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A TRIBUTE TO PROF. DR. LAVINEL G. IONESCU ON HIS 70th BIRTHDAY

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ABSTRACT

Professor Dr. Lavinel G. Ionescu was born of Romanian parents in Vârset (Vrsac, Werschetz), Banat, Yugoslavia (present day Serbia) on May 19, 1943. He attended primary and secondary schools in Yugoslavia, Italy and Switzerland. He did his undergraduate studies at Compton College, University of California at Los Angeles and the University of New Mexico. He obtained the B.S. Degree in Chemistry from the University of New Mexico, Albuquerque, USA in 1964 and the M.S. Degree in 1966. He was awarded the Ph.D. Degree in Physical Chemistry by New Mexico State University, Las Cruces, USA in 1970. He also attended Medical School. Prof. L. G. Ionescu is a U.S. citizen. He did postdoctoral work at the University of California, Santa Barbara and has held faculty positions at universities in the United States and Brazil. He was instrumental in the establishment of many graduate or undergraduate programs in chemistry, chemical engineering, pharmacy. materials science and engineering and science education in Brazil and the United States. His research work includes liquid scintillators, radioactive isotopes, noble gases, solution thermodynamics, surfactants and micelles, micellar catalysis, respiratory pigments, membrane models and history and philosophy of science. He has trained more than one hundred scientists from different parts of the world, is the author of approximately three hundred and fifty scientific works and has been the recipient of many prizes and awards.

RESUMO

Professor Dr. Lavinel G. Ionescu nasceu de pais romênos em Vârset (Vrsac, Werschetz), Banat, Iugoslávia (atualmente Sérvia) em 19 de Maio de 1943. Fez os estudos de primeiro e segundo grau na Iugoslávia, Itália e Suiça. Realizou os estudos de graduação em Compton College, University of California at Los Angeles e University of New Mexico. Ele obteve o título de B.S. em Química na University of New Mexico, Albuquerque, USA em 1964 e o título de M.S. em Química em 1966. Ele obteve o título de Ph.D. em Físico-Química em 1970 em New Mexico State University, Las Cruces, USA. Ele também cursou a Faculdade de Medicina. O Prof. Dr. L. G. Ionescu é cidadão dos Estados Unidos. Realizou estudos de pós-doutorado na University of California, Santa Barbara, USA e ocupou cargos de professor em várias universidades nos Estados Unidos e no Brasil. A sua contribuição foi importante no estabelecimento de cursos à nível de graduação e pós-graduação em química. engenharia química, farmácia, ciência e engenharia dos materiais e educação em ciência no Brasil e nos Estados Unidos. As suas atividades de pesquisa incluem cintiladores líquidos, isótopos radioativos, gases nobres, termodinâmica de soluções, surfatantes e micelas, catálise micelar, pigmentos respiratórios, modelos de membranas e história e filosofia da ciência. Ele preparou mais de cem pesquisadores de várias partes do mundo, é autor de aproximadamente trezentos e cinqüenta trabalhos científicos e foi honrado com muitos prêmios e distinções.

KEYWORDS: **History of Chemistry, History and Philosophy of Science, Noble Gases, Surfactants and Micelles, Micellar Catalysis, Solution Thermodynamics.**

We have written an extensive article in homage and tribute to Professor Dr. Lavinel G. Ionescu on the occasion of his 55th birthday. *(Cf. A.D. Martinez and B.J. Kid, South. Braz. J. Chem., 6(6), 1-10, 1998).*

Professor Lavinel G. Ionescu was born on May 19, 1943 in Vârset (Vrsac, Werschetz), Banat Yugoslavia (present day Serbia). His father, Gheorghe I. Ionescu, a languages teacher and linguist, was originally from Plopeni, Constanta, Romania and his mother Maria (n. Borlovanu) Ionescu, an accountant, was from Alibunar, Banat Yugoslavia.

Prof. Dr. L. G. Ionescu attended primary and secondary schools in Yugoslavia (Samianas-Barite, Alibunar and Uzdin), Italy (Trieste, Seminario Vescovile and Liceo-Ginnasio Dante Alighieri) and Switzerland (Rohrbach b.H., Bern).

He began his undergraduate studies at Compton College, Compton California in 1959 where he was awarded the *Associate in Arts Degree-Cum Laude* in 1961. Subsequently, he continued his undergraduate studies at the University of California, Los Angeles and the University of New Mexico, Albuquerque. He obtained the *Bachelor of Science Degree with a Major in Chemistry and a Minor in Mathematics with Honors* from the University of New Mexico , Albuquerque, USA, in 1964. In 1965 he became a U.S. citizen.

Prof. Dr. Lavinel G. Ionescu obtained the *Master of Science Degree with a Major in Physical Organic Chemistry and a Minor in Physics* from the University of New Mexico in 1966. His M.S. Thesis dealt with the use of dihydronaphthalenes and dihydrophenanthrenes as liquid scintillators , was done under the supervision of Professors Guido H. Daub and Francis Newton Hayes of the Los Alamos Scientific Laboratory and received financial support from the United States Atomic Energy Commission.

PROF. DR. LAVINEL G. IONESCU

Professor L. G. Ionescu obtained the *Doctor of Philosophy Degree with a Major in Physical Chemistry and Minors in Astrophysics and Biology* from New Mexico State University, Las Cruces, USA in 1970. His Ph. D. Dissertation dealt mainly with solution thermodynamics , included the study of the interaction of leguminous hemoglobin with nitrogen and xenon, the properties of the xenon –water clathrate and the solubility of gases in water and aqueous solutions. The work was performed under the supervision of Professor Gordon J. Ewing and received financial support from the National Science Foundation.

Dr. L. G. Ionescu did postdoctoral work at New Mexico State University and the University of California, Santa Barbara, where he collaborated with Professor Clifford A. Bunton in the area of aggregation colloids and micellar catalysis. He also attended Medical School for several years.

Prof. Dr. Lavinel G. Ionescu began his academic career as Teaching Assistant at the University of New Mexico and New Mexico State University and as Technical Assistant at the University of Alabama, Tuscaloosa, USA, positions held from 1964 to 1970. During the period from 1972 to 1978 he held faculty positions at New Mexico Highlands University, Las Vegas, NM, USA and the University of Detroit, Detroit, Michigan, USA.

In June of 1978, accepting an invitation from the Brazilian Ministry of Education and Culture, Dr. L. G. Ionescu went to Brazil and joined the faculty of the Universidade Federal de Santa Catarina, Florianópolis as *Full Professor of Chemistry*. Together with other American and foreign faculty members he helped establish the Graduate Program in Physical Chemistry and in Physiscs at UFSC in Florianópolis.

In 1983, Prof. Dr. Lavinel G. Ionescu moved to Porto Alegre where he became a faculty member at the Universidade Federal do Rio Grande do Sul. He occupied the positions of Full Professor of Materials Science in the School of Engineering and Professor of Chemistry in the Instituto de Química and played an important role in the establishment of the Doctoral Program in Materials Science and Metallurgical Enginering and the Master Program in Chemistry.

In 1992, after denouncing nationwide on radio, television and newspapers ecologic crimes, embezzlement of public funds, corruption and other administrative irregularities at the Universidade Federal do Rio Grande do Sul (UFRGS) he was stripped of all his academic rights and dismissed from the faculty of UFRGS in an arbitrary act that involved harassment, political persecution and had dictatorial and inquisitional overtones. He was forced to ask for special protection from the Brazilian Federal Police and the American Consul. This shameful and sad event in the history of the Federal University of Rio Grande do Sul (UFRGS) led to legal battles that lasted more than two decades and ended up in the Brazilian Supreme Court.

Soon afterwards in 1992, Prof. Dr. Lavinel G. Ionescu was appointed Professor of Chemistry at the Universidade Luterana do Brasil (ULBRA), Canoas, RS and Pontifícia Universidade Católica do Rio Grande do Sul (PUCRS), Porto Alegre, positions that he held until 2004, when he retired from academics and began to dedicate his effort to the editing of journals and scientific consulting.

