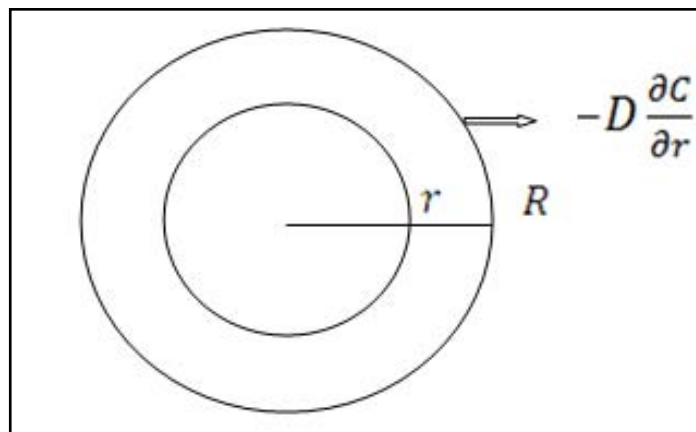


Figure 1 : Schema of the circular cross section of a sphere of radius R.

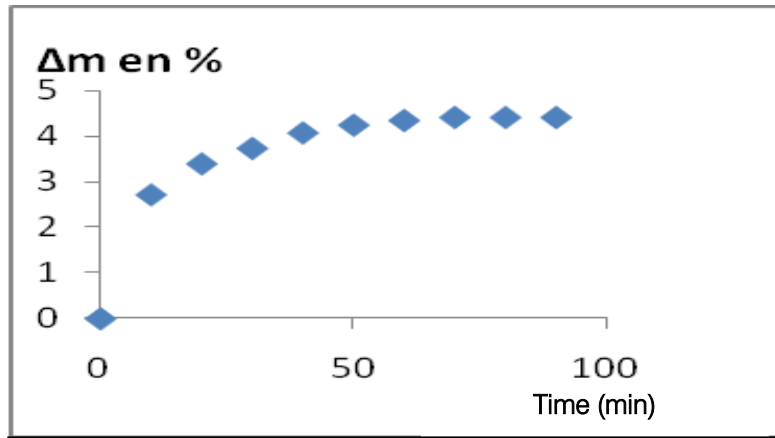


Figure 2 : Variation of the amount of ethanol in the PEVA

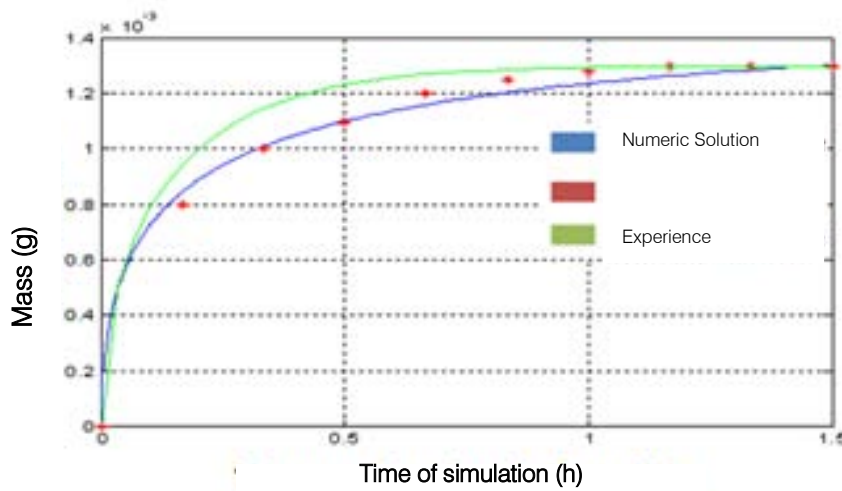


Figure 3 : The amount of ethanol in the material as a function of time for the simulation of three solutions.

