Online ISSN: 2249-4626
Print ISSN: 0975-5896

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

Volume 13 Issue 8 Version 1.0

© 2001-2013 by Global Journal of Science Frontier Research , USA

Volume 13 Issue 50 was originally issued as B8

Global Journal of Science Frontier Research: B
Chemistry

Volume 13 Issue 50
Originally issued as B8

Global Journal of Science Frontier Research: B
Chemistry

Volume 13 Issue 8 (Ver. 1.0)

Open Association of Research Society

© Global Journal of Science Frontier Research .2013.

All rights reserved.

This is a special issue published in version 1.0 of "Global Journal of Science Frontier Research." By Global Journals Inc.

All articles are open access articles distributed under "Global Journal of Science Frontier Research"

Reading License, which permits restricted use. Entire contents are copyright by of "Global Journal of Science Frontier Research" unless otherwise noted on specific articles.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without written permission.

The opinions and statements made in this book are those of the authors concerned. Ultraculture has not verified and neither confirms nor denies any of the foregoing and no warranty or fitness is implied.

Engage with the contents herein at your own risk.

The use of this journal, and the terms and conditions for our providing information, is governed by our Disclaimer, Terms and Conditions and Privacy Policy given on our website http://globaljournals.us/terms-and-condition/menu-id-1463/

By referring / using / reading / any type of association / referencing this journal, this signifies and you acknowledge that you have read them and that you accept and will be bound by the terms thereof.

All information, journals, this journal, activities undertaken, materials, services and our website, terms and conditions, privacy policy, and this journal is subject to change anytime without any prior notice.

Incorporation No.: 0423089
License No.: 42125/022010/1186
Registration No.: 430374
Import-Export Code: 1109007027
Employer Identification Number (EIN):
USA Tax ID: 98-0673427

Global Journals Inc.

*(A Delaware USA Incorporation with "Good Standing"; **Reg. Number: 0423089**)*

Sponsors: Open Association of Research Society
Open Scientific Standards

Publisher's Headquarters office

Global Journals Headquarters
301st Edgewater Place Suite, 100 Edgewater Dr.-Pl,
Wakefield MASSACHUSETTS, Pin: 01880,
United States of America
USA Toll Free: +001-888-839-7392
USA Toll Free Fax: +001-888-839-7392

Offset Typesetting

Global Journals Incorporated
2nd, Lansdowne, Lansdowne Rd., Croydon-Surrey,
Pin: CR9 2ER, United Kingdom

Packaging & Continental Dispatching

Global Journals
E-3130 Sudama Nagar, Near Gopur Square,
Indore, M.P., Pin:452009, India

Find a correspondence nodal officer near you

To find nodal officer of your country, please email us at *local@globaljournals.org*

eContacts

Press Inquiries: *press@globaljournals.org*
Investor Inquiries: *investers@globaljournals.org*
Technical Support: *technology@globaljournals.org*
Media & Releases: *media@globaljournals.org*

Pricing (Including by Air Parcel Charges):

For Authors:
22 USD (B/W) & 50 USD (Color)
Yearly Subscription (Personal & Institutional):
200 USD (B/W) & 250 USD (Color)

Integrated Editorial Board
(Computer Science, Engineering, Medical, Management, Natural Science, Social Science)

John A. Hamilton,"Drew" Jr.,
Ph.D., Professor, Management
Computer Science and Software Engineering
Director, Information Assurance Laboratory
Auburn University

Dr. Henry Hexmoor
IEEE senior member since 2004
Ph.D. Computer Science, University at Buffalo
Department of Computer Science
Southern Illinois University at Carbondale

Dr. Osman Balci, Professor
Department of Computer Science
Virginia Tech, Virginia University
Ph.D.and M.S.Syracuse University, Syracuse, New York
M.S. and B.S. Bogazici University, Istanbul, Turkey

Yogita Bajpai
M.Sc. (Computer Science), FICCT
U.S.A.Email:
yogita@computerresearch.org

Dr. T. David A. Forbes
Associate Professor and Range Nutritionist
Ph.D. Edinburgh University - Animal Nutrition
M.S. Aberdeen University - Animal Nutrition
B.A. University of Dublin- Zoology

Dr. Wenying Feng
Professor, Department of Computing & Information Systems
Department of Mathematics
Trent University, Peterborough,
ON Canada K9J 7B8

Dr. Thomas Wischgoll
Computer Science and Engineering,
Wright State University, Dayton, Ohio
B.S., M.S., Ph.D.
(University of Kaiserslautern)

Dr. Abdurrahman Arslanyilmaz
Computer Science & Information Systems Department
Youngstown State University
Ph.D., Texas A&M University
University of Missouri, Columbia
Gazi University, Turkey

Dr. Xiaohong He
Professor of International Business
University of Quinnipiac
BS, Jilin Institute of Technology; MA, MS, PhD,. (University of Texas-Dallas)

Burcin Becerik-Gerber
University of Southern California
Ph.D. in Civil Engineering
DDes from Harvard University
M.S. from University of California, Berkeley & Istanbul University

Dr. Bart Lambrecht
Director of Research in Accounting and FinanceProfessor of Finance
Lancaster University Management School
BA (Antwerp); MPhil, MA, PhD (Cambridge)

Dr. Carlos García Pont
Associate Professor of Marketing
IESE Business School, University of Navarra
Doctor of Philosophy (Management), Massachusetts Institute of Technology (MIT)
Master in Business Administration, IESE, University of Navarra
Degree in Industrial Engineering, Universitat Politècnica de Catalunya

Dr. Fotini Labropulu
Mathematics - Luther College
University of ReginaPh.D., M.Sc. in Mathematics
B.A. (Honors) in Mathematics
University of Windso

Dr. Lynn Lim
Reader in Business and Marketing
Roehampton University, London
BCom, PGDip, MBA (Distinction), PhD, FHEA

Dr. Mihaly Mezei
ASSOCIATE PROFESSOR
Department of Structural and Chemical Biology, Mount Sinai School of Medical Center
Ph.D., Etvs Lornd University
Postdoctoral Training,
New York University

Dr. Söhnke M. Bartram
Department of Accounting and FinanceLancaster University Management SchoolPh.D. (WHU Koblenz)
MBA/BBA (University of Saarbrücken)

Dr. Miguel Angel Ariño
Professor of Decision Sciences
IESE Business School
Barcelona, Spain (Universidad de Navarra)
CEIBS (China Europe International Business School).
Beijing, Shanghai and Shenzhen
Ph.D. in Mathematics
University of Barcelona
BA in Mathematics (Licenciatura)
University of Barcelona

Philip G. Moscoso
Technology and Operations Management
IESE Business School, University of Navarra
Ph.D in Industrial Engineering and Management, ETH Zurich
M.Sc. in Chemical Engineering, ETH Zurich

Dr. Sanjay Dixit, M.D.
Director, EP Laboratories, Philadelphia VA Medical Center
Cardiovascular Medicine - Cardiac Arrhythmia
Univ of Penn School of Medicine

Dr. Han-Xiang Deng
MD., Ph.D
Associate Professor and Research
Department Division of Neuromuscular Medicine
Davee Department of Neurology and Clinical NeuroscienceNorthwestern University
Feinberg School of Medicine

Dr. Pina C. Sanelli
Associate Professor of Public Health
Weill Cornell Medical College
Associate Attending Radiologist
NewYork-Presbyterian Hospital
MRI, MRA, CT, and CTA
Neuroradiology and Diagnostic Radiology
M.D., State University of New York at Buffalo,School of Medicine and Biomedical Sciences

Dr. Roberto Sanchez
Associate Professor
Department of Structural and Chemical Biology
Mount Sinai School of Medicine
Ph.D., The Rockefeller University

Dr. Wen-Yih Sun
Professor of Earth and Atmospheric SciencesPurdue University Director
National Center for Typhoon and Flooding Research, Taiwan
University Chair Professor
Department of Atmospheric Sciences, National Central University, Chung-Li, TaiwanUniversity Chair Professor
Institute of Environmental Engineering, National Chiao Tung University, Hsin-chu, Taiwan.Ph.D., MS The University of Chicago, Geophysical Sciences
BS National Taiwan University, Atmospheric Sciences
Associate Professor of Radiology

Dr. Michael R. Rudnick
M.D., FACP
Associate Professor of Medicine
Chief, Renal Electrolyte and Hypertension Division (PMC)
Penn Medicine, University of Pennsylvania
Presbyterian Medical Center, Philadelphia
Nephrology and Internal Medicine
Certified by the American Board of Internal Medicine

Dr. Bassey Benjamin Esu
B.Sc. Marketing; MBA Marketing; Ph.D Marketing
Lecturer, Department of Marketing, University of Calabar
Tourism Consultant, Cross River State Tourism Development Department
Co-ordinator , Sustainable Tourism Initiative, Calabar, Nigeria

Dr. Aziz M. Barbar, Ph.D.
IEEE Senior Member
Chairperson, Department of Computer Science
AUST - American University of Science & Technology
Alfred Naccash Avenue – Ashrafieh

President Editor (HON.)

Dr. George Perry, (Neuroscientist)
Dean and Professor, College of Sciences
Denham Harman Research Award (American Aging Association)
ISI Highly Cited Researcher, Iberoamerican Molecular Biology Organization
AAAS Fellow, Correspondent Member of Spanish Royal Academy of Sciences
University of Texas at San Antonio
Postdoctoral Fellow (Department of Cell Biology)
Baylor College of Medicine
Houston, Texas, United States

Chief Author (HON.)

Dr. R.K. Dixit
M.Sc., Ph.D., FICCT
Chief Author, India
Email: authorind@computerresearch.org

Dean & Editor-in-Chief (HON.)

Vivek Dubey(HON.)
MS (Industrial Engineering),
MS (Mechanical Engineering)
University of Wisconsin, FICCT
Editor-in-Chief, USA
editorusa@computerresearch.org

Sangita Dixit
M.Sc., FICCT
Dean & Chancellor (Asia Pacific)
deanind@computerresearch.org

Suyash Dixit
(B.E., Computer Science Engineering), FICCTT
President, Web Administration and
Development , CEO at IOSRD
COO at GAOR & OSS

Er. Suyog Dixit
(M. Tech), BE (HONS. in CSE), FICCT
SAP Certified Consultant
CEO at IOSRD, GAOR & OSS
Technical Dean, Global Journals Inc. (US)
Website: www.suyogdixit.com
Email:suyog@suyogdixit.com

Pritesh Rajvaidya
(MS) Computer Science Department
California State University
BE (Computer Science), FICCT
Technical Dean, USA
Email: pritesh@computerresearch.org

Luis Galárraga
J!Research Project Leader
Saarbrücken, Germany

Contents of the Volume

i. Copyright Notice
ii. Editorial Board Members
iii. Chief Author and Dean
iv. Table of Contents
v. From the Chief Editor's Desk
vi. Research and Review Papers

1. Kinetic Approach to the Mechanism of Reduction of (7-Amino-8-Methyl-Phenothiazin-3-Ylidene)-Dimethyl-Ammonium Chloride by Thiocyanate Ion in Acidic Medium. *1-7*
2. A New Spectrophotometric Determination of Chromium (VI) as $Cr_2O_7^{2-}$ after Cloud-Point Extraction using a Laboratory -Made Organic Reagent. *9-19*
3. Kinetic Approach to the Reduction of Toluidine Blue by Dithionate Ion in Aqueous Acidic Medium. *21-30*
4. Ethanol Diffusion in Polyethylene Vinyl Acetate: Modelling and Experimentation. *31-34*

vii. Auxiliary Memberships
viii. Process of Submission of Research Paper
ix. Preferred Author Guidelines
x. Index

Global Journal of Science Frontier Research
Chemistry
Volume 13 Issue 8 Version 1.0 Year 2013
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

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

Nigerian Defence Academy, Nigeria

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 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.

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

GJSFR-B Classification : FOR Code: 039999



Strictly as per the compliance and regulations of :

© 2013. Babatunde O. A & Nwaji M. U. This is a research/review paper, distributed under the terms of the Creative Commons Attribution-Noncommercial 3.0 Unported License http://creativecommons.org/licenses/by-nc/3.0/), permitting all non commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

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).

Authors α σ: Department of Chemistry, Nigerian Defence Academy, Kaduna Nigeria.

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

© 2013 Global Journals Inc. (US)

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 $0.5 \times 10^{-3} \leq [H^+] \geq 2.5 \times 10^{-3}$ mol dm^{-3} while concentration of TB and SCN ion were kept constant at 1.0×10^{-5} and 20×10^{-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] = 0.2×10^{-5} - 1.0×10^{-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:

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

Product analysis was carried out by reacting equimolar amount of the dye and the thiocyanate at $[H^+] = 1.0 \times 10^{-3}$ 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:

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

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:

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

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

© 2013 Global Journals Inc. (US)

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

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

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.