He has been Visiting Professor at the University of California, Santa Barbara, Universidade de Caxias do Sul, Universidade Regional de Blumenau, Universidade Federal de Santa Maria, Insituto Luterano de Ensino Superior, Manaus, Amazonas and other universities in various continents.

During almost five decades as a faculty member at various universities, Prof. Dr. L. G. Ionescu participated on a wide number of committees and held different administrative positions in the United States and Brazil.

In terms of didactic activities, Professor L. G. Ionescu taught mainly courses in physical chemistry at all levels and occasionally general and inorganic chemistry, biochemistry, quantum mechanics and history and philosophy of science.
He was the first scientist in Brazil to teach a formal advanced course on matter and materials under extreme conditions in Porto Alegre and Manaus, Amazonas.

Prof. Dr. L. G. Ionescu's research activities include liquid scintillators, radio-active isotopes of Fe and Th, noble gases, solution thermodynamics, surfactants and micelles, micellar catalysis, respiratory pigments, membrane models and history and philosophy of science. He has trained more than one hundred scientists from different parts of the world and is the author of approximately 350 scientific papers. A list of representative publications is given at the end of this article.

Prof. Dr. L. G. Ionescu is fluent in many European languages, including Romanian, Serbo-Croatian, Italian, French, Spanish, Portuguese, German, English and others. At times, he surprises people conversing in Chinese, Japanese, Swahili or Hindi.

Prof. L. G. Ionescu is a widely traveled person and his journeys included the Arctic Circle, Sonoran Desert, Sierra Madre, Carpathians, Alps, the Andes and Aconcagua, the Islands of the Pacific and the Amazon.

His hobbies include stamp collecting, mountain climbing, swimming, astronomy, folklore and the traditions of many people.

Prof. Dr, L. G. Ionescu became widely known throughout Brazil as *Leader of the Pró- Ecologia Group of Porto Alegre and Viamão* after denouncing the ecologic crimes of the Campus do Vale of the Federal University of Rio Grande do Sul, widespread corruption and embezzlement of public funds at the same institution. He appeared on all television channels and many radio programs throughout Brazil and his interviews covered entire pages of *Jornal do Brasil*, the country's most important newspaper at the time.

On the streets of Porto Alegre, many people greet him as the "*Courageous Professor*" and in Viamão, city where he lives since 1983, people address him respectfully as *Professor* or *Professor Lavinel*. Dr. Dimitrios Samios, former Dean of the College of Chemistry and UFRGS's best known chemist, has made public depositions considering Prof. D. L. G. Ionescu an *archetype*, a model person or prototype that appeared at the wrong place before his time.

Prof. Dr. Lavinel G. Ionescu has received many prizes, distinctions and awards , has given invited lectures in more than twenty five countries and organized or helped organize many scientific events all over the world.

We cite only the *Symposium on Chemistry in Latin America* during the First Chemical Congress of the North American Continent in Mexico City in 1975 and various *International Symposia on Surfactants in Solution*.

He is a member of the American Chemical Society since 1965, Sigma Xi-Scientific Research Society of America, Sigma Pi Sigma-National Physics Honor Society (USA), New Mexico Academy of Science, Michigan Academy of Arts, Science and Letters, New York Academy of Sciences, Founding Member of the American Romanian Academy of Arts and Sciences together with

Mons. O. Bârlea, Mircea Eliade and George Emil Palade; and Founding President of Sarmisegetusa Research Group of Santa Fe, New Mexico, USA and member of many other learned societies, including the Astronomical Society of Las Cruces.

He was *Researcher IA* of the Brazilian National Research Council (CNPq) and in 2004 he received the *Technology Prize* from PETROBRAS (Brazilian Petroleum Company).

Prof. Dr. L. G. Ionescu is an *Honorary Citizen of the State of New Mexico* and was *Brazilian National Representative* at the International Union of Pure and Applied Chemistry (IUPAC).

When asked about his main contributions in teaching, Prof. L. G. Ionescu cites many courses in *Quantum Chemistry* that opened the frontier in Southern Brazil, the course on *Matter and Materials under Extreme Conditions* and the course on *History and Philosophy of Science*, given to thousands of freshmen students in the sciences and mathematics at ULBRA.

In research he mentions especially the work on relaxation phenomena and liquid dynamics, the use of micelle formation to probe the structure of water and various studies in solution thermodynamics.

He also likes to stress his contributions for several decades, especially as Chief Editor of the *Southern Brazilian Journal of Chemistry* and Editor of the *Brazilian Journal of Materials Science and Engineering*.

We salute Professor Dr. Lavinel G. Ionescu on the occasion of his seventieth birthday, congratulate him for his effort and contributions for almost half a century and wish him happiness, good health, good will and success for the days to come.

REPRESENTATIVE PUBLICATIONS

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THE PRODUCTION OF BIODIESEL MONITORED WITH REAL-TIME LASER SPECTROSCOPY . CONFIRMATION OF THE TECHNIQUE WITH PROTON NUCLEAR MAGNETIC RESONANCE.

19

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ABSTRACT

Biodiesel is a synthetic fuel usually produced by the transesterification reaction. This study was undertaken in order to monitor the kinetics of the transesterification reaction between soybean oil and methanol catalyzed by KOH and determine when the reaction reached chemical equilibrium. A series of reactions was monitored with a laser spectrometer used to analyze the absorption and scattering of light in real time. The monitoring system combined the information received thorough multiple sensors. The correlation of the present technique with ^1H NMR spectra confirmed that the reaction was approaching chemical equilibrium when the monitoring curve showed asymptotic behavior.

KEY WORDS: **Biodiesel, Laser Measurements, ^1H NMR, Chemical Kinetics, Optical Activity of Chemical Reaction, Multiple Sensors**

RESUMO

O biodiesel é um combustível sintético, geralmente produzido através da reação de transesterificção, Este trabalho foi desenvolvido para monitorar a cinética da reação de transesterficação entre oléo de soja e metanol, catalisada por KOH e determinar quando a reação atingiu equilíbrio químico. Uma série de reações foi monitorada com um espectrômetro laser utilizado para analisar a absorção e espalhamento da luz em tempo-real O sistema de monitoramento combinou a informação recebida através de vários sensores. A correlação desta técnica com espetroscopia de RMN de ^1H confirmou que a reação estava se aproximando do equilíbrio químico quando a curva de monitoramento exibia comportamento assintótico.

PALAVRAS CHAVE: Biodiesel, Medidas com Laser, RMN de 1H, Cinética Química, Atividade Ótica de Reações, Vários Sensores

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INTRODUCTION

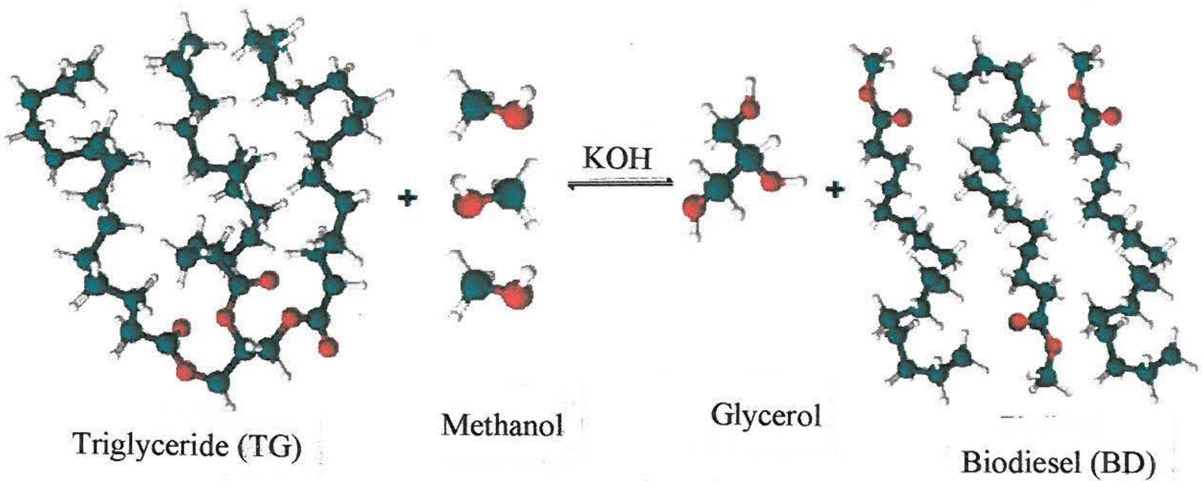
The production of synthetic combustion fuels from biomass is the focus of a large number of research groups in Brazil and the world. Biodiesel is usually produced by the esterification reaction of free fatty acids or the transesterification reaction of triglycerides (1-15).