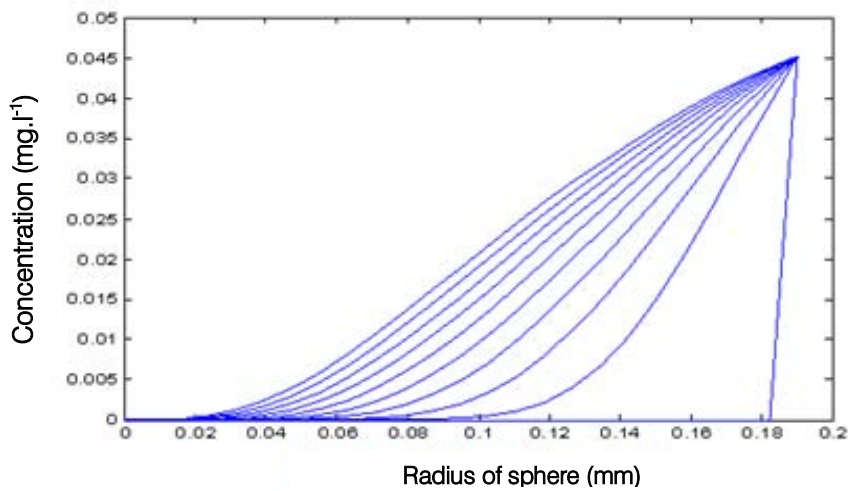


Figure 4 : The profile of the concentration of ethanol after every 10 min

## IV. CONCLUSION

Through this work, we contributed to the study and development of new methods coupling experiments with modeling to understand the behavior of plastic packaging in contact with the food products.

The study was conducted by weighed following the evolution of the mass transferred over time. The polyethylene vinyl acetate contact with ethanol (considered simulating agent) at a temperature of 25°C, showed that the amount of ethanol in the polymer increases with time.

The resulting profile gives better information on concentrations of ethanol inside the package polyethylene vinyl acetate. In addition, we allow a few hours to simulate mass transfer in reality lasting several months.

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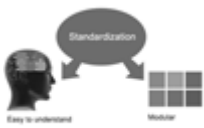
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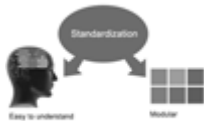
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2. Ethical Guidelines,
3. Submission of Manuscripts,
4. Manuscript's Category,
5. Structure and Format of Manuscript,
6. After Acceptance.

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**25. Take proper rest and food:** No matter how many hours you spend for your research activity, if you are not taking care of your health then all your efforts will be in vain. For a quality research, study is must, and this can be done by taking proper rest and food.

**26. Go for seminars:** Attend seminars if the topic is relevant to your research area. Utilize all your resources.





**27. Refresh your mind after intervals:** Try to give rest to your mind by listening to soft music or by sleeping in intervals. This will also improve your memory.

**28. Make colleagues:** Always try to make colleagues. No matter how sharper or intelligent you are, if you make colleagues you can have several ideas, which will be helpful for your research.

**29. Think technically:** Always think technically. If anything happens, then search its reasons, its benefits, and demerits.

**30. Think and then print:** When you will go to print your paper, notice that tables are not be split, headings are not detached from their descriptions, and page sequence is maintained.

**31. Adding unnecessary information:** Do not add unnecessary information, like, I have used MS Excel to draw graph. Do not add irrelevant and inappropriate material. These all will create superfluous. Foreign terminology and phrases are not apropos. One should NEVER take a broad view. Analogy in script is like feathers on a snake. Not at all use a large word when a very small one would be sufficient. Use words properly, regardless of how others use them. Remove quotations. Puns are for kids, not grunt readers. Amplification is a billion times of inferior quality than sarcasm.

**32. Never oversimplify everything:** To add material in your research paper, never go for oversimplification. This will definitely irritate the evaluator. Be more or less specific. Also too, by no means, ever use rhythmic redundancies. Contractions aren't essential and shouldn't be there used. Comparisons are as terrible as clichés. Give up ampersands and abbreviations, and so on. Remove commas, that are, not necessary. Parenthetical words however should be together with this in commas. Understatement is all the time the complete best way to put onward earth-shaking thoughts. Give a detailed literary review.

**33. Report concluded results:** Use concluded results. From raw data, filter the results and then conclude your studies based on measurements and observations taken. Significant figures and appropriate number of decimal places should be used. Parenthetical remarks are prohibitive. Proofread carefully at final stage. In the end give outline to your arguments. Spot out perspectives of further study of this subject. Justify your conclusion by at the bottom of them with sufficient justifications and examples.

