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Chemistry

Highlights

- Aqueous Acidic Medium
- Spectrophotometric Determination
- Ion in Acidic Medium
- Modelling and Experimentation

Discovering Thoughts, Inventing Future

Volume 13 Issue 8 Version 1.0

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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

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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 $[SCN^-]$ at 30 ± 1°C, $[H^+] = 1 \times 10^{-3}$ mol dm^{-3} and ionic strength, I = 0.50 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

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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 [α] & Nwaji M. U [σ]

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^-] at 30 ± 1°C, [H^+] = 1 x 10^{-3} mol dm^{-3} and ionic strength, I = 0.50 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. The overall reaction conforms to the rate law

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

where a = 2.8 x 10^{-2} dm^3 mol^{-1} s^{-1}, b = 1.20 x 10^{-1} dm^3 mol^{-1} s^{-1}

Variation of the ionic strength and dielectric constant of the medium altered the rate of the reaction, addition anions and cations(X = SO_4^{2-}, NO_3^-, Mg^{2+} and Ca^{2+}) 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).

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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^{-3} and they were prepared by dissolving known quantities in distilled water; hydrochloric acid which was used to investigate the effect of [H^+] on the rate of reaction. This was standardized titrimetrically using standard solution of sodium bicarbonate. The λ_{max} = 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^{-5}mol dm^{-3}, [H^+] = 1 x 10^{-3} moldm^{-3}, I = 0.50 mol dm^{-3}, λ_{max} = 600 nm, T = 30 ±1°C while [SCN^-] was varied from 1.0– 6.0 x 10^{-5} mol dm^{-3} . 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^-] 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^+] =1 x 10^{-3} mol dm^{-3} and I = 0.50 mol dm^{-3}. 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_∞) versus time t were made (where A_t and A_∞ 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:

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

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 x10^{-3} ≤ $[H^+]$ ≥ 2.5 x10^{-3} mol dm^{-3} while concentration of TB and SCN ion were kept constant at 1.0 x10^{-5} and 20 x10^{-5} mol dm^{-3} respectively at 30 ± 1°C and I =0.50 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 mol dm^{-3}, while the concentrations of other reactants were kept constant at 30 ±1°C. The results are presented in Table1.

c) Effect of Added Cation and Anion

The effect of added cation and anion were investigated for [X] = 0.2 x10^{-5} - 1.0 x10^{-5} mol dm^{-3} (X =Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^-) and the concentration of all other reactants were kept constant at 30 ±1°C and the ionic strength was maintained constant at 0.50 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 nm. This was compared with the spectra of the dye alone within the same range. Michaelis-Mentens plot of $1/k_1$ versus 1/ $[SCN^-]$ 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:

$$TB^+ + SCN^- \rightarrow \text{Product} \qquad \text{-- 1}$$

Product analysis was carried out by reacting equimolar amount of the dye and the thiocyanate at $[H^+]$ = 1.0 x 10^{-3} mol dm^{-3} and I = 0.5 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 λ_{max}600 nm. This indicates the destruction of the quinoid structure that gives the dye colour.

Qualitative test forcyanide ion was carried out. Cyanide ion was identified by precipitating with $AgNO_3$.

b) Kinetics

The pseudo-first orders of log (A_t -A_∞) 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 $[TB^+]$. A plot of log k_1 versus log $[SCN^-]$ was linear with a slope of 1.2 showing that the reaction is also first order with respect to $[SCN^-]$(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:

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

where k_2=9.96 x $10^{-2}dm^3$ mol^{-1} 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) x 10^{-3} 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:

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

where a = 2.8 x 10^{-2} dm^3 mol^{-1} s^{-1}, b = 1.20 x 10^{-1} dm^3 mol^{-1} 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 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 Ca^{2+}, Mg^{2+} SO_4^{2-} and 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

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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 $1/[SCN^-]$ 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:

$$SCN^- + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HSCN \qquad \text{-- 4}$$

$$TB^+ + HSCN \xrightarrow[\text{Slow}]{k_2} \text{Products} \qquad \text{-- 5}$$

$$SCN^- + TB^+ \xrightarrow[\text{Slow}]{k_3} \text{Products} \qquad \text{-- 6}$$

The equations 5 and 6 are the rate determining steps

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

From equation 4

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

Substitute equation 8 into equation 7

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

Rearranging equation 9

$$\text{Rate} = k_3 + k_2K_1[H^+] [TB^+] [SCN^-] \qquad \text{-- 10}$$

Where $k_3 = a$

$k_2 K_1 = b$

Equation 10 becomes

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

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

VI. Conclusion

The reaction is found to be second order overall at constant $[H^+]$. And the proposed reaction steps point to an outer sphere electron transfer process, considering the fact that addition of foreign ions led to the inhibition of the reaction rates, when the absorbance of the reaction mixture were measured as the reaction progresses the λ_{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 λ_{max} of TB^+ or appearance of a new peak which was hitherto absent. Also Michaelis-Menten plot of $1/k_1$ against $1/[SCN^-]$ passed through the origin. These points greatly favour the outer sphere mechanistic pathway for this reaction.

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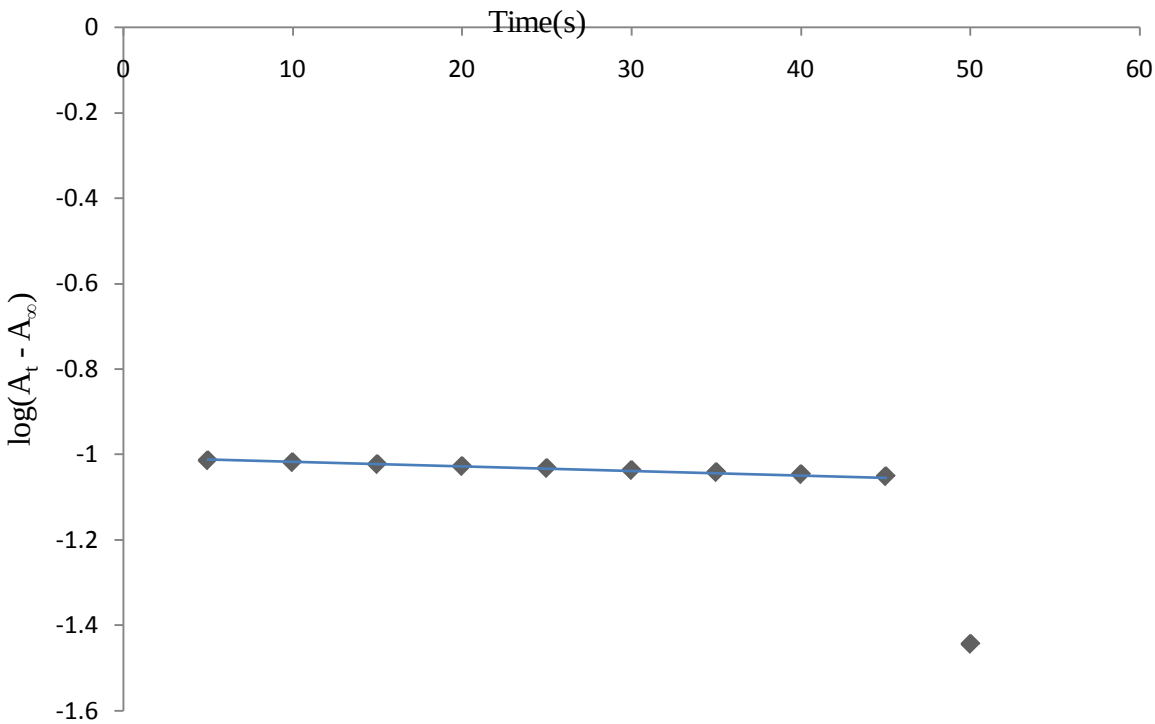

Figure 1 : Pseudo-first Order Plot for the Reduction of TB by SCN

Table 1 : Pseudo – first order and second order rate constants for TBreduction by SCN^- in aqueous HCl medium at $[TB^+] = 1.0 \times 10^{-5}$ mol dm^{-3}, T = 30 ± 1˚C and , λ_{max} = 600 nm

10^5 [SCN^-] mol dm^{-3}	I (NaCl) mol dm^{-3}	10^3 $[H^+]$ mol dm^{-3}	10^1 k_1 s^{-1}	10^3 k_2 dm^3 mol^{-1} s^{-1}
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