© 2013 Global Journals Inc. (US)

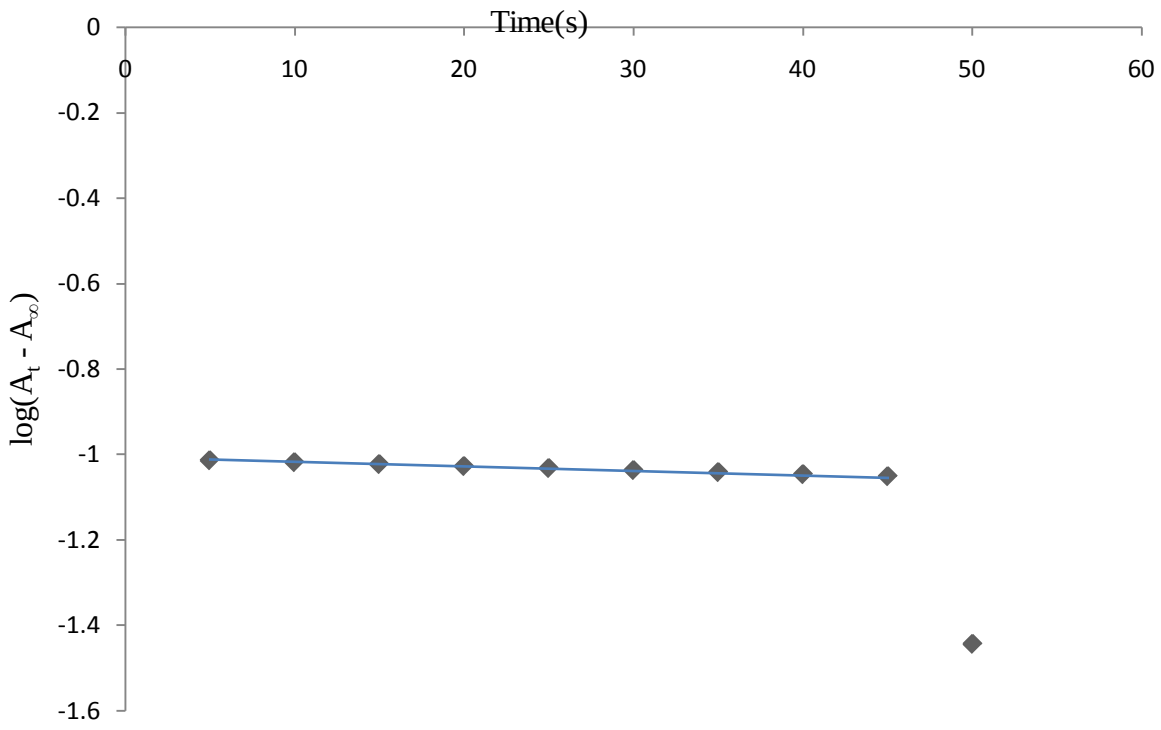

Figure 1 : Pseudo-first Order Plot for the Reduction of TB by SCN

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

© 2013 Global Journals Inc. (US)

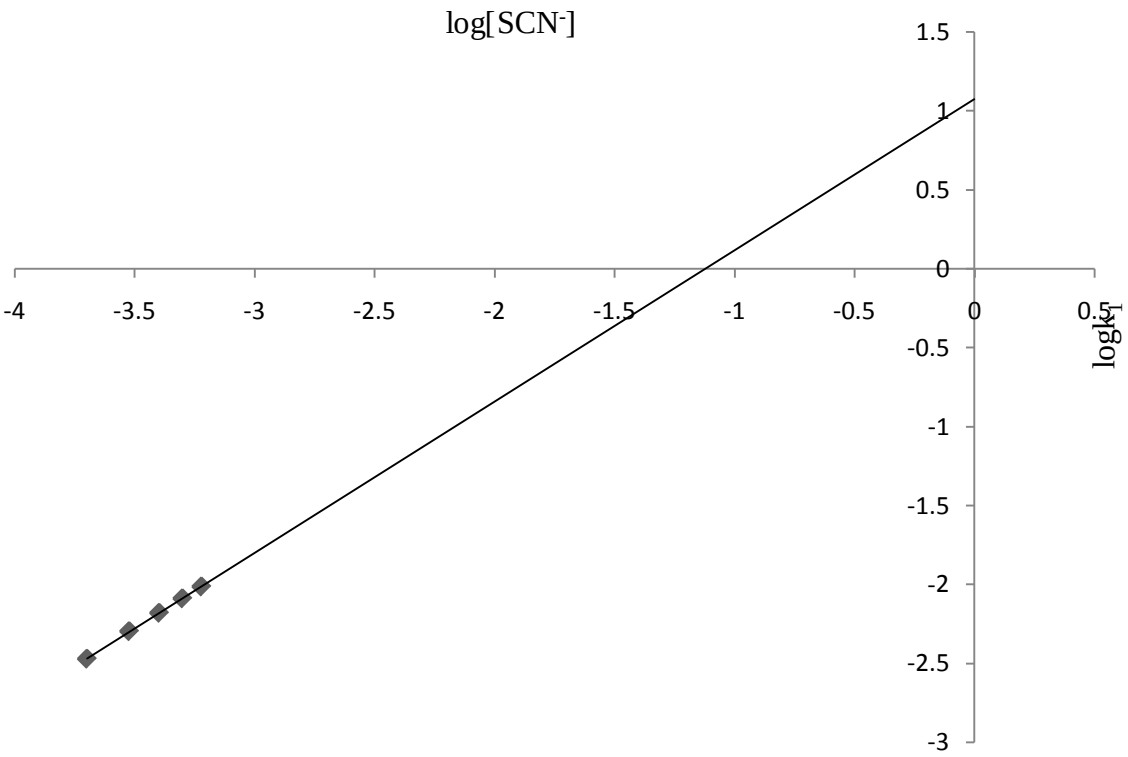

Figure 2 : Plot of log k_1 vs log [SCN^-]for the Reduction of TB by SCN^-

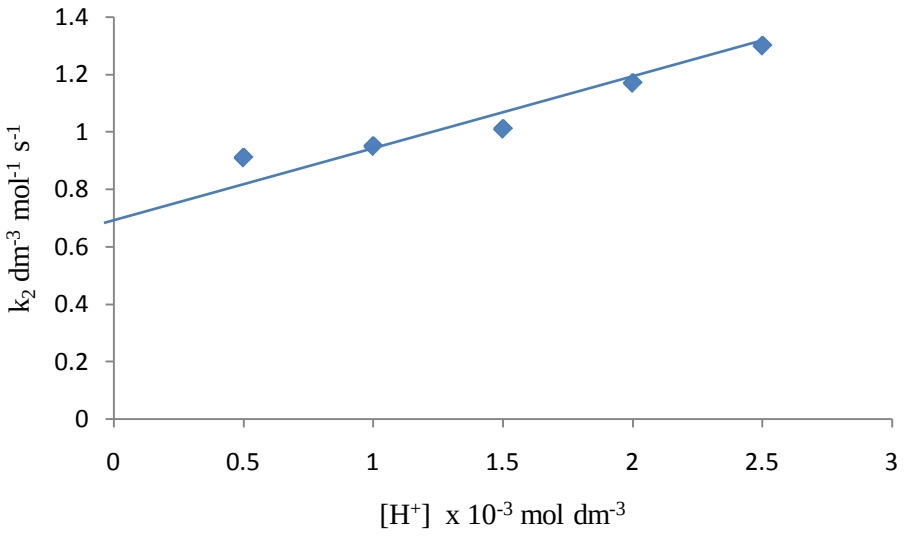

Figure 3 : Plot of k_2 versus [H^+] of reduction of TB by SCN^-

© 2013 Global Journals Inc. (US)

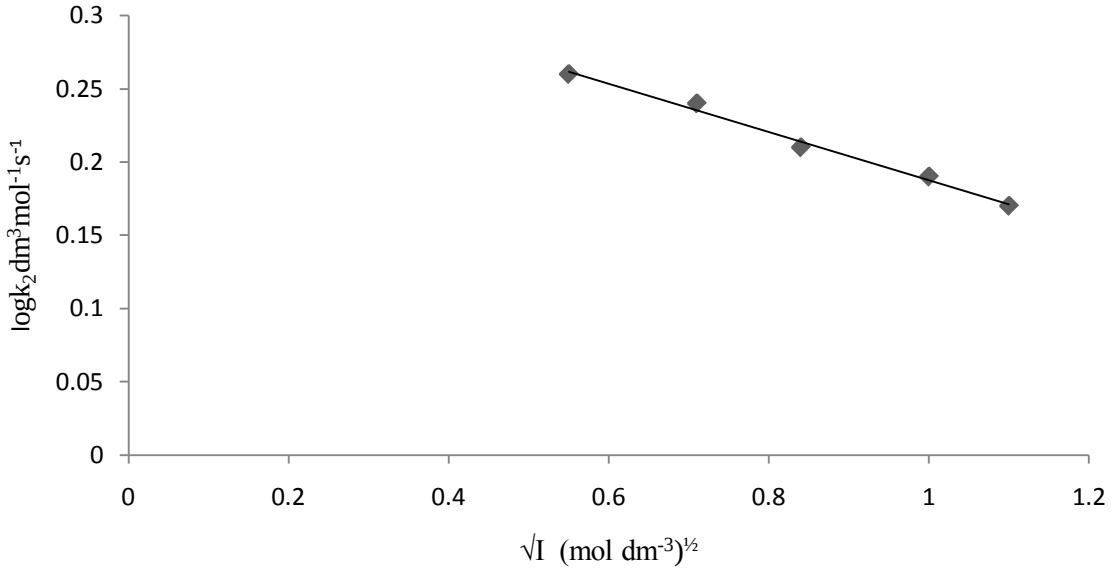

Figure 4 : plot of log $k_2$versus √I for the reduction of TB^+ by $[SCN^-]$

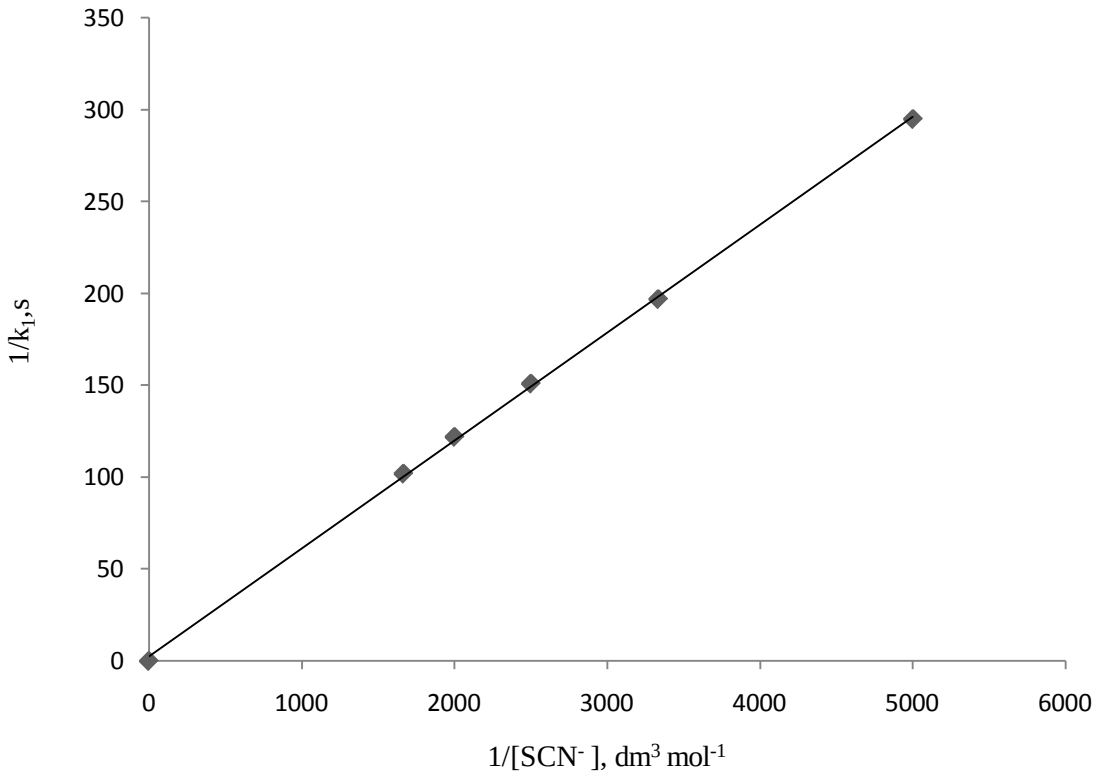

Figure 5 : Michaelis-Menten's plot for the reduction of TB by SCN^-

© 2013 Global Journals Inc. (US)

References Références Referencias

1. J. D. Chandler, B. J. Day, (2012). *BiochemPharmacol.*84(11):1381-7.
2. G. E. Conner, C. Wijkstrom-Frei, S. H. Randell, V. E. Fernandez, M. Salathe, (2007). *FEBS Letters* 581 (2): 271–278.
3. W. E. White, K. M. Pruitt, B. Mansson-Rahemtulla, (1983). *Antimicrobial Agents and Chemotherapy* 23 (2): 267–272.
4. E. L. Thomas, T. M. Aune, (1978). . *Infection and Immunity* 20 (2): 456–463.
5. M. Childers, G. Eckel, A. Himmel, J. Caldwell, (2007). *Medical Hypotheses* 68 (1): 101–112.
6. P. Moskwa, D. Lorentzen, K. J. Excoffon, J. Zabner, P. B. McCray, W. M. Nauseef, C. Dupuy, B. Bánfi, (2007). *American Journal of Respiratory and Critical Care Medicine* 175 (2): 174–183.
7. Y. Xu, S. Szép, Z. Lu, (2009). "*Proceedings of the National Academy of Science U.S.A.* 106 (48): 20515–20519.
8. L. Minarowski, D. Sands, A. Minarowska, A.Karwowska, A.Sulewska, M. Gacko, E. Chyczewska, (2008) *Folia Histochemicaet Cytobiologica* 46 (2): 245–246.
9. M. Junaid,M. M. Choudhary, Z. A. Sobani, G. Murtaza, S. Qadeer, N. S. Ali, M. J. Khan, A. Suhail, (2012)..*World J SurgOncol.*10: 57
10. O. P. Panwar, A. Kumar, R. Amet, S. C.Ameta, (2008). *Macedonian Journal of Chemistry and Chemical Engineering.*27 (2): 133–139
11. M. Kiese,W. Lorcher,N. Weger,A. Zierer,(1972) *Eur. J. Clin. Pharmacol*, 4, 115-118.
12. M. Kiese, H. D. Waller,(1951). *Naunyn-Schmiedebergs Arch Pharmakol*, 213, 44(in German).
13. J. F.Iyun,A. O. Peters, O. A. Babatunde, (2005). *J. Chem. Soc. Nig*. 30.2, 114-118.
14. S. A. Hamza, J. F Iyun, S. O. Idris, (2012). *Der PharmaChemica*, 4 (1):1-9
15. [15] S. A. Hamza, J. F. Iyun, S. O. Idris, (2012). *Journal of Chemical and Pharmaceutical Research.*4(1): 6-13.
16. S. O. Idris, J. F. Iyun, E. B. Agbaji, (2005). *Nig.J. Sci. Res.,* 5(1): 83-89.
17. D. Benson, (1969). Mechanism of inorganic reactions in solution. McGraw- Hill U.K pp: 153.