. This study was undertaken to monitor the kinetics of the transesterification reaction between soybean oil and methanol catalyzed by KOH and determine when the reaction reached equilibrium. The reaction under consideration is given in Figure 1. A triglyceride (TG) reacts with methanol in the presence of KOH to give the corresponding esters (biodiesel,BD) and glycerol. The detailed mechanism of the transesterification reaction is given in Figure 2.

The improvement and the efficient use of energy for the production of biofuels is of paramount importance since it avoids unnecessary energy input in the reaction and consequently contributes to reduce a nation's dependence on external sources of energy.

The principal aim of this study was to monitor the transesterification reaction by laser spectroscopy, determine when it reached equilibrium and avoid unnecessary energy use for the reaction, improve reaction time, reduce energy intake, reduce the generation of secondary products and residues and increase the profitability of the process.

A series of reactions was monitored with a laser spectrometer used to analyze the absorption and scattering of light in real time. The monitoring system combined the information received through multiple sensors. A correlation was performed between the experimental results obtained by laser spectroscopy and proton nuclear magnetic resonance (6-10).



$TG + 3CH_3OH \leftrightharpoons C_3H_8O_3 + BD$

Figure 1. The Transesterification Reaction Leading to Biodiesel.

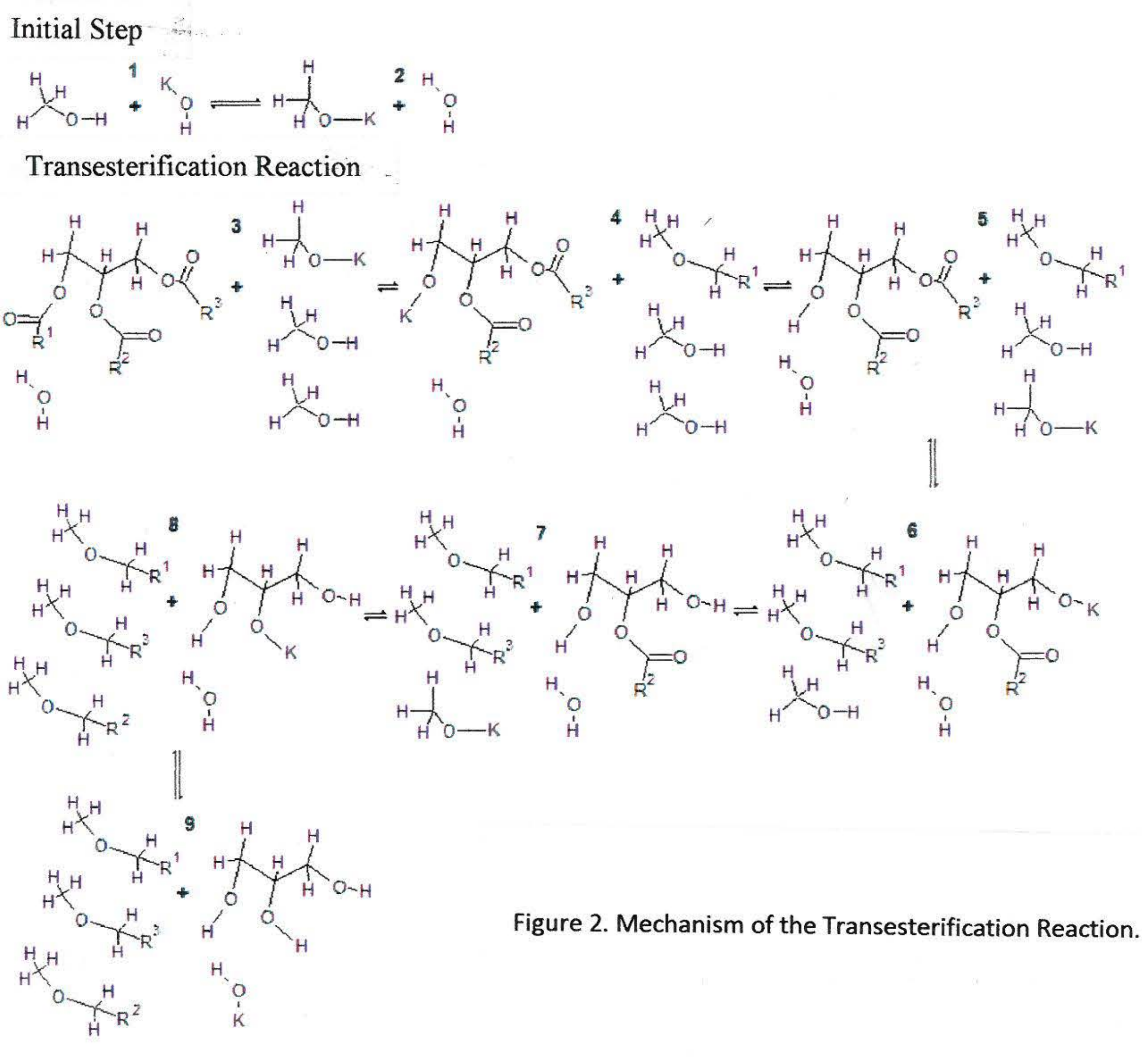


Figure 2. Mechanism of the Transesterification Reaction.

MATERIALS AND METHODS

The experimental technique has been described in detail in the literature (1-15).

The transesterification reaction was performed at 60 C using a stoichiometric molar ratio of soybean oil/methanol of 3:1 and 1% KOH was used as catalyst. The methanol (pure commercial grade) and potassium hydroxide of 85% purity were obtained from Nuclear. The soybean oil was purchased from a local supermarket. The reaction was monitored for 2 hours and samples were taken every second.

The monitoring technique was computer assisted. An illustration of the experimental equipment is shown in Figure 3. It consisted of an optronic sensor that was inserted into the reaction medium and was able to measure the change of light as a function of the reaction development. As the reaction tended to chemical equilibrium, the change in the light captured by the sensors became nearly constant. At this time interval it was possible to arbitrate that the reaction reached chemical equilibrium. This made possible the separation of glycerin from the biodiesel and the continuation of the fuel refining operations(1-5).

The results obtained by laser spectroscopy at 650 nm in real time were correlated directly to data obtained by 1H nuclear magnetic resonance using a method similar to that described by Knothe (10). Specifically, the results obtained by laser spectroscopy were correlated and compared to results of samples collected during the reaction and analyzed by nuclear magnetic resonance, NMR.

RESULTS AND DISCUSSION

Typical experimental results obtained for the transesterification reaction by laser spectroscopy and 1H nuclear magnetic resonance are summarized and illustrated in Figures 4-10.