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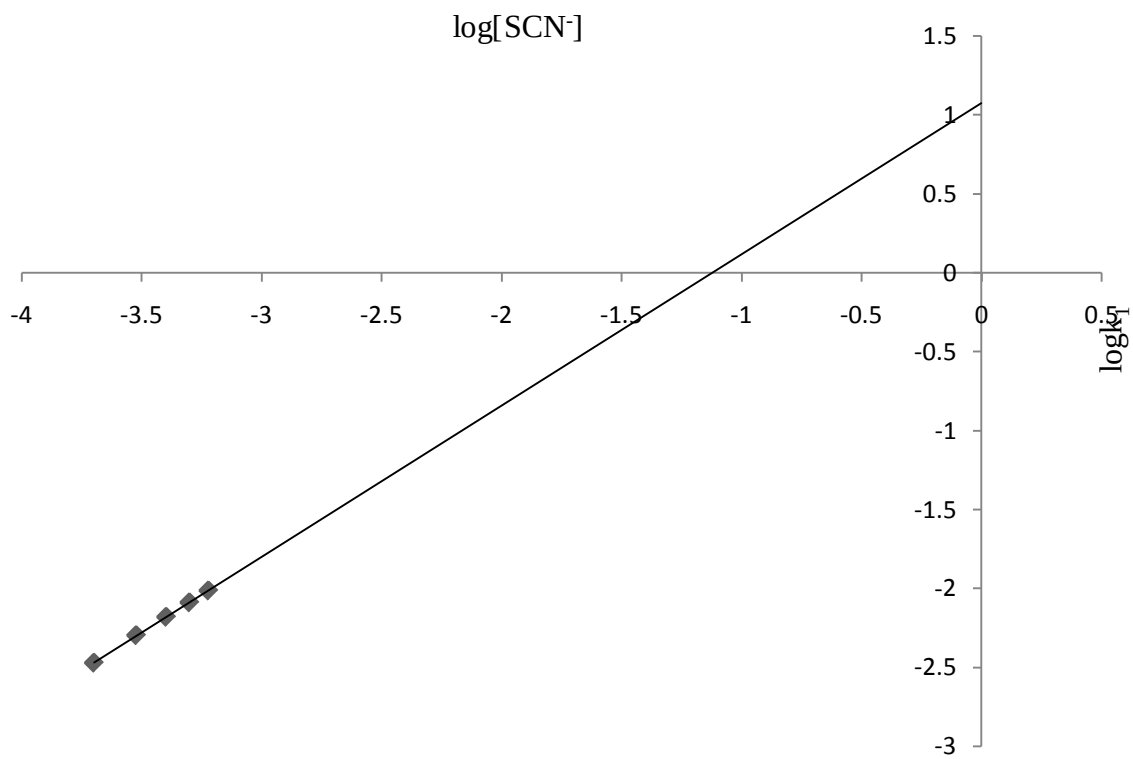

Figure 2 : Plot of log k_1 vs log [SCN^-]for the Reduction of TB by SCN^-

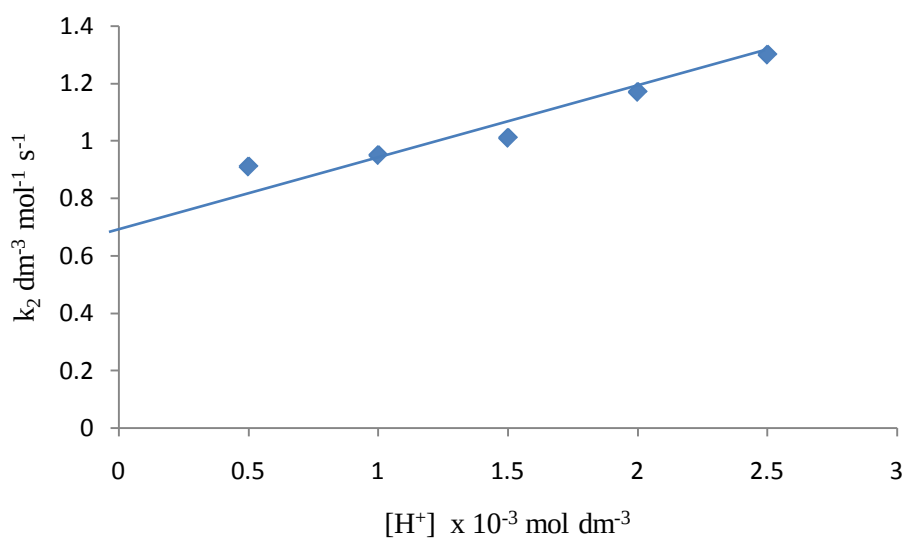

Figure 3 : Plot of k_2 versus [H^+] of reduction of TB by SCN^-

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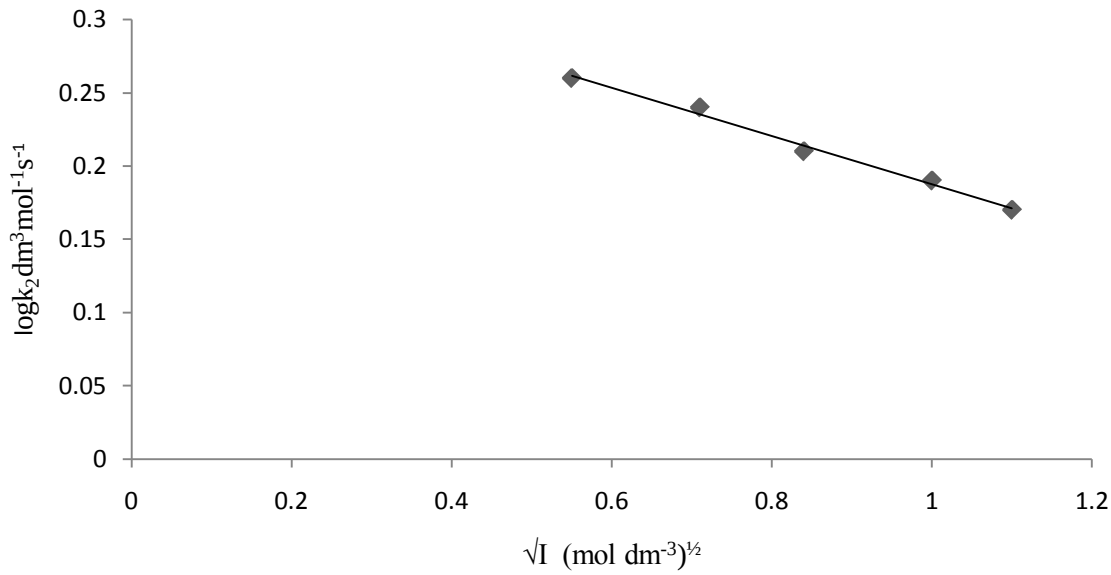

Figure 4 : plot of log k_2 versus √I for the reduction of TB^+ by $[SCN^-]$

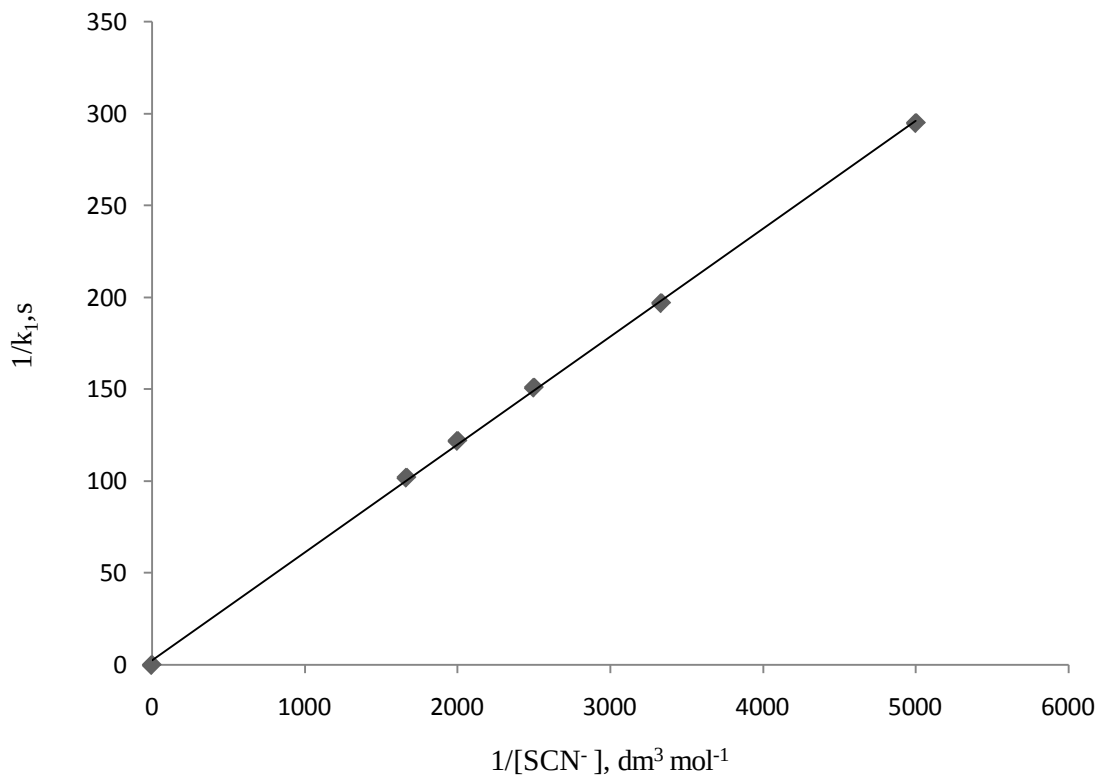

Figure 5 : Michaelis-Menten's plot for the reduction of TB by SCN^-

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A New Spectrophotometric Determination of Chromium (VI) as $Cr_2O_7^{2-}$ After Cloud-Point Extraction Using a Laboratory-Made Organic Reagent