© 2013 Global Journals Inc. (US)

This page is intentionally left blank

© 2013 Global Journals Inc. (US)

Global Journal of Science Frontier Research
Chemistry
Volume 13 Issue 8 Version 1.0 Year 2013
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

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

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

University of Baghdad, Iraq

Abstract- A new trend in extraction and preconcentration of chromium (VI) using laboratory-made azo dye reagent 2- [benzenethiazolylazo]-4-benzenenaphthol (BTABN) after cloud-point extraction (CPE) and its determination by spectrophotometrically. The method involved the reaction of $Cr_2O_7^{2-}$ with BTABN in acidic medium forming a hydrophobic ion-association complex [HBTABN][HCr_2O_7] which is entrapped into micelle-mediating solvent (Triton X-100) and the Cr(VI) detected spectrophotometrically at λ_{max} of 475 nm. The effect of the several factors on the CPE efficiency is optimized by one-factor-at-a-time (OFAT). Extensive thermodynamic study has been presented to understand the mechanism of extraction and solubilisation of ion-association complex in micelles. The interferences effect of divers ions is also considered. Under the optimized conditions, enrichment factor of 270 is achieved leading to limit of detection and limit of quantitation of 0.017 and 0.0568 µg mL^{-1} respectively. The linearity of 0.1-2.0 µg mL^{-1} and sensitivity in term of molar absorptivity is 4.47x104 $L.mol^{-1}.cm^{-1}$ are obtained .The precision (RSD%; n=7) of the proposed method is of 0.31% % at 2.0 µg Cr (VI) mL^{-1}. This method is applied in the determination of Cr (VI) in various environmental and botanical samples.

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

GJSFR-B Classification : FOR Code: 030599



Strictly as per the compliance and regulations of :

© 2013. Zuhair A-A Khammas, Shawkat K. Jawad & Ibtehaj R. Ali. This is a research/review paper, distributed under the terms of the Creative Commons Attribution-Noncommercial 3.0 Unported License http://creativecommons.org/licenses/by-nc/3.0/), permitting all non commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

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

Zuhair A-A Khammas [α], Shawkat K. Jawad [σ] & Ibtehaj R. Ali [ρ]

Abstract- A new trend in extraction and preconcentration of chromium (VI) using laboratory-made azo dye reagent 2-[benzenethiazolylazo]-4-benzenenaphthol (BTABN) after cloud-point extraction (CPE) and its determination by spectrophotometrically. The method involved the reaction of $Cr_2O_7^{2-}$ with BTABN in acidic medium forming a hydrophobic ion-association complex [HBTABN][HCr_2O_7] which is entrapped into micelle-mediating solvent (Triton X-100) and the Cr(VI) detected spectrophotometrically at λ_{max} of 475 nm. The effect of the several factors on the CPE efficiency is optimized by one-factor-at-a-time (OFAT). Extensive thermodynamic study has been presented to understand the mechanism of extraction and solubilisation of ion-association complex in micelles. The interferences effect of divers ions is also considered. Under the optimized conditions, enrichment factor of 270 is achieved leading to limit of detection and limit of quantitation of 0.017 and 0.0568 μg mL^{-1} respectively. The linearity of 0.1-2.0 μg mL^{-1} and sensitivity in term of molar absorptivity is $4.47x10^4$ $L.mol^{-1}.cm^{-1}$ are obtained .The precision (RSD%; n=7) of the proposed method is of 0.31% % at 2.0 μg Cr (VI) mL^{-1}. This method is applied in the determination of Cr (VI) in various environmental and botanical samples.

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

Authors α ρ: Department of Chemistry, College of Science for Women, University of Baghdad, Jadiryiah, Baghdad, Iraq.
e-mail: dr_zuhair@yahoo.com
Author σ : Department of Chemistry, College of Education for Women, University of Kufa, Kufa. Najaf, Iraq. e-mail: shawkat22@yahoo.com

© 2013 Global Journals Inc. (US)

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.

© 2013 Global Journals Inc. (US)

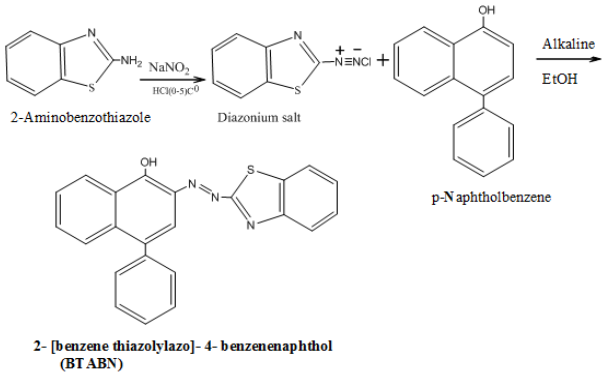

Figure 1 : Synthetic path of BTABN reagent

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

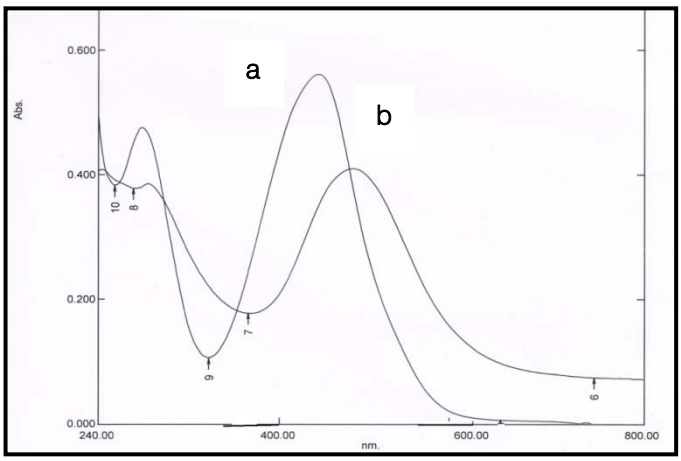

Figure 2 : Absorption spectra of (a) $5x10^{-4}$ M of (BTABN) 10 mL of 20 μg $Cr_2O_7^{2-}$, 0.1 M HCl, ($5x10^{-4}$ M) (BTABN) reagent and 0.5mL (1 % Triton X-100)].

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

© 2013 Global Journals Inc. (US)

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;

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

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

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

or

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

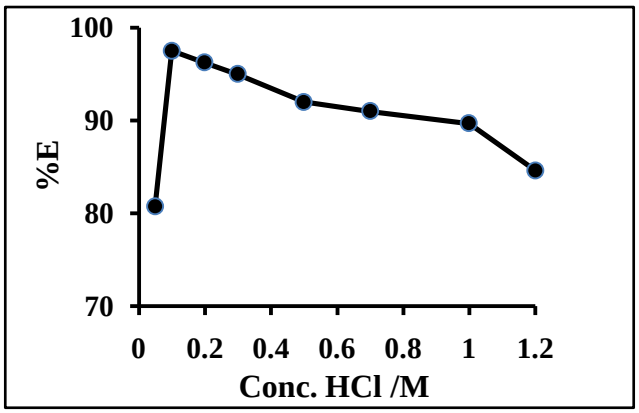

Figure 3 : Effect of HCl on extractability of Cr(VI)

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.

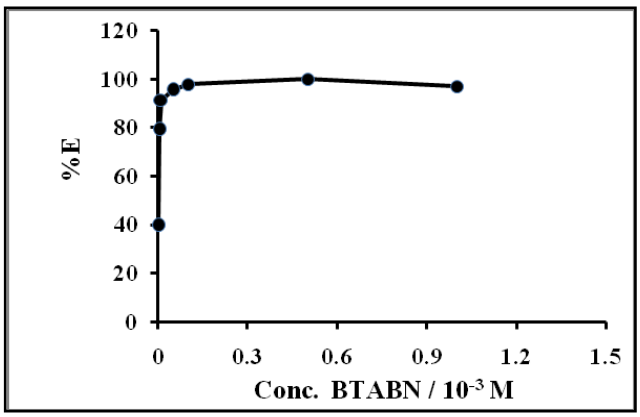

Figure 4 : Effect of BTABN concentration

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

© 2013 Global Journals Inc. (US)

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.

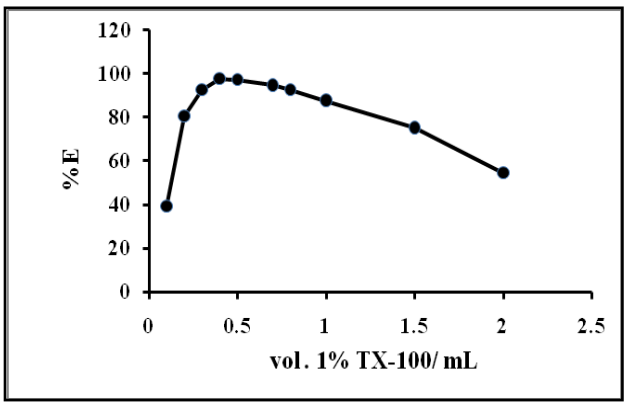

Figure 5 : Effect of Triton X-100 amount

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 [ΔGex=- 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.

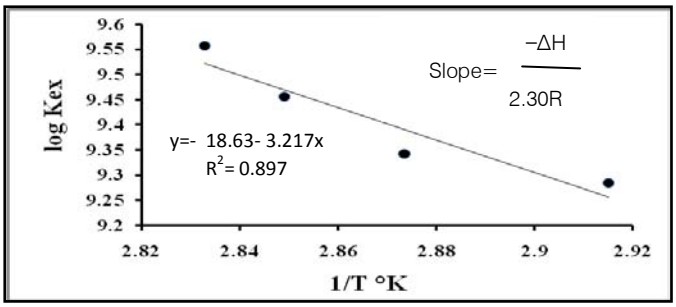

Figure 6 : Extraction constant K_{ex} as a function of equilibrium temperature for ion pair complex of $Cr_2O_7^{2-}$ with (BTABN)

© 2013 Global Journals Inc. (US)

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] .

© 2013 Global Journals Inc. (US)

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 $[H\text{-}BTABN]^+$;$HCrO_4^-$.

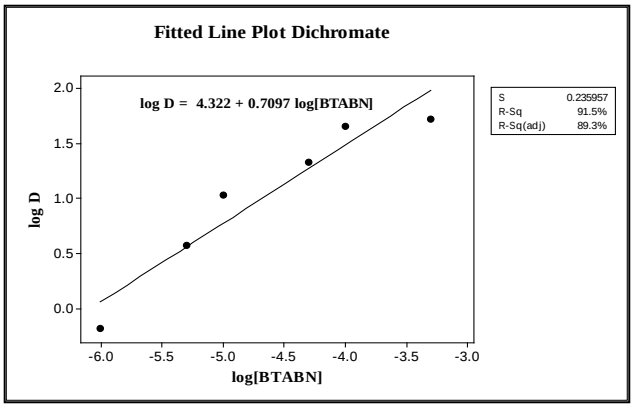

Figure 7 : log D = *f* (logC_{BTABN})

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.

© 2013 Global Journals Inc. (US)

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})	0.1-2.0
Limit of Detection (μg mL^{-1})	0.0170
Limit of Quantitation (μg mL^{-1})	0.0568
Sandell's sensitivity (μg cm^{-2}/0.001A.U)	1.16 x 10^{-7}
Molar absorptivity (L.mol^{-1}.cm^{-1})	4.47x10^4
Composition of complex (M: L)*	1:1
RSD% (n=7) at 2 μg 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
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

© 2013 Global Journals Inc. (US)

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

© 2013 Global Journals Inc. (US)

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.

References Références Referencias

1. Prasad, M.N.V. (2008) Trace elements as contaminates and nutrients-Consequences in ecosystems and human health. John Wiley & Sons, Inc., USA, pp.511 .
2. World Health Organization: Guidelines for Drinking Water Quality, Geneva(1998) WHO, , Vol. 2.
3. EPA (2005) The drinking water criteria document on Chromium, EPA 440/5- 84-030, Office of Drinking Water, U.S. Environment Protection Agency, Washington D.C..
4. Srivastava, N.K.., Jha ,M.K., Mall ,I.D. Singh,D. (2010) Application of genetic engineering for chromium removal from industrial wastewater", World Academy Sci. Eng. Techn. 48,434-439
5. Mizuike,A..(2010) Enrichment techniques for inorganic trace analysis. Springer–Verlag, New York,
6. Dadfarnia S., Shabani, M. A. H. Kamranzadeh E.(2010) Selective cloud point extraction and preconcentration of trace amounts of cadmium prior to flame atomic absorption spectrometric determination. J. Braz. Chem. Soc. 21 ,2353-2358 .
7. Katsaounos, C, Z, Giokas, D.L., Vlessidis, A.G. Paleologos, E.K. and Karayannis, M.I, "The use of surfactant-based separation techniques for monitoring of orthophosphate in natural waters and wastewater", Sci. Total Environ. , 305,157-167(2003)
8. Khammas, Z. A-A., Ali. I.R. Jawad,S.K..(2012) Cloud point extraction and micro amount determination of cadmium as chloro anion complex in realsSamples by using molecular spectrophotometry. J. Kufa Chem. Sci. 6 ,67-85
9. Khammas,Z.A-A, Jawad, A.K., Ali, I.R. (2013) A new approach for extraction and determination of manganese in environmental samples using cloud-point extraction coupled with spectrophotometry. Accepted in C.S.T. ID 505.
10. Langová-Hniličková,M. Sommer ,L.(1969) Reaction of gallium and indium with 4-(2-Thiazolylazo) resorcinol. Talanta,16, 681-690.
11. Standard method for the examination of water and wastewater(1995) 19th edn. American public health association, Washington DC
12. Yıldız, Z., Arslan, G. Tor, A.(2011) Preconcentrative separation of chromium (III) speciesf rom chromium (VI) by cloud point extraction and determination by flame atomic absorption spectrometry. ", Microchim. Acta 174, 399-405 .
13. .Al-Mutawali. N.F. (2000)"Extraction of Mo (VI) ,W (VI) by use crown ether DB18C6 ,M.Sc.Thesis, college of science, Babylon University
14. Purkait, M.K., De, D.S.(2009) Determination of thermodynamic parameters for the cloud point extraction of different dyes using TX-100 and TX-114. Desalination 244, 130–138
15. . Hinze W.L. Pramauro, E. A (1993)Critical review of surfactant-mediated phase separations (cloud-Point extractions): theory and applications", Crit. Rew. Anal. Chem. 24, 133-177
16. .Doroschuk,V.O, Lelyushok,S.O.,Ishchenko, V.B., Kulichenko,S.A.(2004) Flame atomic absorption determination of manganese (II) in natural water after cloud point extraction. Talanta 64, 853-856
17. Madhuchandr, L.M., Nanda, N. Jayaveera, K .N.(2011) Determination of chromium in different water samples using cloud point extraction (CPE) coupled with flame atomic absorption spectrometry (FAAS). R.J.PB.C.S 2, 1119- 1127
18. Suvardhan, K., Lekkala, R.B. Janardhanam, K.(2008) Speciation determination of chromium (III) and (VI) using preconcentration cloud point extraction with flame atomic absorption spectrometry (FAAS). J. Hazard. Mater., 150, 582–586
19. Li, Y.J., Hu, B., Jiang, Z.C. Wu, T.W. Speciation of chromium in water samples by cloud point extraction combined with low temperature electrothermal vaporization ICP-OES. Anal. Lett. , 39, 809-822
20. Shemirani, F., Abkenar, S. D., Mirroshandel, A. A., Salavati-Niasari, M. Kozania, R. R., (2003) Preconcentration and speciation of chromium in water samples by atomic absorption spectrometry after cloud-point extraction. Anal. Sci., 19, 1453-1456 .
21. Minitab® Statistical Software 14(2011)State College, Pennsylvania, USA
22. A protocol for the derivation of environmental and human health soil quality guidelines (1999) CCME, Winnipeg. [A summary of the protocol appears in Canadian environmental quality guidelines, Chapter 7, Canadian Council of Ministers of the Environment, Winnipeg.].
23. Iqbal, M.A., , Chaudhary , M.N., , Zaib , S. , Imran ,M., Ali , K.. Iqbal, A. (2011) Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb) in agricultural soils and spring seasonal plants, irrigated by industrial waste water.J.Environ. Tech. Manag.., 2, 1-7
24. .Dudka, S.(1992) Evaluation of total content of macro- and microelements in the surface layer of soil in Poland. IUNG Pu3awy, R (293), 1 (in Polish)

© 2013 Global Journals Inc. (US)

25. Fendorf S.E.(1995) Surface reactions of chromium in soils and waters, Geoderma ., 67, 55-71
26. Scottish Environmental Protection Agency (SEPA) (2013) Supporting Guidance (WAT-SG-53) Environmental Standards for Discharges to Surface Waters" Vol.4 ,1-28
27. Srivastava, N.K., M. K. Jha, M.K., Mall , I.D. Singh, D.(2010) Application of genetic engineering for chromium removal from industrial wastewater. World Academy Sci. Eng. Techn. 48,434-439

© 2013 Global Journals Inc. (US)

This page is intentionally left blank

© 2013 Global Journals Inc. (US)

Global Journal of Science Frontier Research
Chemistry
Volume 13 Issue 8 Version 1.0 Year 2013
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

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

By Babatunde O.A & Ajayi J.O

Nigerian Defence Academy, Nigeria

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, $[H+] = 1 \times 10^{-2}$ 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.