**34. After conclusion:** Once you have concluded your research, the next most important step is to present your findings. Presentation is extremely important as it is the definite medium through which your research is going to be in print to the rest of the crowd. Care should be taken to categorize your thoughts well and present them in a logical and neat manner. A good quality research paper format is essential because it serves to highlight your research paper and bring to light all necessary aspects in your research.

## INFORMAL GUIDELINES OF RESEARCH PAPER WRITING

### Key points to remember:

- Submit all work in its final form.
- Write your paper in the form, which is presented in the guidelines using the template.
- Please note the criterion for grading the final paper by peer-reviewers.

### Final Points:

A purpose of organizing a research paper is to let people to interpret your effort selectively. The journal requires the following sections, submitted in the order listed, each section to start on a new page.

The introduction will be compiled from reference matter and will reflect the design processes or outline of basis that direct you to make study. As you will carry out the process of study, the method and process section will be constructed as like that. The result segment will show related statistics in nearly sequential order and will direct the reviewers next to the similar intellectual paths throughout the data that you took to carry out your study. The discussion section will provide understanding of the data and projections as to the implication of the results. The use of good quality references all through the paper will give the effort trustworthiness by representing an alertness of prior workings.



Writing a research paper is not an easy job no matter how trouble-free the actual research or concept. Practice, excellent preparation, and controlled record keeping are the only means to make straightforward the progression.

**General style:**

Specific editorial column necessities for compliance of a manuscript will always take over from directions in these general guidelines.

To make a paper clear

- Adhere to recommended page limits

Mistakes to evade

- Insertion a title at the foot of a page with the subsequent text on the next page
- Separating a table/chart or figure - impound each figure/table to a single page
- Submitting a manuscript with pages out of sequence

In every sections of your document

- Use standard writing style including articles ("a", "the," etc.)
- Keep on paying attention on the research topic of the paper
- Use paragraphs to split each significant point (excluding for the abstract)
- Align the primary line of each section
- Present your points in sound order
- Use present tense to report well accepted
- Use past tense to describe specific results
- Shun familiar wording, don't address the reviewer directly, and don't use slang, slang language, or superlatives
- Shun use of extra pictures - include only those figures essential to presenting results

**Title Page:**

Choose a revealing title. It should be short. It should not have non-standard acronyms or abbreviations. It should not exceed two printed lines. It should include the name(s) and address (es) of all authors.



## Abstract:

The summary should be two hundred words or less. It should briefly and clearly explain the key findings reported in the manuscript-- must have precise statistics. It should not have abnormal acronyms or abbreviations. It should be logical in itself. Shun citing references at this point.

An abstract is a brief distinct paragraph summary of finished work or work in development. In a minute or less a reviewer can be taught the foundation behind the study, common approach to the problem, relevant results, and significant conclusions or new questions.

Write your summary when your paper is completed because how can you write the summary of anything which is not yet written? Wealth of terminology is very essential in abstract. Yet, use comprehensive sentences and do not let go readability for brevity. You can maintain it succinct by phrasing sentences so that they provide more than lone rationale. The author can at this moment go straight to shortening the outcome. Sum up the study, with the subsequent elements in any summary. Try to maintain the initial two items to no more than one ruling each.

- Reason of the study - theory, overall issue, purpose
- Fundamental goal
- To the point depiction of the research
- Consequences, including definite statistics - if the consequences are quantitative in nature, account quantitative data; results of any numerical analysis should be reported
- Significant conclusions or questions that track from the research(es)

## Approach:

- Single section, and succinct
- As an outline of job done, it is always written in past tense
- A conceptual should situate on its own, and not submit to any other part of the paper such as a form or table
- Center on shortening results - bound background information to a verdict or two, if completely necessary
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## Introduction:

The **Introduction** should "introduce" the manuscript. The reviewer should be presented with sufficient background information to be capable to comprehend and calculate the purpose of your study without having to submit to other works. The basis for the study should be offered. Give most important references but shun difficult to make a comprehensive appraisal of the topic. In the introduction, describe the problem visibly. If the problem is not acknowledged in a logical, reasonable way, the reviewer will have no attention in your result. Speak in common terms about techniques used to explain the problem, if needed, but do not present any particulars about the protocols here. Following approach can create a valuable beginning:

- Explain the value (significance) of the study
- Shield the model - why did you employ this particular system or method? What is its compensation? You strength remark on its appropriateness from a abstract point of vision as well as point out sensible reasons for using it.
- Present a justification. Status your particular theory (es) or aim(s), and describe the logic that led you to choose them.
- Very for a short time explain the tentative propose and how it skilled the declared objectives.