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

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A NEW SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM VI AS CRO AFTER CLOUD-POINT EXTRACTION USING A LABORATORY-MADE ORGANIC REAGENT

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

I. 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 [(1)]. Due to sever toxicity of Cr (VI), WHO and USEPA have set the guideline for drinking water with upper limit of 50 µg L^{-1}[(2-4)], 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 µg L^{-1}[(5)]. 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 $Cr_2O_7^{2-}$ and 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 (MX_4^-) metal oxyanions (MO_4^-) and metal cyanoanions $[M(CN)_6]^{3-}$, $[M(CN)_4]^{2-}$, $[M(CN)_2]^-$ or metal thiocynoanion $[M(SCN)_4]^{2-}$ 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 attemptts based on the above conception for the determination of Cd (II) as CdI_4^{2-} by CPE with flame atomic absorption spectrometry [(6)] and the reaction of CTAB with the heteropoly acid formed between MoO_4^{2-} and *o*-$PO_4^{2-}$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 [7] beside our two papers recently published elsewhere [8-9] 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 $Cr_2O_7^{2-}$ 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 spectromphotometry at λ_{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 (±0.3nm accuracy at D_2 peak 656.1 nm, 486.0 nm and ± 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 $C_8H_{17}C_6H_4(OC_2H_4)n$ 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-aminobenozthiazol (99%), NaOH (99%) , HCl (37%), $NaNO_2$;(99%) were purchased from BDH(UK), p-benzenenaphthol(98%) from Fluka (Germany) and diphenylcarbazide(>98%) from Chem. Supply Pty limited(Australia). The stock solution of Cr (VI) at 1000 μg mL^{-1} was prepared by dissolving of 0.2829 ±0.0010 g of $K_2Cr_2O_7$ 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 thiazolylazo]- 4- benzenenaphthol (BTABN) reagent solution at concentration of $1x10^{-2}$ 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 Diphenylcarbazide solution was prepared by dissolving 0.25 g of 1, 5-diphenylcarbazide ($C_{13}H_{14}N_4O$) 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 thiazolylazo] - 4-benzenenaphthol reagent was prepared according to the procedure published elsewhere [10] 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 $CaCl_2$ .Yield 77% ; mp 127-128˚C ; anal calcd for $C_{23}H_{15}N_3OS$(382.48 g mol^{-1}); 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) ν_{max}/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, δ, bend aromatic,C-H); ^{1}HNMR(DMSO-*d*6, 298 K,) d/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 thiazolylazo]- 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.

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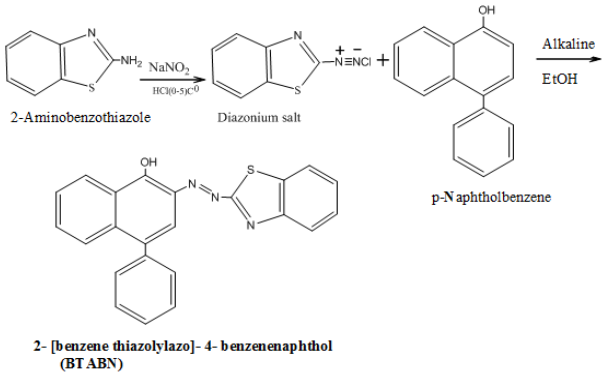

Figure 1 : Synthetic path of BTABN reagent

d) General Procedure for CPE

To an aliquot of 10 mL of a solution containing known amount of Cr (VI) as $Cr_2O_7^{2-}$ standard or sample solution in 0.1M HCl, $5x10^{-4}$ 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 λ_{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 $Cr_2O_7^{2-}$ in surfactant-poor phase (i.e. aqueous phase) was determined spectrophotometrically at λ_{max} of 540 nm by using the diphenylcarbazide method[11] 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 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 HNO_3, 5 mL of concentration $H_2SO_4$and 4mL H_2O_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 filtrated 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 $Cr_2O_7^{2-}$ 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 $Cr_2O_7^{2-}$ oxyanion after CPE procedure. It has been evident that the oxyanion $Cr_2O_7^{2-}$ can form an ion-association complex with BTABN reagent in acidic medium as $[HBTABN]^+[HCr_2O_7]^-$ due to the appearance of another distinct absorption maximum at λ_{max} of 475 nm with molar absorptivity (ε) of $5.5x10^4$ L mol^{-1} cm^{-1} while the BTABN reagent alone gave the absorption maxima at λ_{max} of 452 nm as depicted in the spectra (a) and (b) of Figure 2

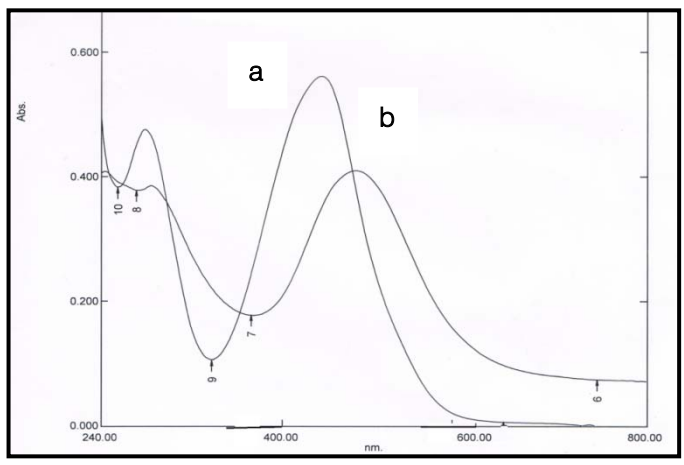

Figure 2 : Absorption spectra of (a) $5x10^{-4}$ M of (BTABN) 10 mL of 20 μg $Cr_2O_7^{2-}$, 0.1 M HCl, ($5x10^{-4}$ M) (BTABN) reagent and 0.5mL (1 % Triton X-100)].

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 $Cr_2O_7^{2-}$ by CPE method involves the formation of ion-association complexes between $Cr_2O_7^{2-}$ oxyanion and the

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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 $Cr_2O_7^{2-}$ ions into $HCr_2O_7^-$ species and the reagent BTABN into ion pair complex $(H\text{-}BTABN)^+$; Cl^-. Consequently, the effect of HCl concentration was studied by measuring the absorbance of 10 mL solution containing 20 μg $Cr_2O_7^{2-}$, $1x10^{-4}$ 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 equilbria 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 inthe following equations below;

$$BTABN + HCl \rightleftharpoons [H\text{-}BTABN]^+; Cl^- \quad \text{or}$$

$$BTABN + 2HCl \rightleftharpoons [2H\text{-}BTABN]^{2+}; 2Cl^-$$

Thereafter, an exchange of small anions Cl^- with large anions of $Cr_2O_7^{2-}$ may occur in micelles as the following;

$$\underset{\text{solution}}{[H\text{-}BTABN]^+; Cl^-} + \underset{\text{solution}}{HCr_2O_7} \rightleftharpoons \underset{\text{micelle}}{[H\text{–}BTABN]^+; HCr_2O_7^-} + \underset{\text{solution}}{Cl^-}$$

or

$$[2H\text{-}BTABN]^+;2Cl^- + Cr_2O_7^{2-} \rightleftharpoons [2H\text{-}BTABN]^+;Cr_2O_7^{2-} + 2Cl^-$$

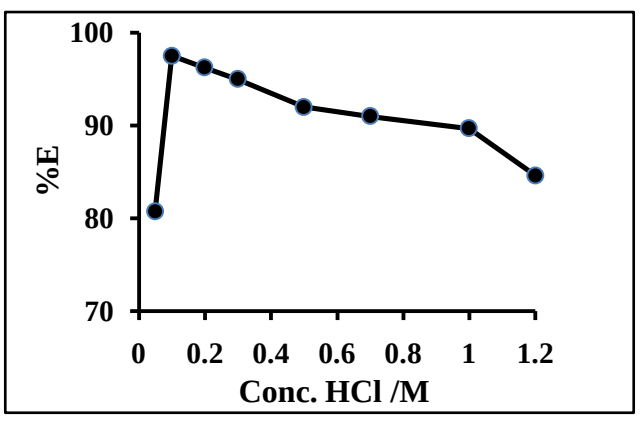

Figure 3 : Effect of HCl on extractability of Cr(VI)

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 $Cr_2O_7^{2-}$ as well as the smaller anion Cl^- to large cation $[H\text{-}BTABN]^+$ thereby led to increase their dissociation equilibrium. This behaviour led to decrease ion pair complex formation with $Cr_2O_7^{2-}$ 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 $Cr_2O_7^{2-}$ 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 μg Cr (VI) as $Cr_2O_7^{-2}$ or 0.1 M HCl, 0.5 mL of 0.1% Triton X100 plus various concentrations ($1x10^{-6}$-$1x10^{-3}$ M) of BTABN and subjected to the general CPE procedure. The results are shown in Figures 4.