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

GJSFR-B Classification : FOR Code: 250000



Strictly as per the compliance and regulations of :

© 2013. Babatunde O.A & Ajayi J.O. This is a research/review paper, distributed under the terms of the Creative Commons Attribution-Noncommercial 3.0 Unported License http://creativecommons.org/licenses/by-nc/3.0/), permitting all non commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

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:

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

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 colourеddyewhich 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].

Author α σ: Department of Chemistry, Nigerian Defence Academy, Kaduna. e-mail: oluwafunmilayo.ajayi@yahoo.com

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^OC 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

© 2013 Global Journals Inc. (US)

(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) Kinectics

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:

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

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:

$k_2 = (a + b [H^+])$ …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

© 2013 Global Journals Inc. (US)

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.

$$S_2O_6^{2-} \quad K_1 \quad 2\cdot SO_3^- \ldots 5$$

$$S_2O_6^{2-} + H^+ \quad K_2HS_2O_6^- \ldots 6$$

$$\cdot SO_3^{2-} + H^+ \quad K_3H\cdot SO_3^- \ldots 7$$

$$HS_2O_6^- + TB^+ \quad K_4 \quad [\ TB^+ \ //\ HS_2O_6^-\ ] \ldots 8$$

$$H\cdot SO_3^- + TB^+ \quad K_5 \quad [\ TB^+ // H\cdot SO_3^-\ ] \ldots 9$$

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

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

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

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

$$\text{Rate} = K_2K_4k_6[\ S_2O_6^{2-}\ ][\ TB^+\ ][\ H^+\ ] + K_1^{1/2}K_3K_5k_7[S_2O_6^{2-}][\ TB^+\ ][\ H^+\ ] \ldots 18$$

Rearrange equation

$$(K_2K_4k_6 + K_1^{1/2}K_3K_5k_7)[\ H^+\ ][\ TB^+][\ S_2O_6^{2-}\ ]^{3/2} \ldots 1$$
$$(a + b\ [\ H^+\ ])^2[\ TB^+][\ S_2O_6^{2-}\ ]^{3/2}$$

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].

© 2013 Global Journals Inc. (US)

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 $\pm$ 1^{O}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	

© 2013 Global Journals Inc. (US)

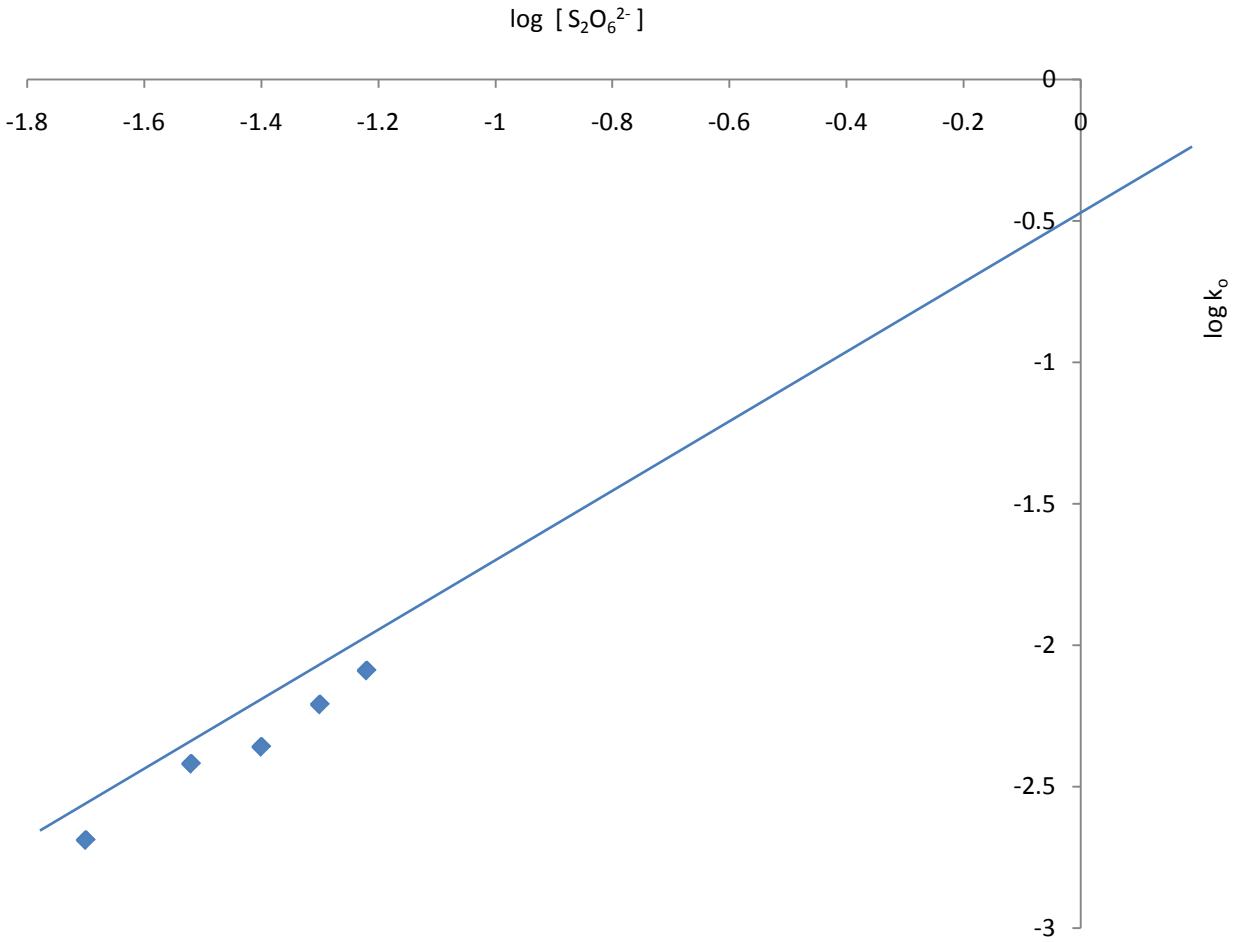

Fig.1 : Pseudo – first order plot oflog k_o versus log [$S_2O_6^{2-}$] for reduction of TB^+ by $S_2O_6^{2-}$ at [TB^+] = 1 x 10^{-3}mol dm^{-3} , [H^+] = 1 x 10^{-2} mol dm^{-3} , I = 0.5 mol dm^{-3} ,λ_{max} = 600 nm , T = 31± 1°C.

© 2013 Global Journals Inc. (US)

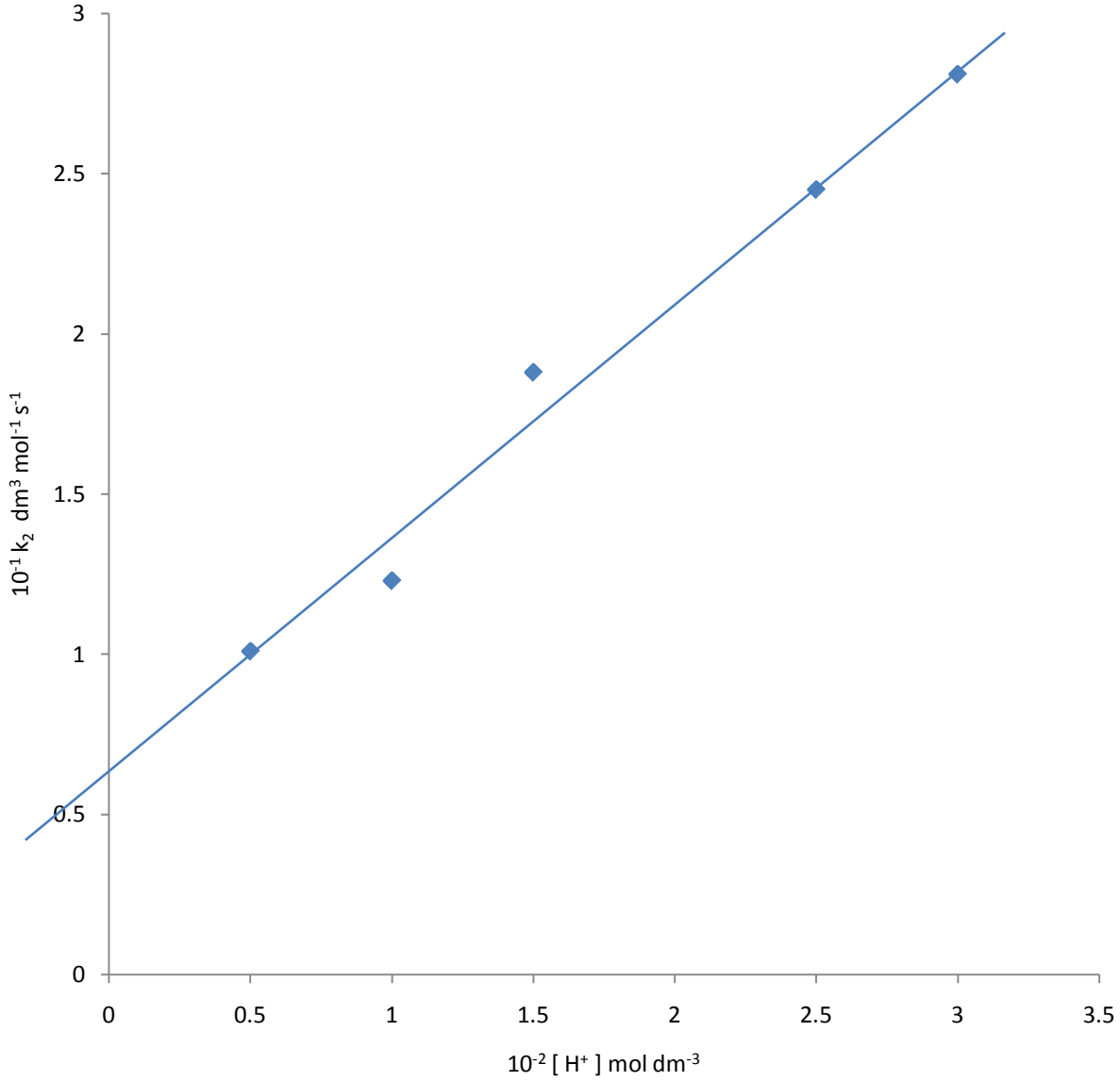

Fig. 2 : Pseudo – first order plot of k_2 versus $[H^+]$ for the reduction of dithionate ion at $[S_2O_6^{2-}] = 30 \times 10^{-3}$ mol dm^{-3}, $[TB^+] = 1 \times 10^{-3}$ mol dm^{-3} , I = 0.5 mol dm^{-3} ,λ_{max} = 600 nm , T = 31 ± 1°C.