## Approach:

- Use past tense except for when referring to recognized facts. After all, the manuscript will be submitted after the entire job is done.
- Sort out your thoughts; manufacture one key point with every section. If you make the four points listed above, you will need a least of four paragraphs.



- Present surroundings information only as desirable in order hold up a situation. The reviewer does not desire to read the whole thing you know about a topic.
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This part is supposed to be the easiest to carve if you have good skills. A sound written Procedures segment allows a capable scientist to replacement your results. Present precise information about your supplies. The suppliers and clarity of reagents can be helpful bits of information. Present methods in sequential order but linked methodologies can be grouped as a segment. Be concise when relating the protocols. Attempt for the least amount of information that would permit another capable scientist to spare your outcome but be cautious that vital information is integrated. The use of subheadings is suggested and ought to be synchronized with the results section. When a technique is used that has been well described in another object, mention the specific item describing a way but draw the basic principle while stating the situation. The purpose is to text all particular resources and broad procedures, so that another person may use some or all of the methods in one more study or referee the scientific value of your work. It is not to be a step by step report of the whole thing you did, nor is a methods section a set of orders.

#### **Materials:**

- Explain materials individually only if the study is so complex that it saves liberty this way.
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- Do not take in frequently found.
- If use of a definite type of tools.
- Materials may be reported in a part section or else they may be recognized along with your measures.

#### **Methods:**

- Report the method (not particulars of each process that engaged the same methodology)
- Describe the method entirely
- To be succinct, present methods under headings dedicated to specific dealings or groups of measures
- Simplify - details how procedures were completed not how they were exclusively performed on a particular day.
- If well known procedures were used, account the procedure by name, possibly with reference, and that's all.

#### **Approach:**

- It is embarrassed or not possible to use vigorous voice when documenting methods with no using first person, which would focus the reviewer's interest on the researcher rather than the job. As a result when script up the methods most authors use third person passive voice.
- Use standard style in this and in every other part of the paper - avoid familiar lists, and use full sentences.

#### **What to keep away from**

- Resources and methods are not a set of information.
- Skip all descriptive information and surroundings - save it for the argument.
- Leave out information that is immaterial to a third party.

#### **Results:**

The principle of a results segment is to present and demonstrate your conclusion. Create this part a entirely objective details of the outcome, and save all understanding for the discussion.

The page length of this segment is set by the sum and types of data to be reported. Carry on to be to the point, by means of statistics and tables, if suitable, to present consequences most efficiently. You must obviously differentiate material that would usually be incorporated in a study editorial from any unprocessed data or additional appendix matter that would not be available. In fact, such matter should not be submitted at all except requested by the instructor.



## Content

- Sum up your conclusion in text and demonstrate them, if suitable, with figures and tables.
- In manuscript, explain each of your consequences, point the reader to remarks that are most appropriate.
- Present a background, such as by describing the question that was addressed by creation an exacting study.
- Explain results of control experiments and comprise remarks that are not accessible in a prescribed figure or table, if appropriate.
- Examine your data, then prepare the analyzed (transformed) data in the form of a figure (graph), table, or in manuscript form.

### What to stay away from

- Do not discuss or infer your outcome, report surroundings information, or try to explain anything.
- Not at all, take in raw data or intermediate calculations in a research manuscript.
- Do not present the similar data more than once.
- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

### Approach

- As forever, use past tense when you submit to your results, and put the whole thing in a reasonable order.
- Put figures and tables, appropriately numbered, in order at the end of the report
- If you desire, you may place your figures and tables properly within the text of your results part.

### Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
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- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

### Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
- Submit to generally acknowledged facts and main beliefs in present tense.



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<i>Methods and Procedures</i>	Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads	Difficult to comprehend with embarrassed text, too much explanation but completed	Incorrect and unorganized structure with hazy meaning
<i>Result</i>	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
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<i>References</i>	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring



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