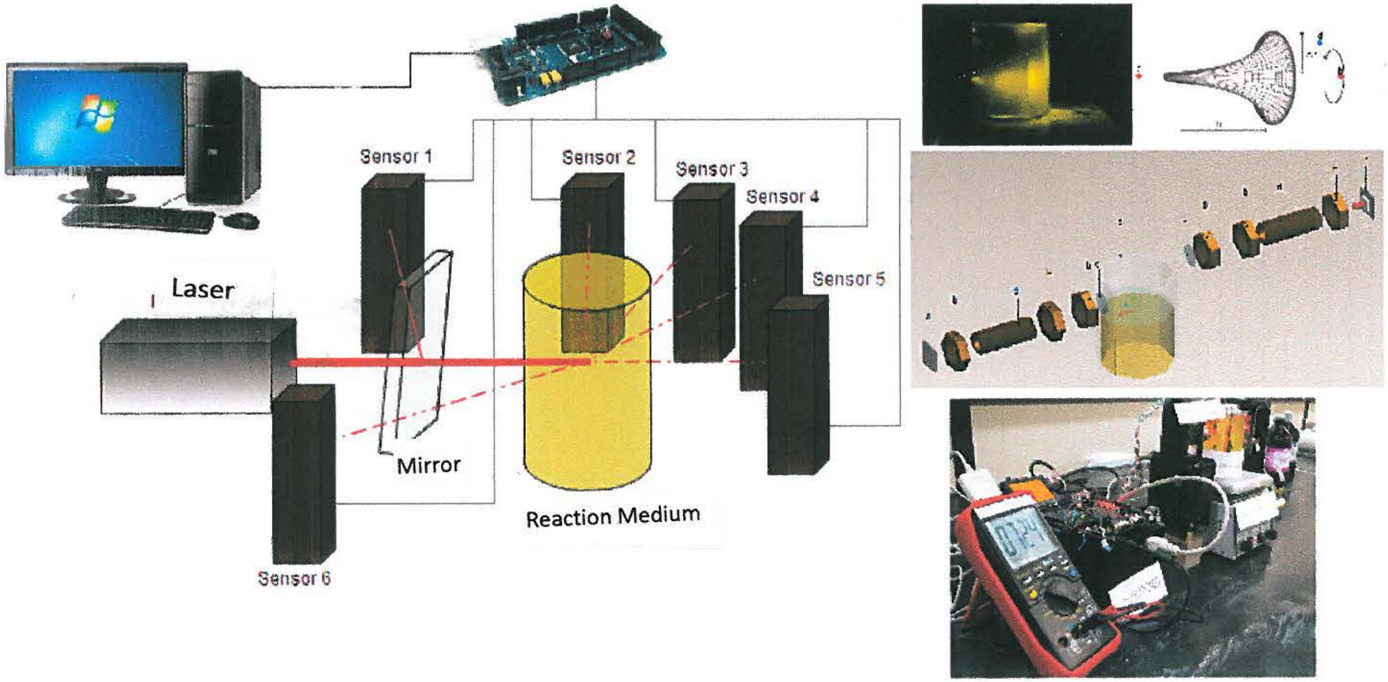


Figure 3. Illustration of the Experimental Equipment.

The prototype includes or shows

- Real-time monitoring of the reaction.
- Easy interpretation of the graphical interface.
- Improves of the reaction time.
- Reduction of the energy intake.
- Reduction of the generation of co-products and waste .
- Raises the profitability of the process.

Figure 4 shows the transesterification reaction being monitored by laser spectroscopy and points of extraction of samples for NMR studies. Time is given in seconds.

Figure 5 illustrates a correlation of the transesterification reaction with 1H nuclear magnetic resonance.

Figures 6-10 show 1H NMR spectra obtained by monitoring the system before, during and after the transesterification reaction.

Figure 6 illustrates a typical NMR spectrum obtained for soybean oil before the reaction begins.

Figure 7 shows the progress of the transesterification reaction for a sample collected at the peak of the curve monitored by laser spectroscopy.

Figure 8 illustrates the NMR spectrum at a point that is near the equilibrium of the reaction.

Figure 9 shows the 1H nuclear magnetic resonance spectrum of the system 15 minutes after decantation.

Finally, Figure 10 shows the NMR spectrum obtained for a sample of biodiesel that was refined with water.

The areas under the NMR spectral curves were calculated using MestReNova software (v.6.0.2-5475).

Subsequently, they were analyzed with Equation (I), proposed by Knothe (10) and given below.

$$C_{ME} = 100 \cdot \frac{5 \cdot I_{ME}}{5 \cdot I_{ME} + 9 \cdot I_{TAG}} \qquad \text{Equation (I)}$$

where CME= Percent (%) conversion of soybean oil into biodiesel

IME= Value of the integration of the methyl ester peak

ITAG= Value of the integration of the glyceride peaks in the triglycerides

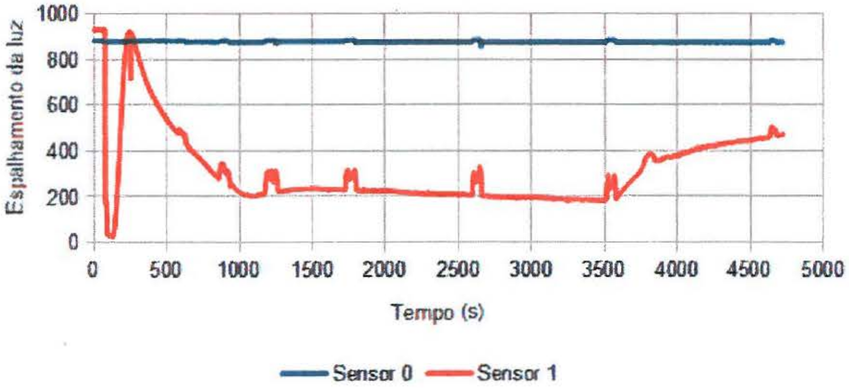


Figure 4. Transesterification Reaction Monitored by Absorption Spectroscopy and Extraction of Samples for Correlation with 1H NMR.

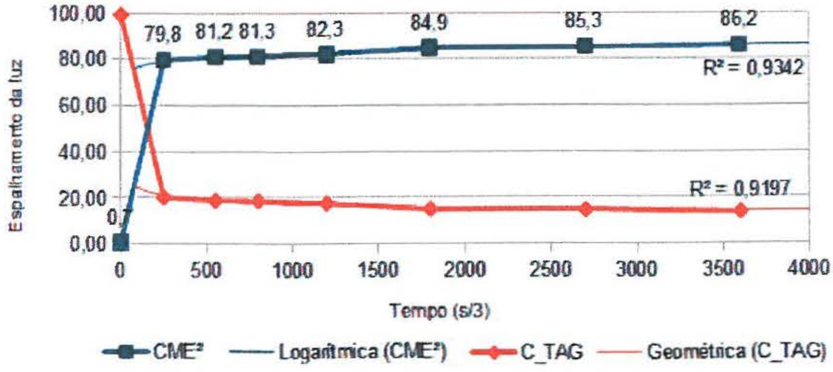


Figure 5 . Correlation of Transesterification Reaction with 1H NMR.

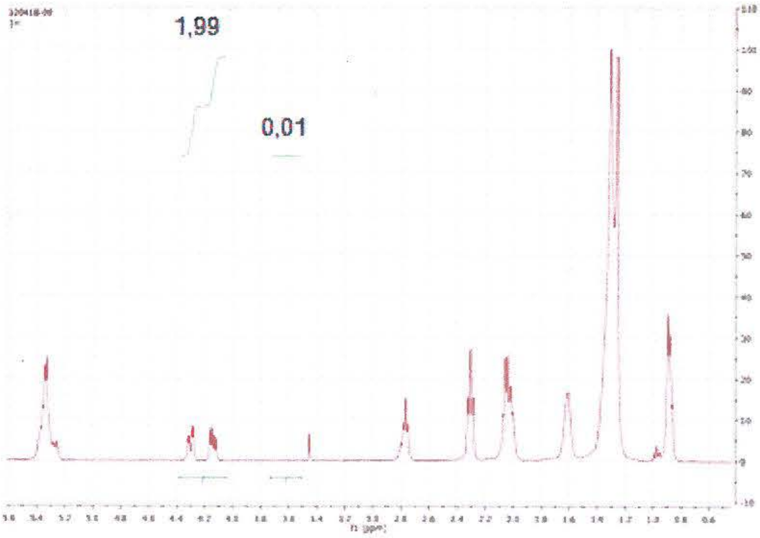


Figure 6. NMR Spectrum of Soybean Oil.