© 2013 Global Journals Inc. (US)

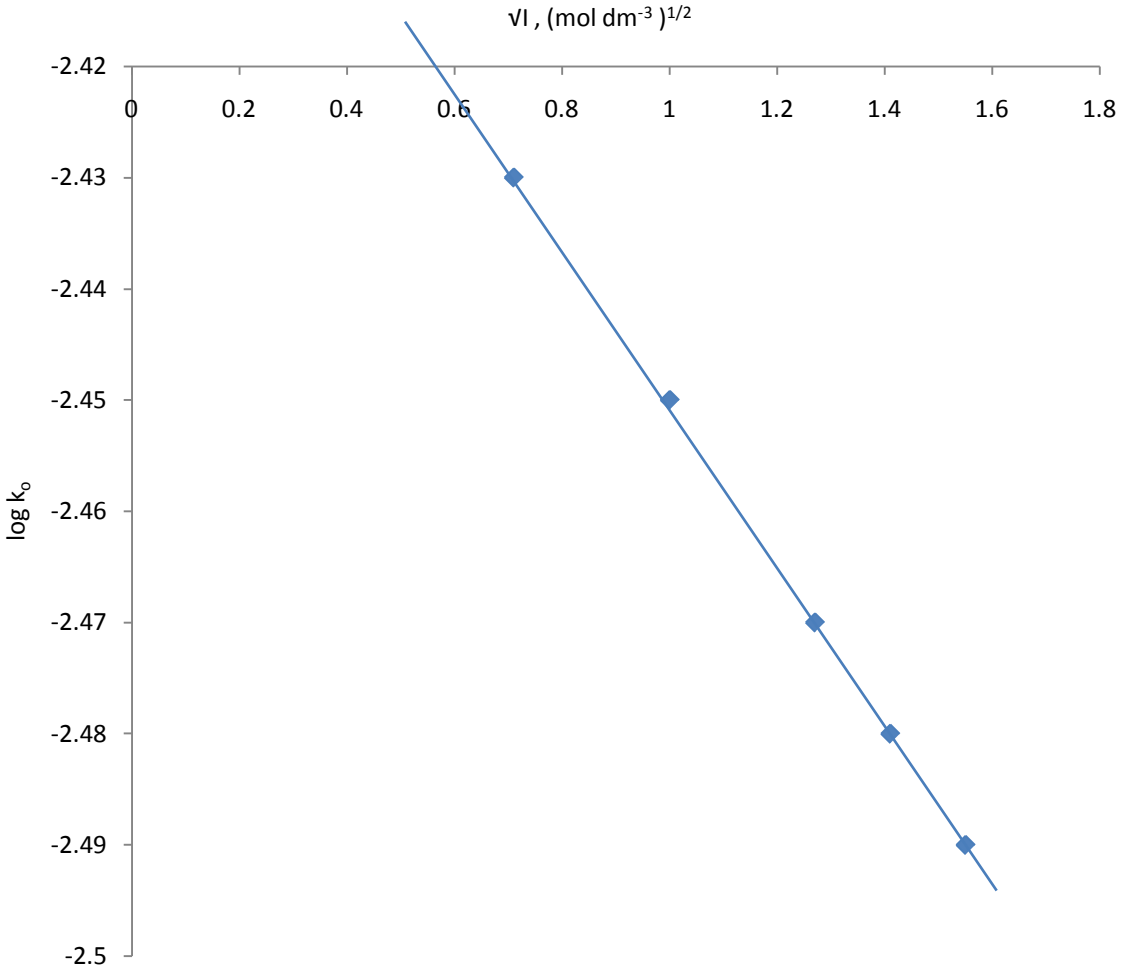

Fig.3 : Plot of logk_o versus √I for the reduction of TB^+ by dithionate ion.

© 2013 Global Journals Inc. (US)

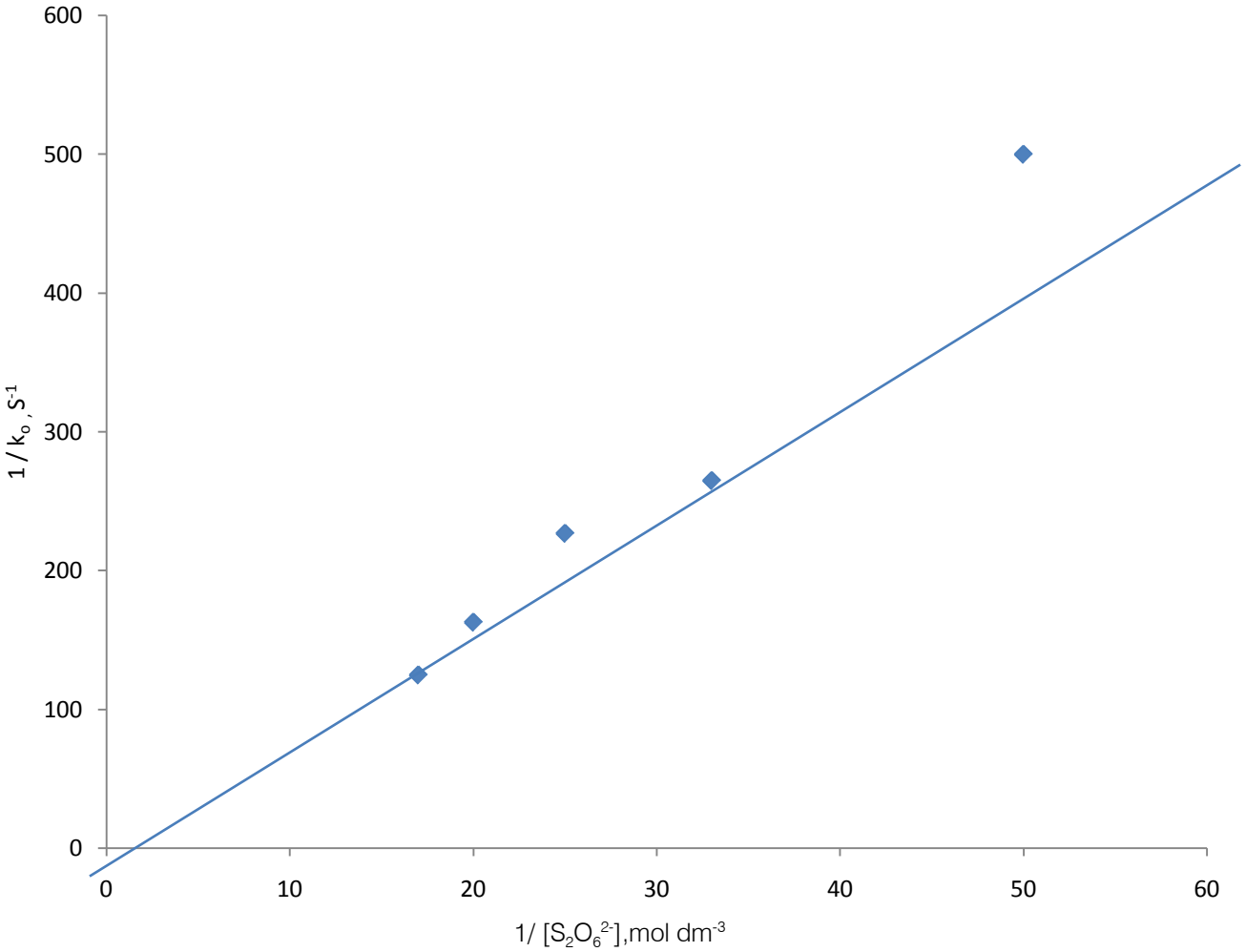

Fig. 4 : Michealis – Menten's plot for the reduction of TB^+ with $S_2O_6^{2-}$ ion at $[TB^+] = 1 \times 10^{-3}$mol dm^{-3}, $[S_2O_6^{2-}] = 30 \times 10^{-3}$mol dm^{-3}, $[H^+] = 1 \times 10^{-2}$mol dm^{-3}, I = 0.5 mol dm^{-3}(NaCl) , λmax = 600 nm, T = 31± 1°C.

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

© 2013 Global Journals Inc. (US)

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

References Références Referencias

1. Elderfield, R.C. (1957). *Heterocyclic compounds.* Chpman and Hall Limited London 6:722.
2. Kiese, M. and Waller, H.D. (1951). Reduction of hemoglobin and oxygen for reversibly reducible dyes in red cells.*Naunyn-Schmiedebergs Arch Pharmacology.*213:44(German).
3. Jeffrey, S. B. and Jones J. S. (2004). Significant of toluidine blue positive findings after speculum examination for sexual assault.*The American journal of emergency medicine.*22(3): 201 – 203.
4. Epstein, J.B. and Guneri, P. (2009). The adjunctive role of toluidine blue in detection of oral premalignant and malignant lesions.*CurrOpinOtolaryngol Head Neck Surg.* 17:79-87.
5. Carson, F. L. and Hladik , C. (2009) . Histotechnology: A Self-Instructional Text (3 ed.). Hong Kong: American Society for Clinical Pathology Press. Pp 188.
6. David, L. M. and Barbara, C.(1999). Fluorescent Tissue Site- Selective Lanthanide Chelate, Tb-PCTMB for Enhanced Imaging of Cancer.*Anal.Chem.* 71(14) :2607-2615.
7. Ko" merik,N.; Nakanishi,H.;Mac, R.; ,A.J. Henderson, A.J.; Speight , B. and Wilson, M.(2003). Invivo killing of porphyromonasgingivalis by toluidine blue –mediated photosensitization in an animal model. Antimicrob . Agents chemother .47(3): 932.
8. Williams, J. A.; Pearson;Colles, G. J. and Wilson,M.J.M.(2004).The photo activated antibacterial action of toluidine blue in a collagen matrix and in carious dentine.*Caries Res.*38 : 530-6.
9. Metersky M. L., Colt H. G., Olson L. K. and Shanks T. G. (1995). AID – related spontaneous pneumothorax, risk factors and treatment. *Chest.*108(4): 946 – 51.
10. Chakaya J. M., Bii C., Ng'ang'a L., Amukoye E., Ouko T., Muita L., Gitau J., Odongo I., Kabanga J. M., Nagai K., Suzumura S., SugiuraY. (2003). Pneumocystis carinii pneumonia in HIV/AIDS patients at an urban district hospital in Kenya.*East Afr. Med. J.* 80(1):30-5.
11. Hamza, S. A., Iyun, J. F. and Idris, S. O. (2012). Kinetics and mechanism of the redox reaction of toluidine blue and nitrite ions in aqueous acidic medium.*Archives of Applied Science Research.*4(1): 10 – 18.
12. Hamza S.A., Iyun J.F. and Idris S.O.(2012). Kinetics and Mechanism of Toluidine blue Reduction by Dithionite Ion in Aqueous Acidic Medium. *Journal of Chemical and Pharmaceutical Research,*4(1): 6-13.
13. Zenovia M. (2011). Kinetic – spectrophotometric determination of nitrite by its accelerating effect on the oxidation of toluidine blue by bromate. *Revue Roumaine de Chimie.* 56(1): 39 – 46.

© 2013 Global Journals Inc. (US)

14. Cizek Z. and Studlova V. (1984). Kinetics and Mechanisms of Toluidine Blue Reduction by Dithionite Ion in Aqueous Acidic Medium. *Talanta*.31:547 – 562.
15. Baran, M. P., Bugay, O. A., Kolesnik, S. P., Maksimenko, V. M., Teslenko,V. V., Petrenko, T. L. and Desrosiers, M. F. (2006). Barium dithionate as a EPR dosemeter. *Radiation Protection Dosimetry*.120: 202.
16. Ishii, M. (2001). Structure of Some Copper (II) Complexes Containing $S_2O_6^{2-}$ Ion. *Bulletin of the Yamagata University* 5(1):7.
17. Greenwood, N. and Earn Shaw, A. (1997). Chemistry of the Elements (2nd Edn.), Oxford: Butterworth-Heinemann. ISBN 0-7506-3365-4.
18. Murthy, G. S. Eager, R. L. and McCallum, K. J. (1971). Radiation Chemistry of Dithionates. *Can. J. Chem.* 49(22): 3733.
19. Babatunde O. A. (2008). A study of the kinetics and mechanism of oxidation of L-ascorbic acid by permanganate ion in acidic medium. *World J. of Chem.*, 3(1):27-31.
20. Babatunde, O. A. (2007). Mechanism of the reduction of Triamino/dimethane chloride by dithionate in acidic medium – kinetic approach. *The Academy Journal of Research and Defence Studies.* 14Pp 232 – 239.
21. Jonnalagada S.B. and Dumba M. (1993). Reduction of toluidine blue by stannous ion at low pH: Kinetics and simulations. *International Journal of Chemical Kinetics.* 25(9): 745-753.
22. Jonnalagada, S B. and Gollapalli, N. R. (2000). Kinetics of reduction of TB^+ with sulfite- kinetic salt effect in elucidation of mechanism. .*J Chem. Educ.*, 77, 4 506.
23. Jonnalagada, S.B. and Nattar, K. (1999). A kinetics and mechanism of autocatalysed reaction between phenyl hydrazine and toluidine blue in aqueous solution. *Int. J. Chem. Kinet.*, 31, 83.
24. Hamza, S.A. (2012). Kinetic and mechanism of the redox reactions of toluidine blue with some oxyanions and ascorbic acid in Aqueous Acidic Medium. *Archives of Applied Science Research.* 4(1):10-18
25. Grases, F., Genester, C. and Amat, E. (1986). Kinetic studies on the oxidation of ascorbic acid by technetium(VII). *International Journal of Chemical Kinetics* 18(8): 899–905.
26. Pryztas T.J. and Sutin, N. (1973). Kinetic studies of anion assisted outer-sphere electron transfer reaction. *J. Am. Chem. Soc.*, 95: 5595.
27. Babatunde, O. A. (2009). Kinetics and Mechanism of reduction of parafuchsin by nitrite ions in aqueous acid medium. *World J. of Chem.*, 4(1),39-44.
28. Iyun, J.F., Peters, A.O. and Babatunde, O.A. (2002). Kinetics of reduction of triaminotolydiphenylmethane chloride (rosanilinehydrochloride) by hydroxide ions in aqueous medium. *Indian Journal of Chemistry*.41A: 967 – 969.

© 2013 Global Journals Inc. (US)

Global Journal of Science Frontier Research
Chemistry
Volume 13 Issue 8 Version 1.0 Year 2013
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Ethanol Diffusion in Polyethylene Vinyl Acetate: Modelling and Experimentation

By Rachid Atmani, Faisal Mobarak, Ibtissam Maghri, Mohamed Elkouali, Mohamed Talbi, Abdlhak Elbrouzi, Samia Yousfi & Driss Boriky

University Hassan II, Morocco

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.

GJSFR-B Classification : FOR Code: 259999p



Strictly as per the compliance and regulations of :

© 2013. Rachid Atmani, Faisal Mobarak, Ibtissam Maghri, Mohamed Elkouali, Mohamed Talbi, Abdlhak Elbrouzi, Samia Yousfi & Driss Boriky. This is a research/review paper, distributed under the terms of the Creative Commons Attribution-Noncommercial 3.0 Unported License http://creativecommons.org/licenses/by-nc/3.0/), permitting all non commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Ethanol Diffusion in Polyethylene Vinyl Acetate: Modelling and Experimentation

Rachid Atmani [α], Faisal Mobarak [σ], Ibtissam Maghri [ρ], Mohamed Elkouali [ω], Mohamed Talbi [¥], Abdlhak Elbrouzi [§], Samia Yousfi [χ] & Driss Boriky [ν]

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.

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

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:

Authors α σ ρ ω ¥ χ ν: Faculty of Sciences Ben M'Sik, BP: 20702 , Casablanca, Morocco. emails: atmanirachid12@gmail.com, moubarak46@hotmail.fr, maghri.ibtissam@gmail.com, m.elkouali@gmail.com, maarifcentre@yahoo.fr, samiaryousfi@yahoo.fr, d.boriky@yahoo.fr

Author §: Faculty of sciences and Technology, Mohammedia, Morocco. e-mail: barouza@hotmail.com

© 2013 Global Journals Inc. (US)

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

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 cm^2/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.