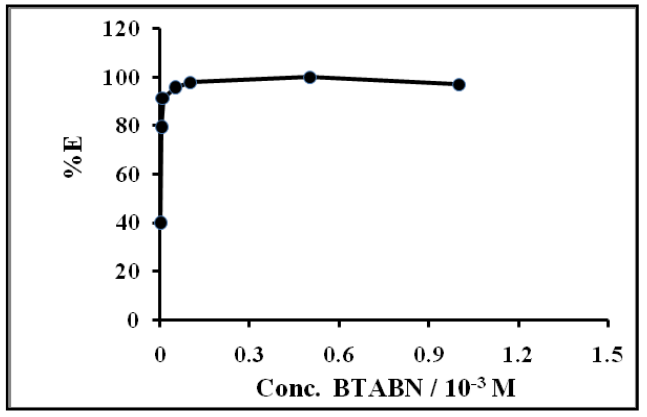

Figure 4 : Effect of BTABN concentration

It was appeared that the magnitude of the extraction efficiency increased sharply by increasing BTABN concentration and reached a plateau up to $1x10^{-4}$M. Therefore, a concentration of $5x10^{-4}$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 $1x10^{-4}$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 preconcentation factor [12]. The effect of Triton X-100 amount was conducted by taking 10 mL solution containing 20 μg $Cr_2O_7^{2-}$, $5x10^{-4}$ 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

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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.

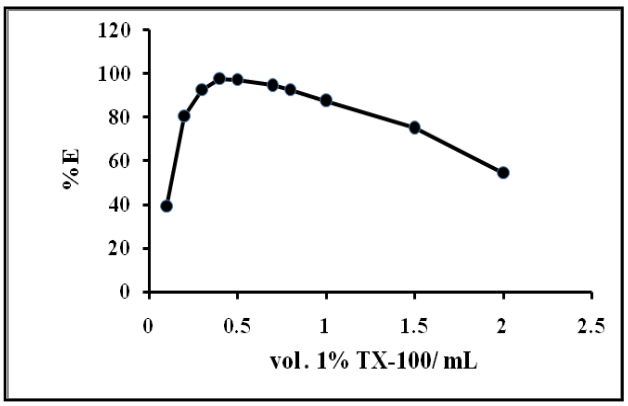

Figure 5 : Effect of Triton X-100 amount

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 µg of $Cr_2O_7^{2-}$ by varying the temperature between 70-80 °C at 25 min and time between 5 and 40 min at 80 °C ,keeping other variables at optimal. A preliminary experiment has indicated that at temperature below 70 ^{0}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 complexe cannot be well separated. However, the results have shown that at temperature of 80 °C and time of 25 min gave a maximum extraction efficiency of 98.56% .But, at higher temperatures than 80 °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 [H–BTABN]$^+$;$HCr_2O_7^-$ 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_{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 $Cr_2O_7^{2-}$ with (BTABN).

T °C	70	75	78	80
T °K	343	348	351	353
1/T	2.915	2.8735	2.849	2.8329
K_{ex}x10^9	1.9263	2.200	2.858	3.606

These thermodynamic equilibrium constants (K_{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_{ex} versus inverse temperature in Kelvin gave a straight line and from its slope, the enthalpy of extraction (ΔH_{ex}) can be calculated for CPE method as shown in Figure 6. While the values of entropy (ΔS_{ex}) and Gibb free energy (ΔG_{ex}) of this extraction process are determined from following thermodynamic relationships [$\Delta G_{ex} = -RT \ln K_{ex}$] and [$\Delta G_{ex} = \Delta H_{ex} - T\Delta S_{ex}$] respectively. Once ($\Delta H_{ex}$) and ($\Delta G_{ex}$) are obtained, the$\Delta S_{ex}$ is calculated from second relationship and the results are summarized in Table 2.

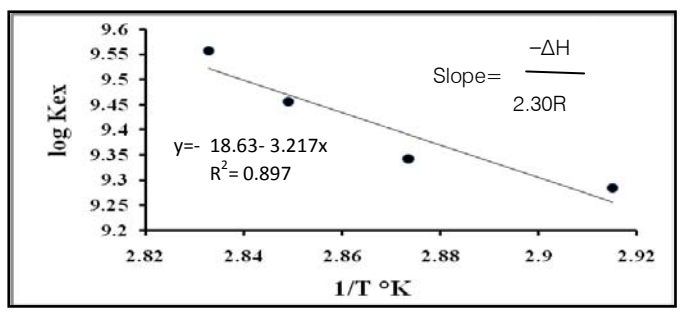

Figure 6 : Extraction constant K_{ex} as a function of equilibrium temperature for ion pair complex of $Cr_2O_7^{2-}$ with (BTABN)

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Table 2 : Thermodynamic parameters for the extraction of $Cr_2O_7^{2-}$ ion-pair complex by CPE

T° (°K)	ΔH_{ex} (KJ mol^{-1})	$-\Delta G_{ex}$ (KJ mol^{-1})	ΔS_{ex} (J mol^{-1})
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 (ΔH_{ex}) is quite low and equal to 0.0544 KJ mol^{-1}, indicating that the endothermic reaction for the solubilisation process of ion pair (H–BTABN$^+$; $HCr_2O_7^-$) complex is controlled by positive value of ΔH_{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 ΔH_{ex}, the dehydration of micelles (i.e. decrease the value of ΔH_{solv} and increase ΔH_{hyd}) is achieved resulting in increasing the phase-volume ratio thus extraction efficiency enhancement [13].

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

The variation of ΔG_{ex} with temperature at optimum conditions of the extraction system (Table 2) was revealed that ΔG_{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 ΔG_{ex}, the large spontaneous process is. Accordingly, the spontaneity of ion pair complex extraction is governed by the negative value of ΔG_{ex} [14]. The entropy (ΔS_{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	λ_{max}	Absorbance	Molar absorptivity (L mol^{-1} cm^{-1})
Amyl alcohol	443	1.037	2.69x10^4
Methanol	433	1.002	2.60x10^4
Chloroform	colloid	-	-
Acetone	445	0.140	3.636x10^3
Ethanol	475	0.855	2.221x10^4

It can been 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 absorbitivity), (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 (H–BTABN$^+$; $HCr_2O_7^-$) 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 [15] .

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Table 4 : Effect of surfactant type on CPE for the extraction $Cr_2O_7^{2-}$ with BTABN.

Surfactant	Tw-20	Tw-80	SDS	TX-114	TX-100
λ_{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 ±10%. The selectivity of CPE for Cr(VI) ion as $Cr_2O_7^2$ was conducted by studying the effect of some salts containing , for example, both cations (Na^+ and K^+) and metal anions (I^-, WO_4^{2-} and $Mo_7O_{24}^-$) in addition to picrate, $C_2O_4^{2-}$, ClO_4^- ,$S_2O_3^{2-}$ and NO_3^- ions on the extraction efficiency of $Cr_2O_7^{2-}$ 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 interfernts have no appreciable effect on the Cr(VI) extractability expect I^- and 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 $Cr_2O_7^{2-}$ with BTABN (percent extraction = 98.56%).

Interferent	Percent extraction (%E) found	$\%E_{rel}$
$KClO_4$	92.21	-6.4
$Na_2C_2O_4$	96.68	-1.9
Picric acid	92.63	-6.0
NaI	83.09	-15.6
$(NH_4)_2MoO_4$	74.83	-24.0
Na_2WO_4	97.48	-1.1
$Na_2 S_2O_4$	95.28	-3.4

k) Stiochoimetry of the Extracted Complex

It is reported that the analysis of the dependence log D = *f* (log $C_{REAGENT}$) permits the determination of the stiochoimetry in the extracted complex [16]. Consequently, the slope in the Figure 7 for log D = *f* (log C_{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 $[H\text{-}BTABN]^+;HCrO_4^-$.

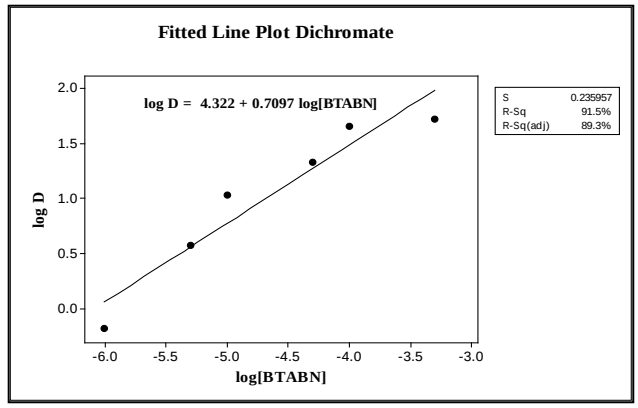

Figure 7 : log D = *f* (logC_{BTABN})

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 μg mL^{-1} were taken and subjected to the general CPE and the Cr (VI) was determined spectrophotometry at λ_{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±0.003534) x-(0.0016±0.00389] was statistically valid. This because of the ratio (MS_{reg}/ MS_{error}] for 1 and 6 degree of freedom (*DOF*), larger than critical values (F16 = 5.987 at 95% CI), indicating that the prediction based on the regression is satisfactory (Table 7).