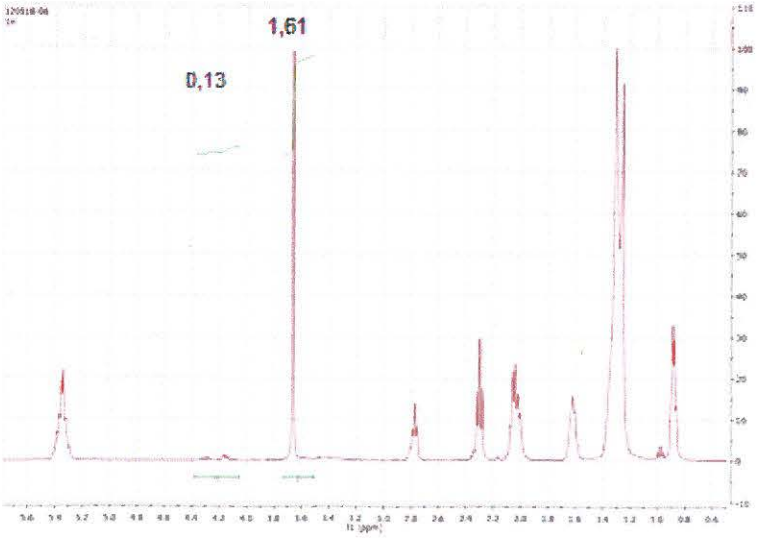


Figure 7. Normalized NMR Spectrum of Sample Collected at the Peak of the Monitoring Curve.

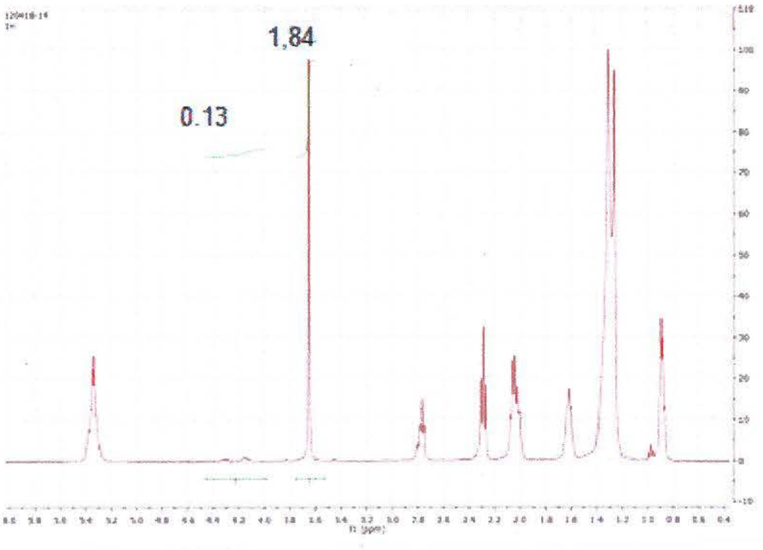


Figure 8. Normalized NMR Spectrum of a Sample Near Equilibrium.

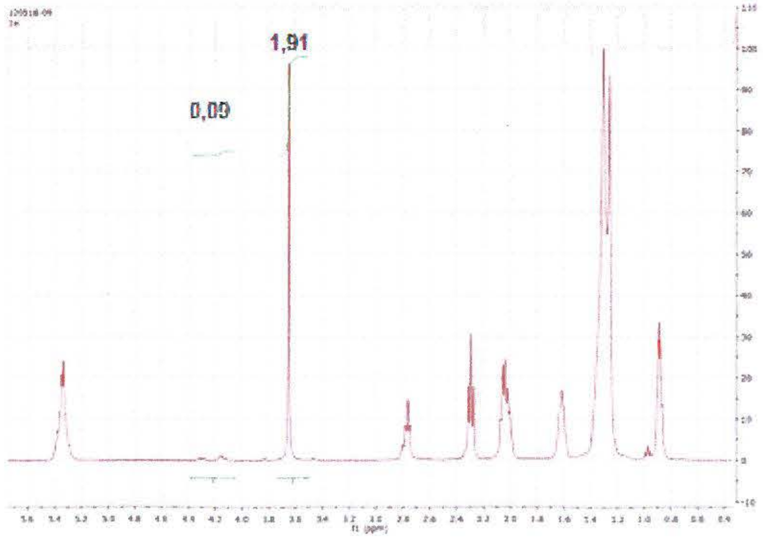


Figure 9. Normalized NMR Spectrum of Sample Collected 15 Minutes after Decantation.

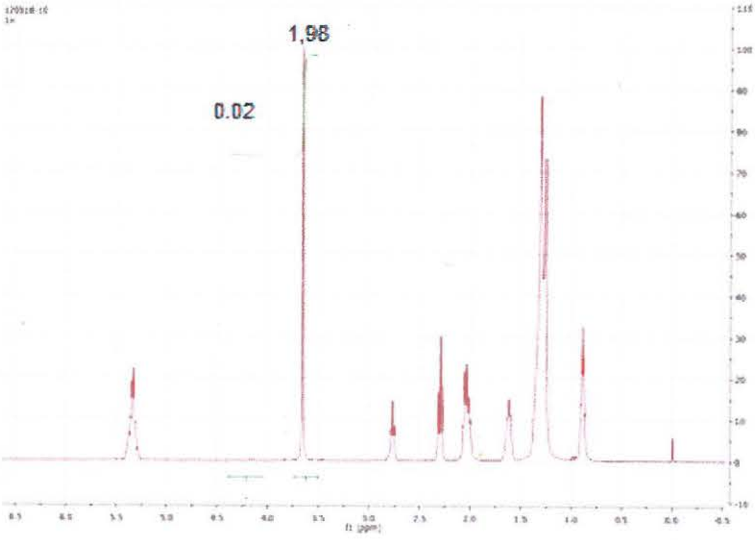


Figure 10. Normalized NMR Spectrum of a Biodiesel Sample Refined with Water.

The results correlated the conversion of monoalkyl glycerides to monoalkyl esters.

The correlation of the results obtained in real-time by laser spectroscopy with those obtained by 1H nuclear magnetic resonance provides evidence for the fact that the reaction reached equilibrium when the monitoring curve for the transesterification reaction began to exhibit asymptotic behavior. According to the data presented in Figure 5, the reaction reached 80% conversion during the initial first 10 minutes. An additional 50 minutes of reaction time increased the conversion only about 6%.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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SOLVENT EFFECTS ON THE THERMODYNAMICS OF SOLVATION OF BARIUUM DIPHENYLAMINESULFONATE IN ETHANOL-WATER MIXED SOLVENTS

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ABSTRACT

Aims: *The aim of this study was to determine the thermodynamic functions, Gibbs energy, enthalpy and entropy for the solution processes of barium diphenylaminesulfonate in the mixed solvent (ethanol+water) were calculated from solubility values obtained at temperatures ranging from 293.15 K to 308.15 K. The respective thermodynamic functions for mixing and solvation processes as well as the activity coefficients for the solute were calculated. The solubility of solutes in mixed solvents depends primarily on the solvation of the solutes or their constituent ions by the components of the solvent mixtures. In this study, the solubility of this barium diphenylaminesulfonate in the mixed solvent (ethanol + water by value percent of ethanol = 0, 20, 40, 60, 80 and 100% by volume), was determined at different temperature by the solvent evaporation method. The results enable us to estimate the value of thermodynamic solubility product,* $K_{op(th)}$*, of barium diphenylaminesulfonate in the mixed solvent. In addition, Gibbs energy, enthalpy, entropy for the solution processes and free energies of transfer of barium diphenylaminesulfonate units from water to the ethanol solutions were also calculated in order to estimate the contributions solute-solvent interactions related ion association are based on changes in the electrostatic properties of the solvent, solute and ion solvation as well as on the ionic strength of the medium.*

KEY WORDS: Solubility; thermodynamics; solubility product; mixed solvents; barium diphenylaminesulfonate

Place and Duration of Study:

1. Chemistry Department, Faculty of Science, Mansoura University, Egypt
2. Basic Science Department, Delta Higher Institute of Engineering and Technology, Dakhlia, Mansoura, Egypt between June 2012 and July 2013

RESUMO

O propósito deste estudo foi determinar as propriedades termodinâmicas tais com energia livre de Gibbs, entalpia e entropia para o processo de solubilização de difenilaminesulfonato de bário em solvente misto consistindo de etanol-água a várias temperaturas. Foi determinada a constante de solubilidade, Ksp , e foram analisados também fatores tais como interações soluto-solvente, propriedades eletrostáticas, solvatação de íons e a força iônica do meio.