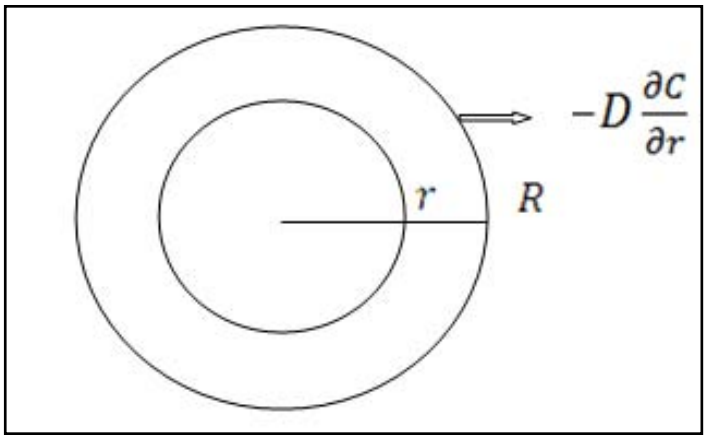

Figure 1 : Schema of the circular cross section of a sphere of radius R.

© 2013 Global Journals Inc. (US)

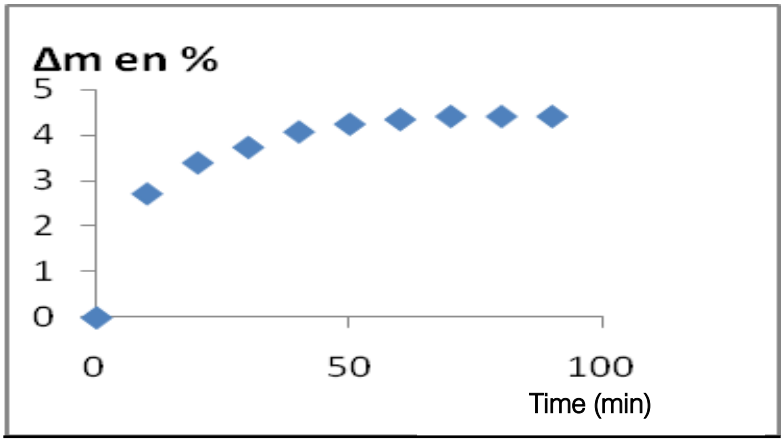

Figure 2 : Variation of the amount of ethanol in the PEVA

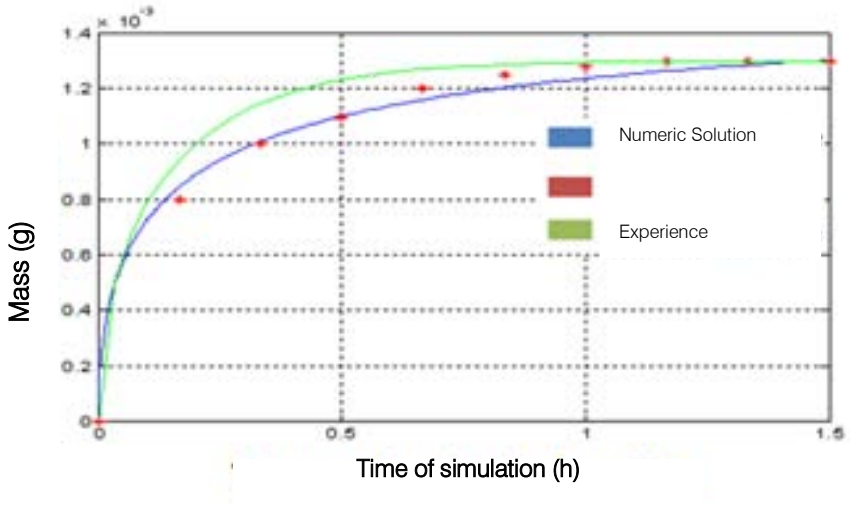

Figure 3 : The amount of ethanol in the material as a function of time for the simulation of three solutions.

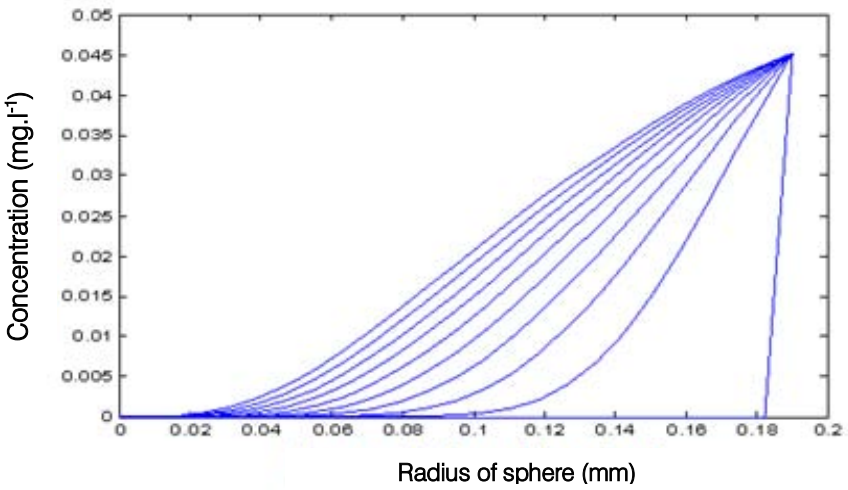

Figure 4 : The profile of the concentration of ethanol after every 10 min

© 2013 Global Journals Inc. (US)

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.

References Références Referencias

1. Giuseppe Allegra, 2008, Theories and simulations of polymer-based nanocomposites: From chain statistics to reinforcement, Prog. Polym. Sci. 33, 683–731.
2. Q.H. Zeng, 2008, Multiscale modeling and simulation of polymer nanocomposites, Prog. Polym. Sci. 33, 191–269.
3. E. Tocci; A. Gugliuzza,; L. De Lorenzo; M. Macchione; G. De Luca; E. J. Drioli, , 2008, Membr. Sci, 323, 316-327.
4. O. Hölck; M. Heuchel; M. Böhning; D. J. Hofmann, 2008, Polym. Sci., Part B: Polym. Phys., 46, 59-71.
5. H.L. CHOO, P.J. MARTIN, E.M.A. HARKIN-JONES, published online on 5 April 2008, Measurement of Heat Transfer for Thermoforming Simulations, International Journal of Material Forming.
6. V.I. Triantafyllou, 2007, A study on the migration of organic pollutants from recycled paperboard packaging materials to solid food matrices, Food Chemistry, vol 101, 1759–1768.
7. S.M. Kitty Sheung, 2007, «Diffusion coefficient of orange juice flavor compounds into packaging Materials: A mathematical model, LWT, vol 40, 157–163.
8. M. Geoghegan, 2003, Wetting at polymer surfaces and interfaces, Prog. Polym. Sci. 28, 261–302.
9. I.D. Rosca, J.M. Vergnaud, 1997, transfer of contaminant into solid from a bottle made of bilayer polymer with a recycled and virgin layer - effect of thicknesses of these polymer layers, journal of applied polymer science, vol 66, 1291-1301.

© 2013 Global Journals Inc. (US)

Global Journals Inc. (US) Guidelines Handbook 2013

www.GlobalJournals.org

FELLOWS

FELLOW OF ASSOCIATION OF RESEARCH SOCIETY IN SCIENCE (FARSS)

Global Journals Incorporate (USA) is accredited by Open Association of Research Society (OARS), U.S.A and in turn, awards "FARSS" title to individuals. The 'FARSS' title is accorded to a selected professional after the approval of the Editor-in-Chief/Editorial Board Members/Dean.



- The "FARSS" is a dignified title which is accorded to a person's name viz. Dr. John E. Hall, Ph.D., FARSS or William Walldroff, M.S., FARSS.

FARSS accrediting is an honor. It authenticates your research activities. After recognition as FARSB, you can add 'FARSS' title with your name as you use this recognition as additional suffix to your status. This will definitely enhance and add more value and repute to your name. You may use it on your professional Counseling Materials such as CV, Resume, and Visiting Card etc.

The following benefits can be availed by you only for next three years from the date of certification:

FARSS designated members are entitled to avail a 40% discount while publishing their research papers (of a single author) with Global Journals Incorporation (USA), if the same is accepted by Editorial Board/Peer Reviewers. If you are a main author or co-author in case of multiple authors, you will be entitled to avail discount of 10%.

Once FARSB title is accorded, the Fellow is authorized to organize a symposium/seminar/conference on behalf of Global Journal Incorporation (USA). The Fellow can also participate in conference/seminar/symposium organized by another institution as representative of Global Journal. In both the cases, it is mandatory for him to discuss with us and obtain our consent.





You may join as member of the Editorial Board of Global Journals Incorporation (USA) after successful completion of three years as Fellow and as Peer Reviewer. In addition, it is also desirable that you should organize seminar/symposium/conference at least once.

We shall provide you intimation regarding launching of e-version of journal of your stream time to time.This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.



© Copyright by Global Journals Inc.(US) | Guidelines Handbook

The FARSS can go through standards of OARS. You can also play vital role if you have any suggestions so that proper amendment can take place to improve the same for the benefit of entire research community.



As FARSS, you will be given a renowned, secure and free professional email address with 100 GB of space e.g. johnhall@globaljournals.org. This will include Webmail, Spam Assassin, Email Forwarders,Auto-Responders, Email Delivery Route tracing, etc.



The FARSS will be eligible for a free application of standardization of their researches. Standardization of research will be subject to acceptability within stipulated norms as the next step after publishing in a journal. We shall depute a team of specialized research professionals who will render their services for elevating your researches to next higher level, which is worldwide open standardization.



The FARSS member can apply for grading and certification of standards of their educational and Institutional Degrees to Open Association of Research, Society U.S.A.
Once you are designated as FARSS, you may send us a scanned copy of all of your credentials. OARS will verify, grade and certify them. This will be based on your academic records, quality of research papers published by you, and some more criteria. After certification of all your credentials by OARS, they will be published on your Fellow Profile link on website https://associationofresearch.org which will be helpful to upgrade the dignity.

The FARSS members can avail the benefits of free research podcasting in Global Research Radio with their research documents. After publishing the work, (including published elsewhere worldwide with proper authorization) you can upload your research paper with your recorded voice or you can utilize chargeable services of our professional RJs to record your paper in their voice on request.



The FARSS member also entitled to get the benefits of free research podcasting of their research documents through video clips. We can also streamline your conference videos and display your slides/ online slides and online research video clips at reasonable charges, on request.

© Copyright by Global Journals Inc.(US)| Guidelines Handbook



The FARSS is eligible to earn from sales proceeds of his/her researches/reference/review Books or literature, while publishing with Global Journals. The FARSS can decide whether he/she would like to publish his/her research in a closed manner. In this case, whenever readers purchase that individual research paper for reading, maximum 60% of its profit earned as royalty by Global Journals, will be credited to his/her bank account. The entire entitled amount will be credited to his/her bank account exceeding limit of minimum fixed balance. There is no minimum time limit for collection. The FARSS member can decide its price and we can help in making the right decision.

The FARSS member is eligible to join as a paid peer reviewer at Global Journals Incorporation (USA) and can get remuneration of 15% of author fees, taken from the author of a respective paper. After reviewing 5 or more papers you can request to transfer the amount to your bank account.



MEMBER OF ASSOCIATION OF RESEARCH SOCIETY IN SCIENCE (MARSS)

The ' MARSS ' title is accorded to a selected professional after the approval of the Editor-in-Chief / Editorial Board Members/Dean.



The "MARSS" is a dignified ornament which is accorded to a person's name viz. Dr. John E. Hall, Ph.D., MARSS or William Walldroff, M.S., MARSS.

MARSS accrediting is an honor. It authenticates your research activities. After becoming MARSS, you can add 'MARSS' title with your name as you use this recognition as additional suffix to your status. This will definitely enhance and add more value and repute to your name. You may use it on your professional Counseling Materials such as CV, Resume, Visiting Card and Name Plate etc.

The following benefitscan be availed by you only for next three years from the date of certification.



MARSS designated members are entitled to avail a 25% discount while publishing their research papers (of a single author) in Global Journals Inc., if the same is accepted by our Editorial Board and Peer Reviewers. If you are a main author or co-author of a group of authors, you will get discount of 10%.

As MARSS, you will be given a renowned, secure and free professional email address with 30 GB of space e.g. johnhall@globaljournals.org. This will include Webmail, Spam Assassin, Email Forwarders,Auto-Responders, Email Delivery Route tracing, etc.



© Copyright by Global Journals Inc.(US) | Guidelines Handbook



We shall provide you intimation regarding launching of e-version of journal of your stream time to time.This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.

The MARSS member can apply for approval, grading and certification of standards of their educational and Institutional Degrees to Open Association of Research, Society U.S.A.





Once you are designated as MARSS, you may send us a scanned copy of all of your credentials. OARS will verify, grade and certify them. This will be based on your academic records, quality of research papers published by you, and some more criteria.

It is mandatory to read all terms and conditions carefully.

© Copyright by Global Journals Inc.(US)| Guidelines Handbook

AUXILIARY MEMBERSHIPS

Institutional Fellow of Global Journals Incorporation (USA)-OARS (USA)

Global Journals Incorporation (USA) is accredited by Open Association of Research Society, U.S.A (OARS) and in turn, affiliates research institutions as "Institutional Fellow of Open Association of Research Society" (IFOARS).



The "FARSC" is a dignified title which is accorded to a person's name viz. Dr. John E. Hall, Ph.D., FARSC or William Walldroff, M.S., FARSC.

The IFOARS institution is entitled to form a Board comprised of one Chairperson and three to five board members preferably from different streams. The Board will be recognized as "Institutional Board of Open Association of Research Society"-(IBOARS).

The Institute will be entitled to following benefits:

The IBOARS can initially review research papers of their institute and recommend them to publish with respective journal of Global Journals. It can also review the papers of other institutions after obtaining our consent. The second review will be done by peer reviewer of Global Journals Incorporation (USA) The Board is at liberty to appoint a peer reviewer with the approval of chairperson after consulting us.

The author fees of such paper may be waived off up to 40%.

The Global Journals Incorporation (USA) at its discretion can also refer double blind peer reviewed paper at their end to the board for the verification and to get recommendation for final stage of acceptance of publication.





The IBOARS can organize symposium/seminar/conference in their country on behalf of Global Journals Incorporation (USA)-OARS (USA). The terms and conditions can be discussed separately.

The Board can also play vital role by exploring and giving valuable suggestions regarding the Standards of "Open Association of Research Society, U.S.A (OARS)" so that proper amendment can take place for the benefit of entire research community. We shall provide details of particular standard only on receipt of request from the Board.