The limit of detection (LOD= 0.017 μg mL^{-1}) and limit of quantitation (LOQ= 0.0568 μg 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; LOD = 3 σ_B/s; LOQ = 10 σ_B/*s*, where (σ_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 [17] and Suvardhan et al [18] who used the combined CPE-ETAAS and FAAS, respectively. But, it was worse than that obtained by Li et al [19] and Shemirani et al [20] 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 μg L^{-1}, the detection limit was of 0.34 μg 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.

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Table 6 : Figures of merit for the determination of $Cr_2O_7^{2-}$ by the proposed method

Parameter	value
λ_{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± tsb) at 95%	0.428±0.003534
C.L. for the intercept (a± tsa) at 95%	-0.0016±0.00389
Concentration range (μg mL^{-1})	
Limit of Detection (μg mL^{-1})	0.1-2.0
Limit of Quantitation (μg mL^{-1})	0.0170
Sandell's sensitivity	0.0568
(μg cm^{-2}/0.001A.U)	1.16 x 10^{-7}
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	
Composition of complex (M: L)*	$4.47x10^4$
RSD% (n=7) at 2 μg mL^{-1}	1:1
Preconcentration factor**	0.31
Enrichment factor***	250
	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
l 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 [21] 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_o) 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 μg 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 μg g^{-1} [22] while the permissible limit for Cr in Dutch standards is 100 µg g^{-1}[23]. 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 µg g^{-1} and in dusty and loamy soil is of 14.8 – 81.0 µg g^{-1} [24].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 µg g $-^{1}$ [25].

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 µg g^{-1} with concentration range of 0.24 to 2.72 µg 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 µg g^{-1} respectively, indicating that all water samples analyzed were mostly above the maximum permitted concentration for protection of aquatic life and drinking [26].

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 μg g^{-1} and ranged from 0.40 to 2.65 μg 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±0.055 μg g^{-1}) in Tanning site of the

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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 µg L^{-1} (27).

Table 8 : Cr (VI) content (µg 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	
2	5.84±0.161	4.98±0.136	$\overline{X}_d$ = 0.0160
3	7.20±0.451	6.90±0.368	S_d=0.035777
4	4.88±0.205	5.33±0.311	$t_{cal(n=5)}$= 1.0
5	5.44±0.417	5.21±0.224	$t_{crit.}$at95%
			df;4=2.78
			P-value=0.374

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 (µg 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	
2	1.00±0.903	0.97±0.341	$\overline{X}_d$=0.115714
3	0.80±0.168	0.77±0.624	S_d= 0.144897
4	1.20±0.569	1.10±0.335	$t_{cal(n=8)}$=
5	BDL*	BDL*	2.11$t_{crit.}$at 95%
6	1.60±0.611	1.55±0.258	df;7=2.36
7	0.72±0.187	0.69±0.038	P-value=0.079
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 (µg 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	
2	0.56±0.127	0.52±0.627	$\overline{X}_d$=0.236000
3	0.80±0.519	0.81±0.253	S_d =0.455006
4	2.72±0.492	1.69±0.085	$t_{cal(n=5)}$= 1.19
5	0.24±0.620	0.20±0.710	$t_{crit.}$at95%
6	BDL*	BDL*	df;4=2.78
7	BDL*	BDL*	P=0.301

**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 (µg g^{-1}) in plants and vegetable samples withstatistical paired t-test at 95% confidence level.

Sample	Proposed method	AAS method	Paired t -test
1	BDL	BDL	
2	2.65±0.400	1.8±0.059	$\overline{X}_d$= 0.323333
3	BDL	BDL	S_d= 0.456216
4	BDL	BDL	$t_{cal(n=3)}$= 1.23
5	BDL	BDL	$t_{crit.}$at95%
6	0.40±0.625	0.35±0.026	df;2=4.30
7	0.80±0.183	0.73±0.53	P-value=0.344
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) (µg 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	
2	3360±0.2	3358.4±0.17	$\overline{X}_d$= 0.992500
3	500.0±0.3	499.2±0.26	S_d=0.710557
4	0.8±0.05	0.730±0.17	$t_{cal(n=4)}$=2.79
			$t_{crit.}$at 95% df;3
			=3.18
			P-value=0.068

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 $Cr_2O_7^{2-}$ 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

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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 speectrophotometric 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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Abstract- The kinetics of redox reduction of Toluidine blue (hereafter referred to as TB^+) by dithionate ion have been studied in acidic medium under pseudo-first order condition of excess $[S_2O_6^{2-}]$ at 31± 1°C, [H+] = 1 x 10^{-2} mol dm^{-3}, ionic strength (I) = 0.5 mol dm^{-3} (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.

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KINETIC APPROACH TO THE REDUCTION OF TOLUIDINE BLUE BY DITHIONATE ION IN AQUEOUS ACIDIC MEDIUM

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

Babatunde O.A [α] & Ajayi J.O [σ]

Abstract- The kinetics of redox reduction of Toluidine blue (hereafter referred to as TB^+) by dithionate ion have been studied in acidic medium under pseudo-first order condition of excess $[S_2O_6^{2-}]$ at 31± 1ºC, $[H^+]$ = 1 x 10^{-2} mol dm^{-3}, ionic strength (I) = 0.5 mol dm^{-3} (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:

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

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

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 coloureddyewhich is a phenothiazinethat 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 pneumocysticscarinii 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].

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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^+ 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^+ were prepared by dissolving known quantities in distilled water and the observed λ max =600nm whichagrees 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 constantat 1x10^{-3}mol dm^{-3}, $[H^+]$ = 1x10^{-2}mol dm^{-3}, I= 0.5mol dm^{-3}, λ max=600nm, T= 31± 1^{O}C and varying the concentration of $S_2O_6^{2-}$from (1 – 6) x 10^{-3}moldm^{-3}. The absorbance of the reacting mixture was obtained after the reaction had gone to completion by the steady readings recorded after 24hours. The stoichiometry was then evaluated from the plot of absorbance against different concentrations of $S_2O_6^{2-}$.

c) Kinectic Measurements

The kinetics of the reaction was monitored under various conditions by following decrease in the absorbance of TB^+ at λ max = 600 nm on a colorimeter 252. All measurements were made under pseudo - first order conditions with $[S_2O_6^{2-}]$ in large excess over $[TB^+]$. The pseudo-first order plots of log(A_t A_∞) versus time were made, where$A_t$and$A_\infty$are the absorbance attime (t)and at theend of the reaction respectively. From the slope of the plots, the pseudo-first order rate constants (k_o) were determined and second order rate constant

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(k_2) were obtained fromk_o as k_o / $[S_2O_6^{2-}]$. 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) x 10^{-2} mol dm^{-3} while $[TB^+]$ and $[S_2O_6^{2-}]$ were kept constant at T = 31 ± 1°C , λ max = 600 nm and I = 0.5 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) moldm^{-3}(NaCl) while the concentration of other reactants were kept constant at 31± 1°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 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)x 10^{-3}mol dm^{-3} where X = Ca^{2+}, Mg^{2+}, NO_3^- and SO_4^{2-}while the concentration of other reagents were kept constant.

h) Test for intermediate complex formation

The spectrophotometric testwas carriedout by comparing the electronic spectra of the reaction mixture and that of TB^+ alone within 400 – 700 nm.Michealis – Mentens plot of $1/k_o$ 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 ± 1°C, $[H^+]$ = 1x10^{-2}mol dm^{-3} and I = 0.5mol dm^{-3}. After the completion of the reaction a colorless solution was obtained.This indicates the destruction of the quinoid (chromophore) group. $BaCl_2$ 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:

$TB^+ + S_2O_6^{2-}$ Products…1

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_∞) 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_o(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 constant$k_2$were calculated as k_o / $[S_2O_6^{2-}]$ and the reading were found to be fairly constant, the results are presented in Table 1. Thus the overall order of the reaction is 5/2at constant $[H^+]$ and the rate equation for the reaction is:

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

wherek_2 = 1.19 x 10^{-1} $dm^3mol^{-1}s^{-1}$

Similar fractional order has been reported for redox reaction of TB^+ with dithionite ion, stannous ion andphenylhydrazine (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 ofk_2 versus $[H^+]$ was linear with an intercept on k_2 axis. The acid dependence rate constant is therefore given as:

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

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

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

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

From equation 4it 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 $HS_2O_6^-$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 √I gave a slope of 0.07 (Fig.3).This suggests that some other interactions

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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 enhancingeffects 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 throughthe origin fig. 4. This further suggests the absence of formation of intermediate complex thereby supporting the outer – sphere mechanism for this reactionBabatunde [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 λ 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 excessdilute HCl indicating the presence of SO_4^{2-} ions.