PALAVRAS CHAVE: Solubilidade, termodinâmica, solventes mistos,
Ksp, difenilaminesulfonato de bário

1. INTRODUCTION

The solubility of solutes of all kinds in mixed solvents is of great practical importance, since many industrial process as well as laboratory procedures call for the use of solvent mixtures, or such mixtures are used by default [1]. Most physicochemical properties of ionic solutions are influenced by ionic strength and the solvent's dielectric constant. Indeed, in the context of solution chemistry, solvent polarity, the dielectric constant of the solvent, and the ionic strength of the medium are of great interest as a measure of the solvent's ability to stabilize charges or dipoles. As an example, the dissolution of an ionic salt in a solvent or in a mixed solvent depends on the relative permittivity and the polarity of the solvent as well as on the lattice energy of the solute and the ionic strength of the medium [2-4].

The solvation of dissolved ions determines many of the properties of electrolyte solutions [5–7], including their redox, complexation, and kinetic behavior. Its particular importance to solubilities, the central topic of the international symposium on solubility phenomena, is illustrated by the thermodynamic cycle in Fig. 1. As shown, the (standard) Gibbs energy of solution, $\Delta_{soln}G°$, is seen to be the sum of (the negative of the) lattice energy of the salt, $\Delta_{latt}G°$, and the solvation energies of the ions, $\Delta_{solv}G°$. This cycle makes it clear that the only reason that salts dissolve in solvents is because the very large lattice energies that are lost upon dissolution are compensated by the even larger solvation energies of the ions.

$$\begin{tikzcd}
\mathbf{MX(s)} \arrow[r, shift left, "-\Delta_{latt}G"] \arrow[dr, shift left, "\Delta_{sln}G"] & \mathbf{M^+(g) + X^-(g)} \arrow[l, shift left] \arrow[d, shift left, "\Delta_{solv}G"] \\
 & \mathbf{M^+(sln) + X^-(sln)} \arrow[u, shift left] \arrow[ul, shift left]
\end{tikzcd}$$

Fig. 1 Born–Haber cycle for dissolution of the salt MX.

Because both $\Delta_{latt}G°$ and $\Delta_{solv}G°$ are very large (negative) quantities, typically of the order of −1000 kJ/mol, it follows that relatively small changes in either, for example, arising from minor changes in the nature of the solvent or the salt, can result in dramatic changes in solubility. Given that $\Delta_{sln}G^{o} = -RT \ln K_{sp}^{o} = 2.303\ RT\ pK_{sp}^{o}$

where R and T have their usual meanings and $\mathbf{K_{sp}^{o}}$ is the (standard) solubility product of the salt:
In turn, most of the theories that have been used to predict the extend of solubility of an ionic compound in a given solvent or in a mixed solvent and related ion association are based on changes in the electrostatic properties of the solvent, solute and ion solvation as well as on the ionic strength of the medium [8-15].

2. EXPERIMENTAL

2.1 Chemicals and Reagents

Barium diphenylaminesulfonate and ethanol were purchased from Merck Company with high degree of purity and used without further purification.

2.2 Preparation of mixed solvent and saturated solutions

The mixed solvent, (ethanol + water by value percent of ethanol = 0, 20, 40, 60, 80 and 100% by volume), were prepared from deionized water and fairly pure ethanol. Then, saturated solutions of barium diphenylaminesulfonate were prepared by dissolving different amounts in closed test tubes containing different (ethanol + water) mixtures. These mixtures were then saturated with nitrogen gas an inert atmosphere. The tubes were placed in a shaking thermostat (Model Gel) for a period of four days till equilibrium reached. The solubility, S (g.mole/Kg.solvent), of barium diphenylaminesulfonate in the mixed solvent at different temperature was determined gravimetrically by the solvent evaporating method. All the solubility experiments were repeated at least three times and the results were averaged.

3. RESULTS AND DISCUSSION

For an ionic compound, with the formula BA_2, we may consider the following equilibrium in its saturated solution at a given constant temperature.

$$\mathbf{BA_2(s) \leftrightarrow B^{2+}{}_{(aq)} + 2A^{-}{}_{(aq)}, \qquad K_{sp(th)} = a_{+} \cdot a_{-}^{2}} \qquad (1)$$

Where $K_{sp(th)}$ denotes the thermodynamic solubility product constant and a_+ and a_- refer to activity of B^{2+} and A^- in the solution, respectively. If the solubility of BA_2 is very low, it may replace the activity of each ion by its concentration, S_o

$$K_{sp(th)} = 4S_o^3 \qquad (2)$$

Where S_o represents the molarity of BA_2 in the very dilute solution. The electrostatic interaction becomes very small and the ion association phenomenon may be negligible (the activity coefficient $\gamma_{\pm} \sim 1$) [16-21].
At low concentration, the activity coefficient may be determined by using the Debye-Huckel limiting law:

$$\log \gamma_{\pm} = -Z_{+}Z_{-}A\sqrt{I} \quad \textbf{applicable for } I < 10^{-2}\,M \qquad (3)$$

Where Z_+ and Z_- are the charges of ions in solutions, **$A = 1.823 \times 10^{6}(\varepsilon.T)^{-3/2}$**, the ionic strength, I, defined as, $I = \frac{1}{2}\sum_i m_i Z_i^2$ (z_i is the charge on ion i, and m_i is the molality of ion i) and the ionic strength, I emphasizes the charges of ions because the charge numbers occur as their squares. The values of dielectric constant **(ε)** for ethanol-water mixtures were taken from previous publications [22].

On the other hand, it can be considered that at high concentration, the solubility product constant (K_{sp}) is given by:

$$K_{sp} = 4S^3\,\gamma_{\pm}^3 \qquad (4)$$

where S is the molal solubility of BA_2 and $\gamma_{\pm}$ is the mean molal activity coefficient. There are several theoretically-based expressions that can be used to estimate single ion activity coefficients [15]. At relatively high concentration, the electrostatic interaction becomes very large [23-26]. The activity coefficient may be determined using the extend Debye-Hückel law:

$$\log \gamma_{\pm} = -\frac{Z_{+}Z_{-}A\sqrt{I}}{I + Br^{\circ}\sqrt{I}} \qquad \textbf{for} \quad I < 10^{-1}\,M \qquad (5)$$

Where **$B = 50.29\,(\varepsilon.T)^{-1/2}$**, and r° is the solvated radius.

At high concentrations, activity coefficients of electrolyte solutions can be determined by using the Davies equation [27] which is an empirical extension of Debye–Hückel theory. The final form of the equation gives the mean molal activity coefficient, $\gamma_{\pm}$, of an electrolyte which dissociates into ions having charges z_+ and z_- as a function of ionic strength, I.

$$\log \gamma_{\pm} = -Z_{+}Z_{-}A\left(\frac{\sqrt{I}}{I+\sqrt{I}} - 0.3I\right) \qquad (6)$$

The second term, 0.3 *I*, goes to zero as the ionic strength goes to zero, so the equation reduces to the Debye–Hückel equation at low concentration. However, as concentration increases, the second term becomes increasingly important, so the Davies equation can be used for solutions too concentrated to allow the use of the Debye–Hückel equation.

The molal solubility , S (g.mole/Kg.solvent), of barium diphenylaminesulfonate in the mixed solvent at different temperature was determined gravimetrically by the solvent evaporating method. The solubility values and activity coefficients are cited in Table (1).

The solubility of saturated solution of barium diphenylaminesulfonate in mixed solvents found to decrease with the increase the mole fraction of EtOH in the mixed solvent and increase with increase temperature depends primarily on the solvation of the solutes or their constituent ions by the components of the solvent mixtures. The saturated solution of diphenyl amine barium salt in the mixed solvent is perfectly non-ideal. The non-ideality is partly due to the mean activity coefficient of ions in the solution and partly due to the ion association phenomenon.