The board members can also join us as Individual Fellow with 40% discount on total fees applicable to Individual Fellow. They will be entitled to avail all the benefits as declared. Please visit Individual Fellow-sub menu of GlobalJournals.org to have more relevant details.

© Copyright by Global Journals Inc.(US) | Guidelines Handbook

We shall provide you intimation regarding launching of e-version of journal of your stream time to time. This may be utilized in your library for the enrichment of knowledge of your students as well as it can also be helpful for the concerned faculty members.



After nomination of your institution as "Institutional Fellow" and constantly functioning successfully for one year, we can consider giving recognition to your institute to function as Regional/Zonal office on our behalf.
The board can also take up the additional allied activities for betterment after our consultation.

The following entitlements are applicable to individual Fellows:



Open Association of Research Society, U.S.A (OARS) By-laws states that an individual Fellow may use the designations as applicable, or the corresponding initials. The Credentials of individual Fellow and Associate designations signify that the individual has gained knowledge of the fundamental concepts. One is magnanimous and proficient in an expertise course covering the professional code of conduct, and follows recognized standards of practice.

Open Association of Research Society (US)/ Global Journals Incorporation (USA), as described in Corporate Statements, are educational, research publishing and professional membership organizations. Achieving our individual Fellow or Associate status is based mainly on meeting stated educational research requirements.



Disbursement of 40% Royalty earned through Global Journals : Researcher = 50%, Peer Reviewer = 37.50%, Institution = 12.50% E.g. Out of 40%, the 20% benefit should be passed on to researcher, 15 % benefit towards remuneration should be given to a reviewer and remaining 5% is to be retained by the institution.

We shall provide print version of 12 issues of any three journals [as per your requirement] out of our 38 journals worth $ 2376 USD.

Other:

The individual Fellow and Associate designations accredited by Open Association of Research Society (US) credentials signify guarantees following achievements:

- The professional accredited with Fellow honor, is entitled to various benefits viz. name, fame, honor, regular flow of income, secured bright future, social status etc.

© Copyright by Global Journals Inc.(US)| Guidelines Handbook

- In addition to above, if one is single author, then entitled to 40% discount on publishing research paper and can get 10%discount if one is co-author or main author among group of authors.
- The Fellow can organize symposium/seminar/conference on behalf of Global Journals Incorporation (USA) and he/she can also attend the same organized by other institutes on behalf of Global Journals.
- The Fellow can become member of Editorial Board Member after completing 3yrs.
- The Fellow can earn 60% of sales proceeds from the sale of reference/review books/literature/publishing of research paper.
- Fellow can also join as paid peer reviewer and earn 15% remuneration of author charges and can also get an opportunity to join as member of the Editorial Board of Global Journals Incorporation (USA)
- • This individual has learned the basic methods of applying those concepts and techniques to common challenging situations. This individual has further demonstrated an in–depth understanding of the application of suitable techniques to a particular area of research practice.

Note :

"

- In future, if the board feels the necessity to change any board member, the same can be done with the consent of the chairperson along with anyone board member without our approval.
- In case, the chairperson needs to be replaced then consent of 2/3rd board members are required and they are also required to jointly pass the resolution copy of which should be sent to us. In such case, it will be compulsory to obtain our approval before replacement.
- In case of "Difference of Opinion [if any]" among the Board members, our decision will be final and binding to everyone.

"

Process of submission of Research Paper

The Area or field of specialization may or may not be of any category as mentioned in 'Scope of Journal' menu of the GlobalJournals.org website. There are 37 Research Journal categorized with Six parental Journals GJCST, GJMR, GJRE, GJMBR, GJSFR, GJHSS. For Authors should prefer the mentioned categories. There are three widely used systems UDC, DDC and LCC. The details are available as 'Knowledge Abstract' at Home page. The major advantage of this coding is that, the research work will be exposed to and shared with all over the world as we are being abstracted and indexed worldwide.

The paper should be in proper format. The format can be downloaded from first page of 'Author Guideline' Menu. The Author is expected to follow the general rules as mentioned in this menu. The paper should be written in MS-Word Format (*.DOC,*.DOCX).

The Author can submit the paper either online or offline. The authors should prefer online submission.Online Submission: There are three ways to submit your paper:

(A) (I) First, register yourself using top right corner of Home page then Login. If you are already registered, then login using your username and password.

(II) Choose corresponding Journal.

(III) Click 'Submit Manuscript'. Fill required information and Upload the paper.

(B) If you are using Internet Explorer, then Direct Submission through Homepage is also available.

(C) If these two are not conveninet , and then email the paper directly to dean@globaljournals.org.

Offline Submission: Author can send the typed form of paper by Post. However, online submission should be preferred.

© Copyright by Global Journals Inc.(US)| Guidelines Handbook

Preferred Author Guidelines

MANUSCRIPT STYLE INSTRUCTION (Must be strictly followed)

Page Size: 8.27" X 11'"

- Left Margin: 0.65
- Right Margin: 0.65
- Top Margin: 0.75
- Bottom Margin: 0.75
- Font type of all text should be Swis 721 Lt BT.
- Paper Title should be of Font Size 24 with one Column section.
- Author Name in Font Size of 11 with one column as of Title.
- Abstract Font size of 9 Bold, "Abstract" word in Italic Bold.
- Main Text: Font size 10 with justified two columns section
- Two Column with Equal Column with of 3.38 and Gaping of .2
- First Character must be three lines Drop capped.
- Paragraph before Spacing of 1 pt and After of 0 pt.
- Line Spacing of 1 pt
- Large Images must be in One Column
- Numbering of First Main Headings (Heading 1) must be in Roman Letters, Capital Letter, and Font Size of 10.
- Numbering of Second Main Headings (Heading 2) must be in Alphabets, Italic, and Font Size of 10.

You can use your own standard format also.
Author Guidelines:

1. General,

2. Ethical Guidelines,

3. Submission of Manuscripts,

4. Manuscript's Category,

5. Structure and Format of Manuscript,

6. After Acceptance.

1. GENERAL

Before submitting your research paper, one is advised to go through the details as mentioned in following heads. It will be beneficial, while peer reviewer justify your paper for publication.

Scope

The Global Journals Inc. (US) welcome the submission of original paper, review paper, survey article relevant to the all the streams of Philosophy and knowledge. The Global Journals Inc. (US) is parental platform for Global Journal of Computer Science and Technology, Researches in Engineering, Medical Research, Science Frontier Research, Human Social Science, Management, and Business organization. The choice of specific field can be done otherwise as following in Abstracting and Indexing Page on this Website. As the all Global

Journals Inc. (US) are being abstracted and indexed (in process) by most of the reputed organizations. Topics of only narrow interest will not be accepted unless they have wider potential or consequences.

2. ETHICAL GUIDELINES

Authors should follow the ethical guidelines as mentioned below for publication of research paper and research activities.

Papers are accepted on strict understanding that the material in whole or in part has not been, nor is being, considered for publication elsewhere. If the paper once accepted by Global Journals Inc. (US) and Editorial Board, will become the copyright of the Global Journals Inc. (US).

Authorship: The authors and coauthors should have active contribution to conception design, analysis and interpretation of findings. They should critically review the contents and drafting of the paper. All should approve the final version of the paper before submission

The Global Journals Inc. (US) follows the definition of authorship set up by the Global Academy of Research and Development. According to the Global Academy of R&D authorship, criteria must be based on:

1) Substantial contributions to conception and acquisition of data, analysis and interpretation of the findings.

2) Drafting the paper and revising it critically regarding important academic content.

3) Final approval of the version of the paper to be published.

All authors should have been credited according to their appropriate contribution in research activity and preparing paper. Contributors who do not match the criteria as authors may be mentioned under Acknowledgement.

Acknowledgements: Contributors to the research other than authors credited should be mentioned under acknowledgement. The specifications of the source of funding for the research if appropriate can be included. Suppliers of resources may be mentioned along with address.

Appeal of Decision: The Editorial Board's decision on publication of the paper is final and cannot be appealed elsewhere.

Permissions: It is the author's responsibility to have prior permission if all or parts of earlier published illustrations are used in this paper.

Please mention proper reference and appropriate acknowledgements wherever expected.

If all or parts of previously published illustrations are used, permission must be taken from the copyright holder concerned. It is the author's responsibility to take these in writing.

Approval for reproduction/modification of any information (including figures and tables) published elsewhere must be obtained by the authors/copyright holders before submission of the manuscript. Contributors (Authors) are responsible for any copyright fee involved.

3. SUBMISSION OF MANUSCRIPTS

Manuscripts should be uploaded via this online submission page. The online submission is most efficient method for submission of papers, as it enables rapid distribution of manuscripts and consequently speeds up the review procedure. It also enables authors to know the status of their own manuscripts by emailing us. Complete instructions for submitting a paper is available below.

Manuscript submission is a systematic procedure and little preparation is required beyond having all parts of your manuscript in a given format and a computer with an Internet connection and a Web browser. Full help and instructions are provided on-screen. As an author, you will be prompted for login and manuscript details as Field of Paper and then to upload your manuscript file(s) according to the instructions.



To avoid postal delays, all transaction is preferred by e-mail. A finished manuscript submission is confirmed by e-mail immediately and your paper enters the editorial process with no postal delays. When a conclusion is made about the publication of your paper by our Editorial Board, revisions can be submitted online with the same procedure, with an occasion to view and respond to all comments.

Complete support for both authors and co-author is provided.

4. MANUSCRIPT'S CATEGORY

Based on potential and nature, the manuscript can be categorized under the following heads:

Original research paper: Such papers are reports of high-level significant original research work.

Review papers: These are concise, significant but helpful and decisive topics for young researchers.

Research articles: These are handled with small investigation and applications

Research letters: The letters are small and concise comments on previously published matters.

5.STRUCTURE AND FORMAT OF MANUSCRIPT

The recommended size of original research paper is less than seven thousand words, review papers fewer than seven thousands words also.Preparation of research paper or how to write research paper, are major hurdle, while writing manuscript. The research articles and research letters should be fewer than three thousand words, the structure original research paper; sometime review paper should be as follows:

Papers: These are reports of significant research (typically less than 7000 words equivalent, including tables, figures, references), and comprise:

(a)Title should be relevant and commensurate with the theme of the paper.

(b) A brief Summary, "Abstract" (less than 150 words) containing the major results and conclusions.

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

(d) An Introduction, giving necessary background excluding subheadings; objectives must be clearly declared.

(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.

(f) Results should be presented concisely, by well-designed tables and/or figures; the same data may not be used in both; suitable statistical data should be given. All data must be obtained with attention to numerical detail in the planning stage. As reproduced design has been recognized to be important to experiments for a considerable time, the Editor has decided that any paper that appears not to have adequate numerical treatments of the data will be returned un-refereed;

(g) Discussion should cover the implications and consequences, not just recapitulating the results; conclusions should be summarizing.

(h) Brief Acknowledgements.

(i) References in the proper form.

Authors should very cautiously consider the preparation of papers to ensure that they communicate efficiently. Papers are much more likely to be accepted, if they are cautiously designed and laid out, contain few or no errors, are summarizing, and be conventional to the approach and instructions. They will in addition, be published with much less delays than those that require much technical and editorial correction.

The Editorial Board reserves the right to make literary corrections and to make suggestions to improve briefness.

It is vital, that authors take care in submitting a manuscript that is written in simple language and adheres to published guidelines.

Format

Language: The language of publication is UK English. Authors, for whom English is a second language, must have their manuscript efficiently edited by an English-speaking person before submission to make sure that, the English is of high excellence. It is preferable, that manuscripts should be professionally edited.

Standard Usage, Abbreviations, and Units: Spelling and hyphenation should be conventional to The Concise Oxford English Dictionary. Statistics and measurements should at all times be given in figures, e.g. 16 min, except for when the number begins a sentence. When the number does not refer to a unit of measurement it should be spelt in full unless, it is 160 or greater.

Abbreviations supposed to be used carefully. The abbreviated name or expression is supposed to be cited in full at first usage, followed by the conventional abbreviation in parentheses.

Metric SI units are supposed to generally be used excluding where they conflict with current practice or are confusing. For illustration, 1.4 l rather than 1.4 × 10-3 m3, or 4 mm somewhat than 4 × 10-3 m. Chemical formula and solutions must identify the form used, e.g. anhydrous or hydrated, and the concentration must be in clearly defined units. Common species names should be followed by underlines at the first mention. For following use the generic name should be constricted to a single letter, if it is clear.

Structure

All manuscripts submitted to Global Journals Inc. (US), ought to include:

Title: The title page must carry an instructive title that reflects the content, a running title (less than 45 characters together with spaces), names of the authors and co-authors, and the place(s) wherever the work was carried out. The full postal address in addition with the e-mail address of related author must be given. Up to eleven keywords or very brief phrases have to be given to help data retrieval, mining and indexing.

Abstract, used in Original Papers and Reviews:

Optimizing Abstract for Search Engines

Many researchers searching for information online will use search engines such as Google, Yahoo or similar. By optimizing your paper for search engines, you will amplify the chance of someone finding it. This in turn will make it more likely to be viewed and/or cited in a further work. Global Journals Inc. (US) have compiled these guidelines to facilitate you to maximize the web-friendliness of the most public part of your paper.

Key Words

A major linchpin in research work for the writing research paper is the keyword search, which one will employ to find both library and Internet resources.

One must be persistent and creative in using keywords. An effective keyword search requires a strategy and planning a list of possible keywords and phrases to try.

Search engines for most searches, use Boolean searching, which is somewhat different from Internet searches. The Boolean search uses "operators," words (and, or, not, and near) that enable you to expand or narrow your affords. Tips for research paper while preparing research paper are very helpful guideline of research paper.

Choice of key words is first tool of tips to write research paper. Research paper writing is an art.A few tips for deciding as strategically as possible about keyword search:

- One should start brainstorming lists of possible keywords before even begin searching. Think about the most important concepts related to research work. Ask, "What words would a source have to include to be truly valuable in research paper?" Then consider synonyms for the important words.
- It may take the discovery of only one relevant paper to let steer in the right keyword direction because in most databases, the keywords under which a research paper is abstracted are listed with the paper.
- One should avoid outdated words.

Keywords are the key that opens a door to research work sources. Keyword searching is an art in which researcher's skills are bound to improve with experience and time.

Numerical Methods: Numerical methods used should be clear and, where appropriate, supported by references.

Acknowledgements: Please make these as concise as possible.