a) Reaction mechanism

The mechanism proposed below accommodates all the experimental findingsfor the reaction of Toluidine blue dye with dithionate ion.

$$S_2O_6^{2-} \underset{}{\overset{K_1}{\rightleftharpoons}} 2\,{}^{\cdot}SO_3^- \ldots 5$$

$$S_2O_6^{2-} + H^+ \underset{}{\overset{K_2}{\rightleftharpoons}} HS_2O_6^- \ldots 6$$

$${}^{\cdot}SO_3^{2-} + H^+ \underset{}{\overset{K_3}{\rightleftharpoons}} H{}^{\cdot}SO_3^- \ldots 7$$

$$HS_2O_6^- + TB^+ \underset{}{\overset{K_4}{\rightleftharpoons}} [\,TB^+ \,//\, HS_2O_6^-\,] \ldots 8$$

$$H{}^{\cdot}SO_3^- + TB^+ \underset{}{\overset{K_5}{\rightleftharpoons}} [\,TB^+ \,//\, H{}^{\cdot}SO_3^-\,] \ldots 9$$

$$[\,TB^+ \,//\, HS_2O_6^-\,] \xrightarrow{k_6} \text{Products} \ldots 10$$

slow

$$[\,TB^+ \,//\, H{}^{\cdot}SO_3^-\,] \xrightarrow{k_7} \text{Products} \ldots 11$$

slow

Equations10 and 11 are the rate determining steps.

$$\text{Rate} = k_6\,[\,TB^+ \,//\, HS_2O_6^-\,] + k_7\,[\,TB^+ \,//\, H{}^{\cdot}SO_3\,] \ldots 12$$

From equation 8

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

And from equation 6

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

From equation 9

$$[\,TB^+ \,//\, H{}^{\cdot}SO_3\,] = K_5\,[\,H{}^{\cdot}SO_3\,]\,[\,TB^+\,] \ldots 15$$

From equation 7

$$[\,H{}^{\cdot}SO_3\,] = K_3\,[\,{}^{\cdot}SO_3^{2-}\,][\,H^+\,] \ldots 16$$

From equation 5

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

$$\text{Rate} = K_2K_4\,k_6\,[\,S_2O_6^{2-}\,][\,TB^+\,]\,[\,H^+\,] + K_1^{1/2}K_3K_5k_7[S_2O_6^{2-}\,][\,TB^+\,]\,[\,H^+\,] \;..18$$

Rearrange equation

$$(K_2K_4\,k_6 + K_1^{1/2}K_3K_5k_7)[\,H^+\,][\,TB^+][\,S_2O_6^{2-}\,]^{3/2} \ldots 1$$

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

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

V. Conclusion

Redox reaction of toluidine blue dye with Dithionate 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].

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Table1 : Pseudo-first order and second order rate constants for the reduction of TB^+ by dithionate ions in aqueous acidic medium at $[TB^+] = 1 \times 10^{-3}$ mol dm^{-3} , λ max = 600 nm , T = 31 ± 1°C.

$[S_2O_6^{2-}] \times 10^{-3}$ x 10^{-2} mol dm^{-3}	$[H^+]$ mol dm^{-3} mol dm^{-3}	I(NaCl) x 10^{-3}	k_o k_2 x 10^{-1}	s^{-1} dm^3 mol^{-1} s^{-1}
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	

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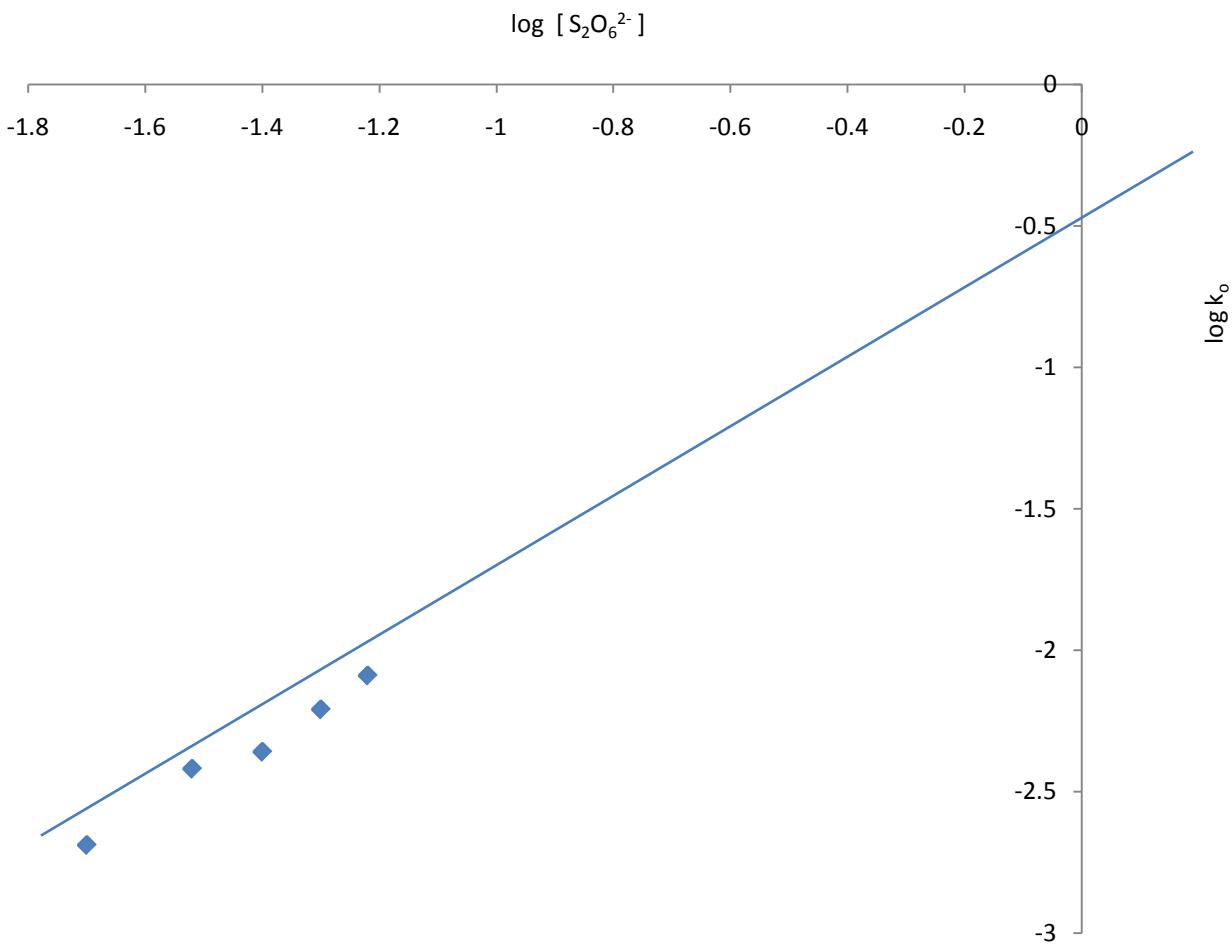

Fig.1 : Pseudo – first order plot oflog k_o versus log [$S_2O_6^{2-}$] for reduction of TB^+ by $S_2O_6^{2-}$ at [TB^+] = 1 x 10^{-3}mol dm^{-3} , [H^+] = 1 x 10^{-2} mol dm^{-3} , I = 0.5 mol dm^{-3} ,λ_{max} = 600 nm , T = 31± 1°C.