The solubility product was calculated by the use of equation (7).

$$pK_{sp} = -4(\log S^3 + \log \gamma_{\pm}^{3}) \ldots\ldots\ldots\ldots (7)$$

The solubility product (pK_{sp}) data are given in Table (2), the Gibbs free energies of solvation and the transfer Gibbs free energies from water to mixed solvents were calculated by using equations (8) and (9) [28-32]. Their values are tabulated also in Table (2) and Table (3).

$$\Delta G^{o} = 2.303\ RT\ pK_{sp} \qquad (8)$$

$$\Delta G_{t} = \Delta G_{s} - \Delta G_{w} \qquad (9)$$

Where (s), (w) denote solvent and water, respectively.

The enthalpy change of solvation $(\Delta H)_s$ were calculated From the plots of log $K_{sp.}$ versus $\frac{1}{T}$ as shown in Figs. 1, where the slope equals $-\Delta H/2.303\ R$ using van 't Hoff equation [33]:-

$$\log \mathbf{K} = -\frac{\Delta \mathbf{H}^{\circ}}{2.303\mathbf{R}}\left(\frac{1}{\mathbf{T}}\right) + \mathbf{constant} \qquad \mathbf{(10)}$$

From equation (18) & (20) the values of $(\Delta G)_s$ and $(\Delta H)_s$ can be used to calculate the values of TΔS at different temperatures according to Gibbs-Helmholtz equation (12) [32] and all the results are reported in Table (3).

$$(\Delta \mathbf{G})_s = (\Delta \mathbf{H})_s - (\mathbf{T}\Delta \mathbf{S})_s \qquad \mathbf{(12)}$$

The magnitude of $\Delta G_{t\ (\text{solute},\ w \rightarrow w+s)}$ as shown in Figs. 2 is a measure of the overall change in the solvation (energy) of an ion upon its transfer from water to an organic–aqueous mixture. Such quantities are usually "well behaved" in the sense that they vary smoothly as a function of solvent composition, even though they may show great diversity. It was concluded that the Gibbs free energies of transfer increase in negativity by increasing the mole fraction of EtOH in the mixed EtOH -H_2O solvents indicating the decrease in spontaneous nature of barium diphenylaminesulfonate solubilization. This is due to more solvation behaviour in water than that of the mixed solvents where the Gibbs free energy values provide information on whether the process conditions favor or disfavor barium diphenylaminesulfonate solubilization in the aqueous carrier solution. Positive Gibbs free energy values indicate disfavourable conditions.

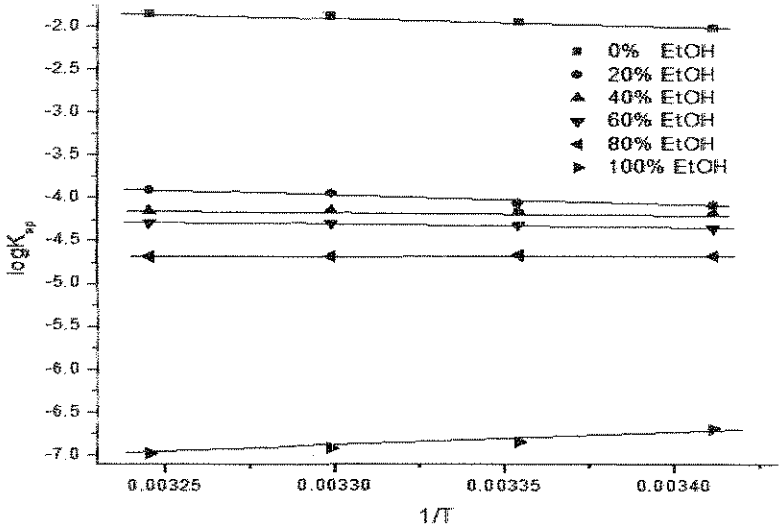

Fig. 1. Plots of log $K_{sp.}$ for barium diphenylaminesulfonate versus $\frac{1}{T}$ at different vol % of EtOH.

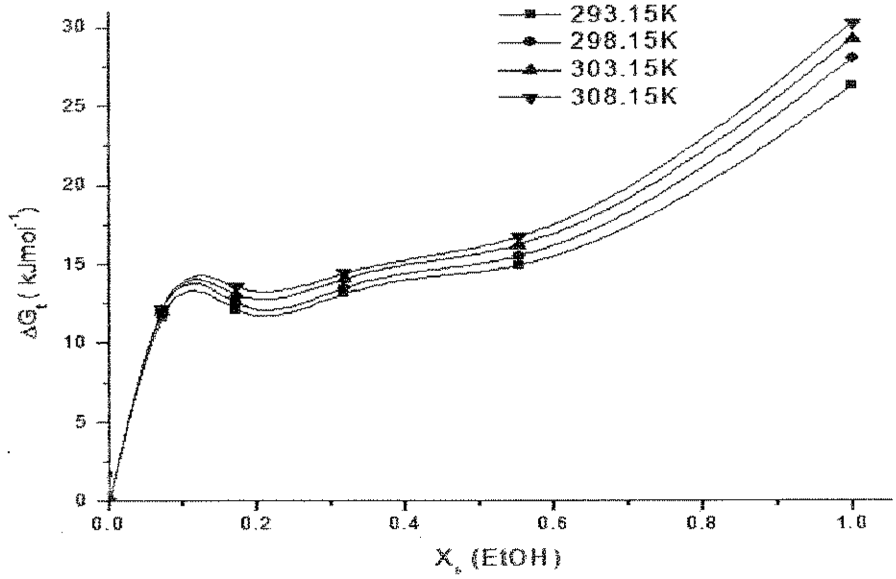

Fig. 2. Gibbs free energies of transfer (ΔGt) for barium diphenylaminesulfonate versus the mole fraction (X_s) of EtOH at different temperature.

Table 1. Solubilities and molal activity coefficients for barium diphenylaminesulfonate in mixed EtOH-H2O solvents at different temperature.

EtOH% By vol.	X_s EtOH	S,g. mol/kg solvent				log $\gamma_\pm$			
		293.15K	298.15K	303.15K	308.15K	293.15K	298.15K	303.15K	308.15K
0	0	0.2416	0.2548	0.2682	0.2753	0.5513	0.5518	0.5516	0.5508
20	0.0717	0.0468	0.0485	0.0538	0.0569	0.5792	0.5729	0.5605	0.5510
40	0.1708	0.046	0.0479	0.0489	0.049	0.5515	0.5428	0.5369	0.5316
60	0.3166	0.0451	0.0468	0.0476	0.0481	0.4924	0.4902	0.4868	0.4844
80	0.5527	0.0446	0.0464	0.0468	0.0474	0.3878	0.3757	0.3702	0.3631
100	1	0.0439	0.0459	0.0468	0.0470	0.0838	0.0711	0.0669	0.0631

Table 2. Solubility products and Gibbs free energies of solvation for barium diphenylaminesulfonate in mixed EtOH-H_2O solvents at different temperature.

X_s, EtOH	pK_{sp}				ΔG_s, kJ/mol			
	293.15K	298.15K	303.15K	308.15K	293.15K	298.15K	303.15K	308.15K
0	2.0246	1.9543	1.8855	1.8553	11.364	11.157	10.944	10.947
0.0717	4.0974	4.0661	3.9608	3.9081	22.999	23.212	22.99	23.059
0.1708	4.1848	4.1526	4.1410	4.1519	23.489	23.706	24.037	24.497
0.3166	4.3591	4.3152	4.3102	4.2963	24.468	24.634	25.019	25.349
0.5527	4.6841	4.6745	4.6807	4.6891	26.292	26.686	27.169	27.667
1	6.7008	6.8562	6.9206	6.9812	37.612	39.141	40.171	41.191

Table 3. Transfer Gibbs free energies, enthalpy and entropy of solvation for barium diphenylaminesulfonate in mixed EtOH-H_2O solvents at different temperature.