References

References follow the Harvard scheme of referencing. References in the text should cite the authors' names followed by the time of their publication, unless there are three or more authors when simply the first author's name is quoted followed by et al. unpublished work has to only be cited where necessary, and only in the text. Copies of references in press in other journals have to be supplied with submitted typescripts. It is necessary that all citations and references be carefully checked before submission, as mistakes or omissions will cause delays.

References to information on the World Wide Web can be given, but only if the information is available without charge to readers on an official site. Wikipedia and Similar websites are not allowed where anyone can change the information. Authors will be asked to make available electronic copies of the cited information for inclusion on the Global Journals Inc. (US) homepage at the judgment of the Editorial Board.

The Editorial Board and Global Journals Inc. (US) recommend that, citation of online-published papers and other material should be done via a DOI (digital object identifier). If an author cites anything, which does not have a DOI, they run the risk of the cited material not being noticeable.

The Editorial Board and Global Journals Inc. (US) recommend the use of a tool such as Reference Manager for reference management and formatting.

Tables, Figures and Figure Legends

Tables: Tables should be few in number, cautiously designed, uncrowned, and include only essential data. Each must have an Arabic number, e.g. Table 4, a self-explanatory caption and be on a separate sheet. Vertical lines should not be used.

Figures: Figures are supposed to be submitted as separate files. Always take in a citation in the text for each figure using Arabic numbers, e.g. Fig. 4. Artwork must be submitted online in electronic form by e-mailing them.

Preparation of Electronic Figures for Publication

Even though low quality images are sufficient for review purposes, print publication requires high quality images to prevent the final product being blurred or fuzzy. Submit (or e-mail) EPS (line art) or TIFF (halftone/photographs) files only. MS PowerPoint and Word Graphics are unsuitable for printed pictures. Do not use pixel-oriented software. Scans (TIFF only) should have a resolution of at least 350 dpi (halftone) or 700 to 1100 dpi (line drawings) in relation to the imitation size. Please give the data for figures in black and white or submit a Color Work Agreement Form. EPS files must be saved with fonts embedded (and with a TIFF preview, if possible).

For scanned images, the scanning resolution (at final image size) ought to be as follows to ensure good reproduction: line art: >650 dpi; halftones (including gel photographs) : >350 dpi; figures containing both halftone and line images: >650 dpi.

Color Charges: It is the rule of the Global Journals Inc. (US) for authors to pay the full cost for the reproduction of their color artwork. Hence, please note that, if there is color artwork in your manuscript when it is accepted for publication, we would require you to complete and return a color work agreement form before your paper can be published.

Figure Legends: Self-explanatory legends of all figures should be incorporated separately under the heading 'Legends to Figures'. In the full-text online edition of the journal, figure legends may possibly be truncated in abbreviated links to the full screen version. Therefore, the first 100 characters of any legend should notify the reader, about the key aspects of the figure.

6. AFTER ACCEPTANCE

Upon approval of a paper for publication, the manuscript will be forwarded to the dean, who is responsible for the publication of the Global Journals Inc. (US).

6.1 Proof Corrections

The corresponding author will receive an e-mail alert containing a link to a website or will be attached. A working e-mail address must therefore be provided for the related author.

Acrobat Reader will be required in order to read this file. This software can be downloaded

(Free of charge) from the following website:

www.adobe.com/products/acrobat/readstep2.html. This will facilitate the file to be opened, read on screen, and printed out in order for any corrections to be added. Further instructions will be sent with the proof.

Proofs must be returned to the dean at dean@globaljournals.org within three days of receipt.

As changes to proofs are costly, we inquire that you only correct typesetting errors. All illustrations are retained by the publisher. Please note that the authors are responsible for all statements made in their work, including changes made by the copy editor.

6.2 Early View of Global Journals Inc. (US) (Publication Prior to Print)

The Global Journals Inc. (US) are enclosed by our publishing's Early View service. Early View articles are complete full-text articles sent in advance of their publication. Early View articles are absolute and final. They have been completely reviewed, revised and edited for publication, and the authors' final corrections have been incorporated. Because they are in final form, no changes can be made after sending them. The nature of Early View articles means that they do not yet have volume, issue or page numbers, so Early View articles cannot be cited in the conventional way.

6.3 Author Services

Online production tracking is available for your article through Author Services. Author Services enables authors to track their article - once it has been accepted - through the production process to publication online and in print. Authors can check the status of their articles online and choose to receive automated e-mails at key stages of production. The authors will receive an e-mail with a unique link that enables them to register and have their article automatically added to the system. Please ensure that a complete e-mail address is provided when submitting the manuscript.

6.4 Author Material Archive Policy

Please note that if not specifically requested, publisher will dispose off hardcopy & electronic information submitted, after the two months of publication. If you require the return of any information submitted, please inform the Editorial Board or dean as soon as possible.

6.5 Offprint and Extra Copies

A PDF offprint of the online-published article will be provided free of charge to the related author, and may be distributed according to the Publisher's terms and conditions. Additional paper offprint may be ordered by emailing us at: editor@globaljournals.org .



Before start writing a good quality Computer Science Research Paper, let us first understand what is Computer Science Research Paper? So, Computer Science Research Paper is the paper which is written by professionals or scientists who are associated to Computer Science and Information Technology, or doing research study in these areas. If you are novel to this field then you can consult about this field from your supervisor or guide.

TECHNIQUES FOR WRITING A GOOD QUALITY RESEARCH PAPER:

1. Choosing the topic: In most cases, the topic is searched by the interest of author but it can be also suggested by the guides. You can have several topics and then you can judge that in which topic or subject you are finding yourself most comfortable. This can be done by asking several questions to yourself, like Will I be able to carry our search in this area? Will I find all necessary recourses to accomplish the search? Will I be able to find all information in this field area? If the answer of these types of questions will be "Yes" then you can choose that topic. In most of the cases, you may have to conduct the surveys and have to visit several places because this field is related to Computer Science and Information Technology. Also, you may have to do a lot of work to find all rise and falls regarding the various data of that subject. Sometimes, detailed information plays a vital role, instead of short information.

2. Evaluators are human: First thing to remember that evaluators are also human being. They are not only meant for rejecting a paper. They are here to evaluate your paper. So, present your Best.

3. Think Like Evaluators: If you are in a confusion or getting demotivated that your paper will be accepted by evaluators or not, then think and try to evaluate your paper like an Evaluator. Try to understand that what an evaluator wants in your research paper and automatically you will have your answer.

4. Make blueprints of paper: The outline is the plan or framework that will help you to arrange your thoughts. It will make your paper logical. But remember that all points of your outline must be related to the topic you have chosen.

5. Ask your Guides: If you are having any difficulty in your research, then do not hesitate to share your difficulty to your guide (if you have any). They will surely help you out and resolve your doubts. If you can't clarify what exactly you require for your work then ask the supervisor to help you with the alternative. He might also provide you the list of essential readings.

6. Use of computer is recommended: As you are doing research in the field of Computer Science, then this point is quite obvious.

7. Use right software: Always use good quality software packages. If you are not capable to judge good software then you can lose quality of your paper unknowingly. There are various software programs available to help you, which you can get through Internet.

8. Use the Internet for help: An excellent start for your paper can be by using the Google. It is an excellent search engine, where you can have your doubts resolved. You may also read some answers for the frequent question how to write my research paper or find model research paper. From the internet library you can download books. If you have all required books make important reading selecting and analyzing the specified information. Then put together research paper sketch out.

9. Use and get big pictures: Always use encyclopedias, Wikipedia to get pictures so that you can go into the depth.

10. Bookmarks are useful: When you read any book or magazine, you generally use bookmarks, right! It is a good habit, which helps to not to lose your continuity. You should always use bookmarks while searching on Internet also, which will make your search easier.

11. Revise what you wrote: When you write anything, always read it, summarize it and then finalize it.

12. Make all efforts: Make all efforts to mention what you are going to write in your paper. That means always have a good start. Try to mention everything in introduction, that what is the need of a particular research paper. Polish your work by good skill of writing and always give an evaluator, what he wants.

13. Have backups: When you are going to do any important thing like making research paper, you should always have backup copies of it either in your computer or in paper. This will help you to not to lose any of your important.

14. Produce good diagrams of your own: Always try to include good charts or diagrams in your paper to improve quality. Using several and unnecessary diagrams will degrade the quality of your paper by creating "hotchpotch." So always, try to make and include those diagrams, which are made by your own to improve readability and understandability of your paper.

15. Use of direct quotes: When you do research relevant to literature, history or current affairs then use of quotes become essential but if study is relevant to science then use of quotes is not preferable.

16. Use proper verb tense: Use proper verb tenses in your paper. Use past tense, to present those events that happened. Use present tense to indicate events that are going on. Use future tense to indicate future happening events. Use of improper and wrong tenses will confuse the evaluator. Avoid the sentences that are incomplete.

17. Never use online paper: If you are getting any paper on Internet, then never use it as your research paper because it might be possible that evaluator has already seen it or maybe it is outdated version.

18. Pick a good study spot: To do your research studies always try to pick a spot, which is quiet. Every spot is not for studies. Spot that suits you choose it and proceed further.

19. Know what you know: Always try to know, what you know by making objectives. Else, you will be confused and cannot achieve your target.

20. Use good quality grammar: Always use a good quality grammar and use words that will throw positive impact on evaluator. Use of good quality grammar does not mean to use tough words, that for each word the evaluator has to go through dictionary. Do not start sentence with a conjunction. Do not fragment sentences. Eliminate one-word sentences. Ignore passive voice. Do not ever use a big word when a diminutive one would suffice. Verbs have to be in agreement with their subjects. Prepositions are not expressions to finish sentences with. It is incorrect to ever divide an infinitive. Avoid clichés like the disease. Also, always shun irritating alliteration. Use language that is simple and straight forward. put together a neat summary.

21. Arrangement of information: Each section of the main body should start with an opening sentence and there should be a changeover at the end of the section. Give only valid and powerful arguments to your topic. You may also maintain your arguments with records.

22. Never start in last minute: Always start at right time and give enough time to research work. Leaving everything to the last minute will degrade your paper and spoil your work.

23. Multitasking in research is not good: Doing several things at the same time proves bad habit in case of research activity. Research is an area, where everything has a particular time slot. Divide your research work in parts and do particular part in particular time slot.

24. Never copy others' work: Never copy others' work and give it your name because if evaluator has seen it anywhere you will be in trouble.

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.



© Copyright by Global Journals Inc.(US)| Guidelines Handbook

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 though 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.



© Copyright by Global Journals Inc.(US)| Guidelines Handbook

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 briefness. 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 a 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
- What you account in an conceptual must be regular with what you reported in the manuscript
- Exact spelling, clearness of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else

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.
- Shape the theory/purpose specifically - do not take a broad view.
- As always, give awareness to spelling, simplicity and correctness of sentences and phrases.

Procedures (Methods and Materials):

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.
- Embrace particular materials, and any tools or provisions that are not frequently found in laboratories.
- 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.



© Copyright by Global Journals Inc.(US)| Guidelines Handbook

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
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

Discussion:

The Discussion is expected the trickiest segment to write and describe. A lot of papers submitted for journal are discarded based on problems with the Discussion. There is no head of state for how long a argument should be. Position your understanding of the outcome visibly to lead the reviewer through your conclusions, and then finish the paper with a summing up of the implication of the study. The purpose here is to offer an understanding of your results and hold up for all of your conclusions, using facts from your research and generally accepted information, if suitable. The implication of result should be visibly described. Infer your data in the conversation in suitable depth. This means that when you clarify an observable fact you must explain mechanisms that may account for the observation. If your results vary from your prospect, make clear why that may have happened. If your results agree, then explain the theory that the proof supported. It is never suitable to just state that the data approved with prospect, and let it drop at that.

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- 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.

Administration Rules Listed Before Submitting Your Research Paper to Global Journals Inc. (US)

Please carefully note down following rules and regulation before submitting your Research Paper to Global Journals Inc. (US):

Segment Draft and Final Research Paper: You have to strictly follow the template of research paper. If it is not done your paper may get rejected.

- The **major constraint** is that you must independently make all content, tables, graphs, and facts that are offered in the paper. You must write each part of the paper wholly on your own. The Peer-reviewers need to identify your own perceptive of the concepts in your own terms. NEVER extract straight from any foundation, and never rephrase someone else's analysis.

- Do not give permission to anyone else to "PROOFREAD" your manuscript.

- Methods to avoid Plagiarism is applied by us on every paper, if found guilty, you will be blacklisted by all of our collaborated research groups, your institution will be informed for this and strict legal actions will be taken immediately.)
- To guard yourself and others from possible illegal use please do not permit anyone right to use to your paper and files.



© Copyright by Global Journals Inc.(US)| Guidelines Handbook

Criterion for Grading a Research Paper (Compilation) by Global Journals Inc. (US)

Please note that following table is only a Grading of "Paper Compilation" and not on "Performed/Stated Research" whose grading solely depends on Individual Assigned Peer Reviewer and Editorial Board Member. These can be available only on request and after decision of Paper. This report will be the property of Global Journals Inc. (US).

Topics	Grades		
	A-B	**C-D**	**E-F**
Abstract	Clear and concise with appropriate content, Correct format. 200 words or below	Unclear summary and no specific data, Incorrect form Above 200 words	No specific data with ambiguous information Above 250 words
Introduction	Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited	Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter	Out of place depth and content, hazy format
Methods and Procedures	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
Result	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
Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

INDEX

B

Benzenenaphthol · 10, 12, 13

D

Diphenylcarbazide · 12
Dithionate · 23, 25, 26, 27, 28, 29, 30, 31, 32, 33

M

Methaemoglobinaemia · 1

P

Phenothiazin · 1, 3, 4, 5, 6, 7, 8, 9
Paleolimnological · 3
Prepeliņele · 68

S

Spectrophotometric · 10, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22
Stoichiometry · 1, 23, 25, 26
Scleroxylon · 26, 30, 32
Seudoacacia · 24
Silvipastoral · 16, 21, 22

T

Thiocyanate · 1, 3, 4, 5, 6, 7, 8, 9
Toluidine · 23, 25, 26, 27, 28, 29, 30, 31, 32, 33
Tendipendidae · 7
Trophochemical · 5, 6

R

Ricinodendron · 24, 26, 28, 31

Z

Zooplankters · 4



Global Journal of Science Frontier Research

Visit us on the Web at www.GlobalJournals.org | www.JournalofScience.org
or email us at helpdesk@globaljournals.org

ISSN 9755896



© Global Journals