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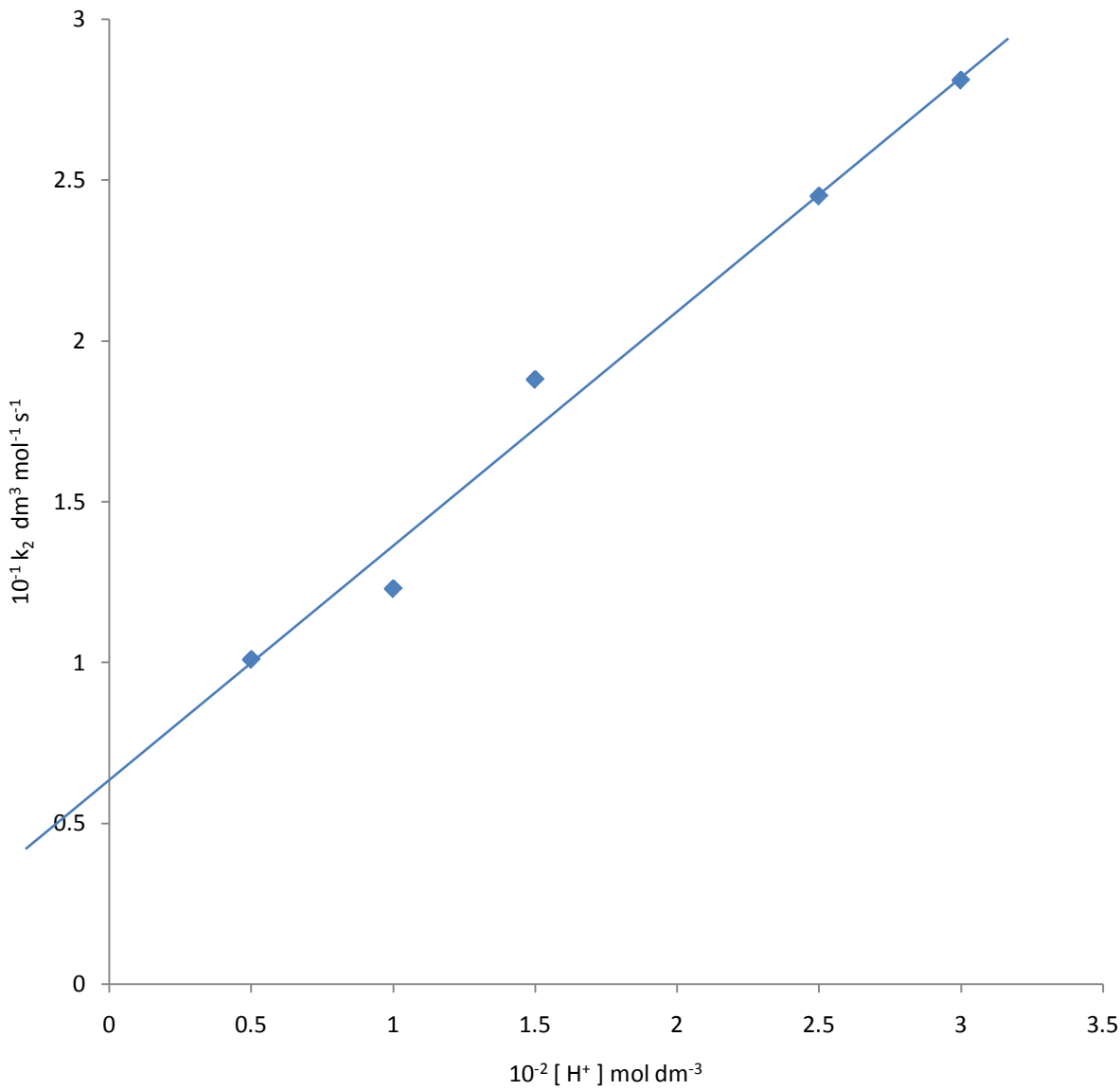

Fig. 2 : Pseudo – first order plot of k_2 versus $[H^+]$ for the reduction of dithionate ion at $[S_2O_6^{2-}] = 30 \times 10^{-3}$ mol dm^{-3}, $[TB^+] = 1 \times 10^{-3}$ mol dm^{-3} , I = 0.5 mol dm^{-3} ,λ_{max} = 600 nm , T = 31 ± 1°C.

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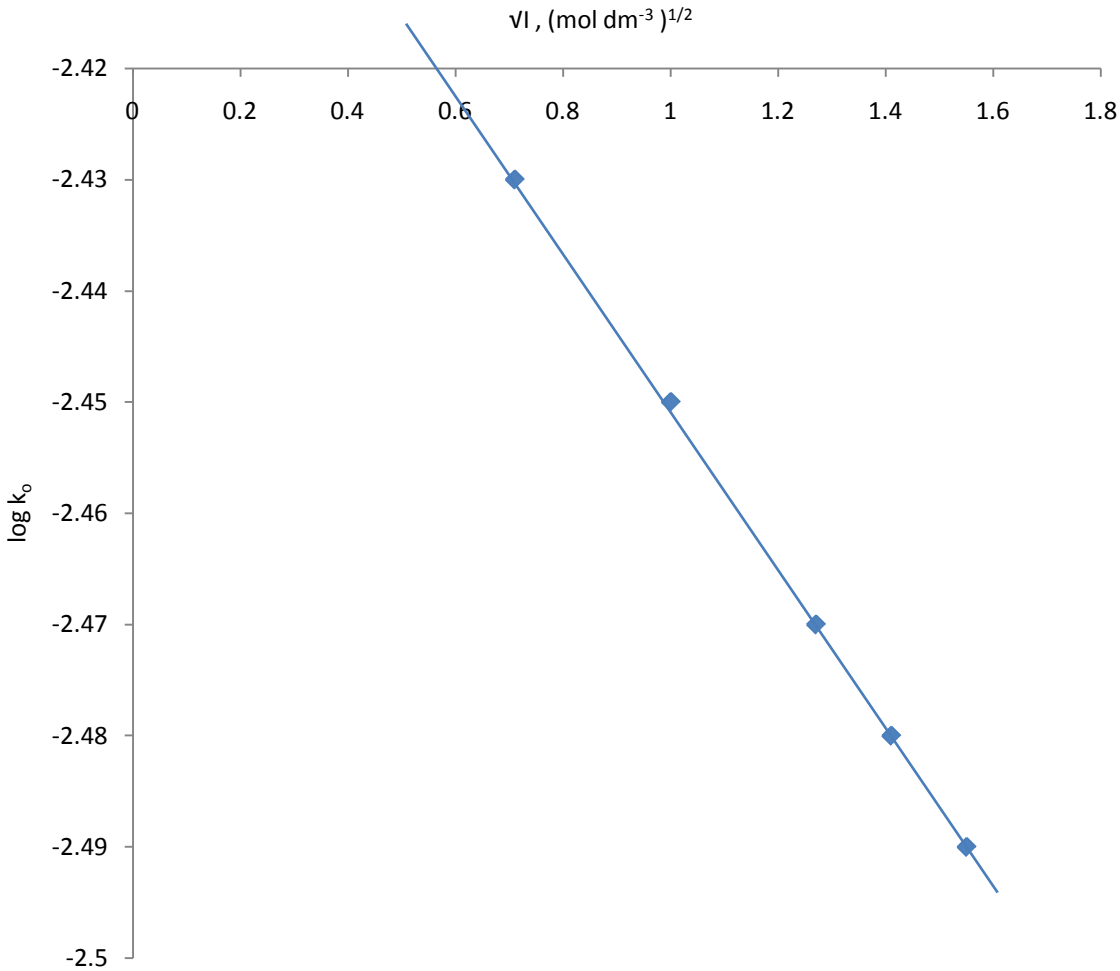

Fig.3 : Plot of $\log k_o$ versus √I for the reduction of TB^+ by dithionate ion.

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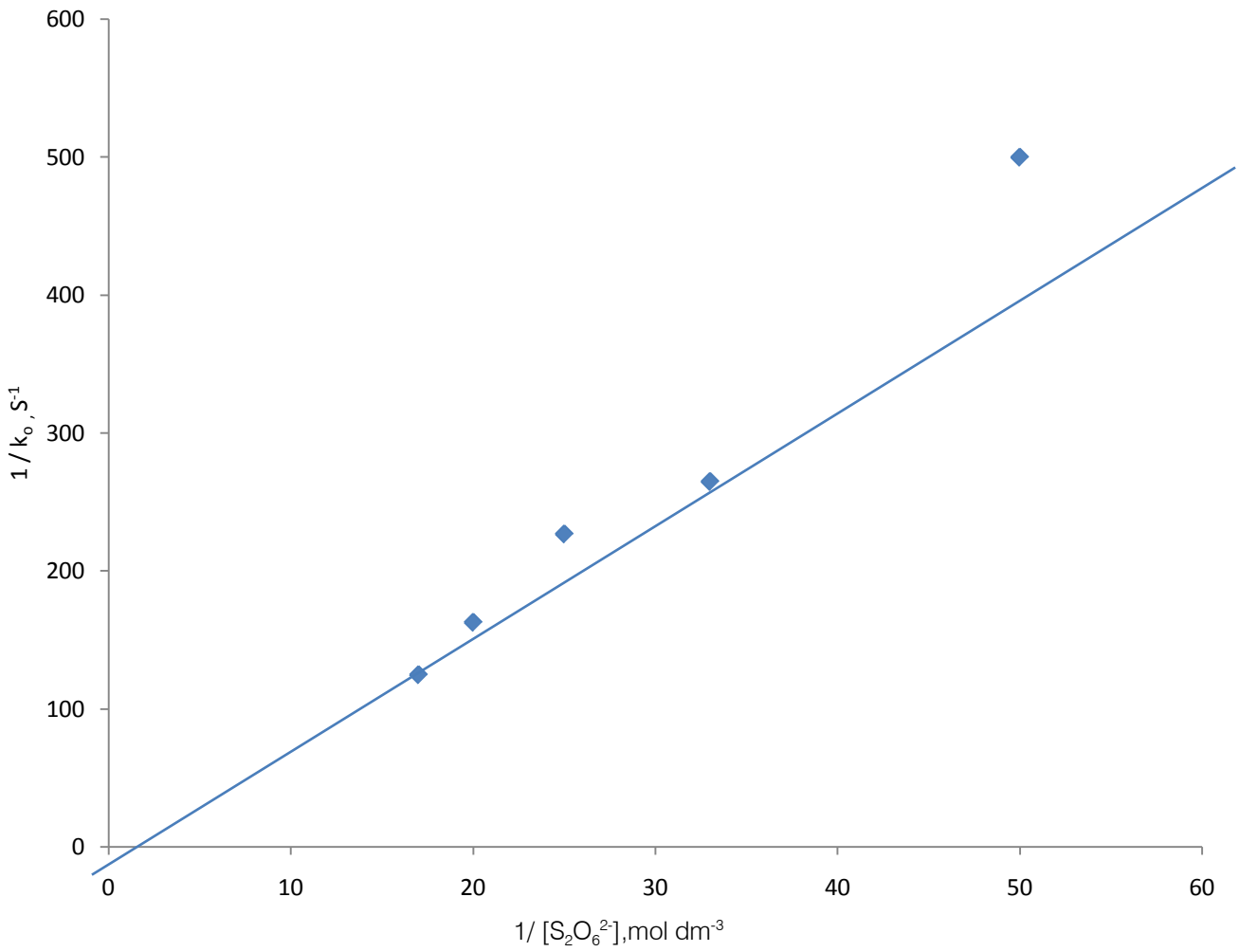

Fig. 4 : Michealis – Menten's plot for the reduction of TB^+ with $S_2O_6^{2-}$ ion at $[TB^+] = 1 \times 10^{-3}$mol dm^{-3}, $[S_2O_6^{2-}] = 30 \times 10^{-3}$mol dm^{-3}, $[H^+] = 1 \times 10^{-2}$mol dm^{-3}, I = 0.5 mol dm^{-3}(NaCl) , λmax = 600 nm, T = 31± 1°C.

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 $[TB^+] = 1 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1 \times 10^{-2}$ mol dm^{-3}, $[S_2O_6^{2-}] = 30 \times 10^{-3}$mol dm^{-3}, I = 0.5 mol dm^{-3} (NaCl) , λmax = 600 nm , T = 31± 1°C.

D s^{-1} dm^3 mol^{-1} s^{-1}	k_o x 10^{-2}	k_2 x 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

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Table 3 : Pseudo-first order and second order rate constants for the effect of added ions on the reaction of TB^+ with dithionate ions at $[TB^+] = 1 \times 10^{-3}$ mol dm^{-3} , $[S_2O_6^{2-}] = 30 \times 10^{-3}$ mol dm^{-3} , $[H^+] = 1 \times 10^{-2}$ mol dm^{-3} , I = 0.5 mol dm^{-3}(NaCl) , λmax = 600 nm, T = 31± 1^{0}C.

X	10^{-3}[X], mol dm^{-3}	$10^{-2}k_o$ s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
SO_4^{2-}	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_3^-	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^{2+}	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^{2+}	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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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).

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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).

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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.

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

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:

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

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

By putting:

$$U = C.r(eq3)$$

Equation (2) becomes:

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

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: Ci.

b) Mathematical model

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

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

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

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

We can obtained:

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

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

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

The kinetics for the matter transported is:

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

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

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

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.

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

This expression can be rewritten using finite difference method.

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

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 CH3-CH2-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:

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

Effect of The diffusion coefficient is given by this relation:

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

En cm²/s:

$$D=1{,}390.10^{-6}cm^2/s$$

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.

a. The ethanol concentration within the sphere is low, however the surfaces.
b. 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.

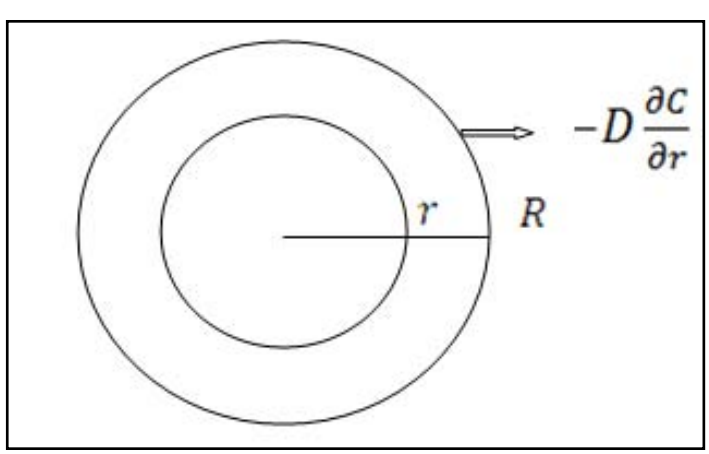

Figure 1 : Schema of the circular cross section of a sphere of radius R.

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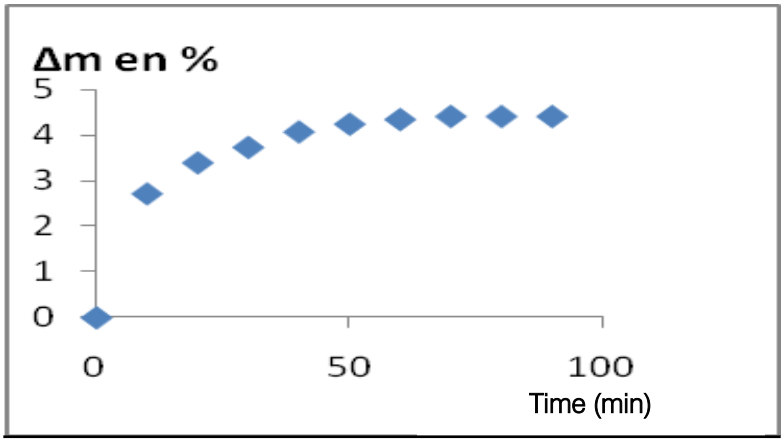

Figure 2 : Variation of the amount of ethanol in the PEVA

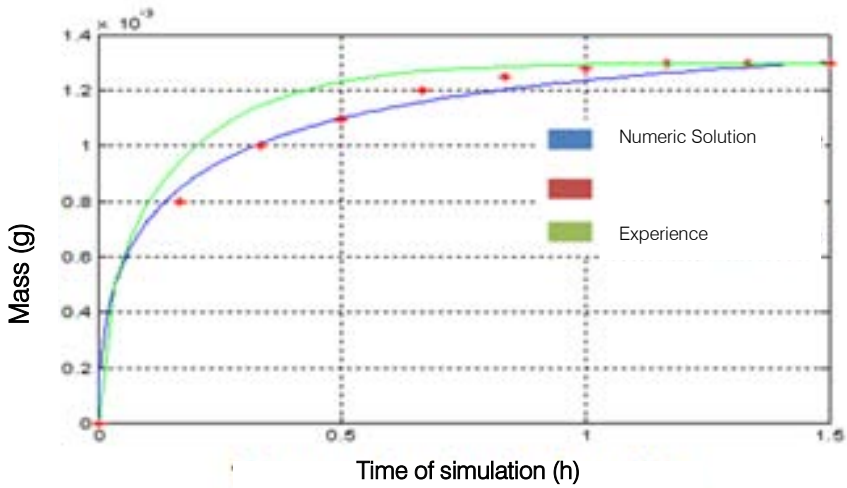

Figure 3 : The amount of ethanol in the material as a function of time for the simulation of three solutions.

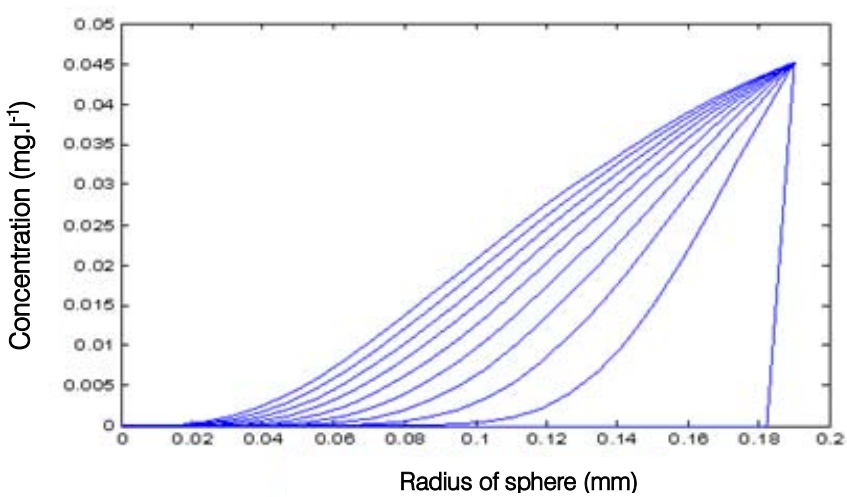

Figure 4 : The profile of the concentration of ethanol after every 10 min

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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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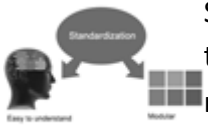

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(c) Up to ten keywords, that precisely identifies the paper's subject, purpose, and focus.

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(e) Resources and techniques with sufficient complete experimental details (wherever possible by reference) to permit repetition; sources of information must be given and numerical methods must be specified by reference, unless non-standard.

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(h) Brief Acknowledgements.

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References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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