X_s, EtOH	ΔG_t, kJ/mol				ΔH_s, kJ/mol	$(T\Delta S)_s$, kJ/mol			
	293.15K	298.15K	303.15K	308.15K		293.15K	298.15K	303.15K	308.15K
0	0.000	0.000	0.000	0.000	20.006	8.642	8.850	9.062	9.060
0.0717	11.634	12.055	12.046	12.112	23.206	0.188	0.205	0.216	0.224
0.1708	12.125	12.549	13.092	13.550	3.889	-19.601	-19.818	-20.148	-20.609
0.3166	13.104	13.478	14.074	14.402	6.714	-17.754	-17.920	-18.305	-18.635
0.5527	14.928	15.529	16.225	16.720	-0.717	-27.009	-27.403	-27.886	-28.384
1	26.247	27.984	29.226	30.244	-31.432	-69.043	-70.572	-71.602	-72.622

4. CONCLUSIONS

The solubility of saturated solution of barium diphenylaminesulfonate in mixed solvents found to decrease with the increase the mole fraction of EtOH in the mixed solvent and increase with increasing the temperature. In addition, Gibbs energy, enthalpy, entropy for the solution processes and free energies of transfer were also calculated in order to estimate the contributions solute-solvent interactions related ion association are based on changes in the electrostatic properties of the solvent, solute and ion solvation as well as on the ionic strength of the medium. The saturated solution of diphenyl amine barium salt in the mixed solvent is perfectly non-ideal. The non-ideality is partly due to the mean activity coefficient of ions in the solution and partly due to the ion association phenomenon. By choosing a suitable model for estimating the mean activity coefficient and using the iteration calculations, we obtained the value of ion-pair concentration and the activity coefficient contribution and ion association contribution to the solubility of the considered ionic compound in the considered mixed solvent at different temperature.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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QUANTUM MECHANICAL STUDIES OF THE KINETICS, MECHANISMS AND THERMODYNAMICS OF THE GAS-PHASE THERMAL DECOMPOSITION OF ETHYLVINYL ETHER.

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ABSTRACT

The thermal decomposition of Ethyl Vinyl Ether was studied using Austin Model (AMI), Re-parameterized Austin Model (RMI), Parameterized Model 3 (PM3) and Modified Neglect of Diatomic Overlap (MNDO) Hamiltonian in the Semi-Empirical method, Hartree – Fock at 3-21G,6-31G, 6-31G** level, and Density Functional method with Becke 3 Lee Yang Parr (B3LYP), 6-31G* in the Ab-initio method of calculation in Spartan'10. The geometric properties such as the bond length, dihedral, bond angles, heat of formation, atomic charges, and vibrational frequencies were obtained. The data were used to calculate the change in enthalpy ΔH, entropy ΔS, free energy ΔG, pre exponential factor A, Rate, k at 624K, and the variation of rate, k with temperatures at 498K - 773K at temperature interval of 25K. It was observed that the values obtained are in good agreement with experimental values for both semi-empirical and ab-initio methods and according to Arrhenius Theory, calculated rate k, increases with increase in temperature.*

KEYWORDS: Kinetics, ethyl vinyl ether, semi-empirical,ab-initio, transition state

RESUMO

A decomposição térmica do éter de etil vinila foi estudada usando os modelos Austin (AMI), Reparametrizado Austin (RMI), Parametrizado 3 (PM3) , Negligenciando a Superposição Molecular (MNDO), Hartree-Fock, Densidade Funcional Becke3 Lee Young Parr e o método Ab-initio em Spartan 10. Foram obtidos propriedades tais com comprimentos de ligações, ângulos, calor de formação, cargas atômicas e freqüência vibracional. Foram calculados parâmetros tais como a entalpia, energia livre, fator pré-exponencial A, velocidade, k à 624K. Os valores calculados concordaram com resultados experimentais.

PALAVRAS CHAVE: Cinética, éter de etil vinila , métodos semi-empíricos, ab-initio, estado de transição

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INTRODUCTION

Although there are numbersof experimental studies onthermal gas phase decomposition of aliphatic ethers and vinyl ethers but few work has been done on the kinetics,thermodynamics and mechanism using computational approach. However, semi empirical self –consistent field theory (SCF) molecular orbital method MNDO was used to study the kinetics of the pyrolysis of ethyl vinyl ether (Bamkole, 1990). The gas-phase thermal decomposition of alkylvinyl ethers proceeds through a retro–eneand in some cases through H-transfer molecular mechanism,through a six – membered cyclic transition state in which the $\beta - H$ atom,attracting the terminal vinyl carbon atoms is part of the six membered cyclic transition state which involves a C-H bond making, C-H and C-O bond breaking.

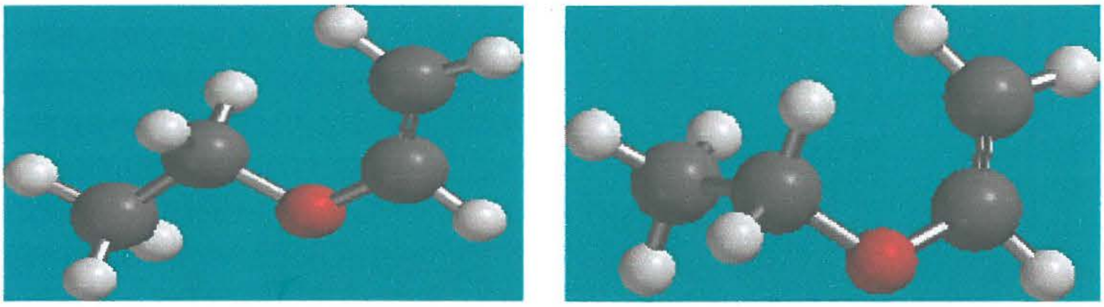
A large number of the gas- phase unimolecular reaction which have been studied, appeared to take place by way of 4-center and 6-center cyclic process (O' Neal and Benson, 1967). The thermal decomposition of ethyl vinyl ether gives acetaldehyde and acetylene as the products.

The aim of this study is to take a closer look through the computational method to study the kinetics, thermodynamics and mechanism of the thermal decomposition of ethyl vinyl ether through a procedure devised by Adejoro and Bamkole (2005) using semi –empirical and ab-initio method in Spartan '10.

COMPUTATIONAL METHOD

Conformational search was performed on the molecule to locate the structure with the lowestenergy. The conformational search was carried out using molecular mechanics force field (MMFF) which is quite successful in assigning low energy conformers and in providing quantitative estimates of conformational energy differences (Warren, J.Hehre, 2003). Using semi-empirical and ab initio methods the geometry of the lowest energy conformer in Spartan reactant was optimized. There are four different conformersand the heat of formation with AMI calculation is as shown in fig. 1 below:

Fig 1: CONFORMERS OF ETHYL VINYL ETHERS

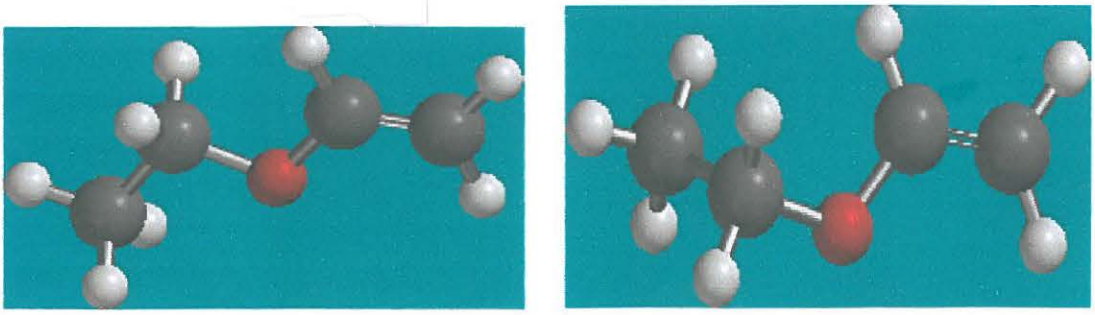


Energy = 16.384 **kJ/Mol**

HOF = -139.650 kJ/mol

Energy = 24.798 **kJ/Mol**

HOF = -139.282 kJ/mol



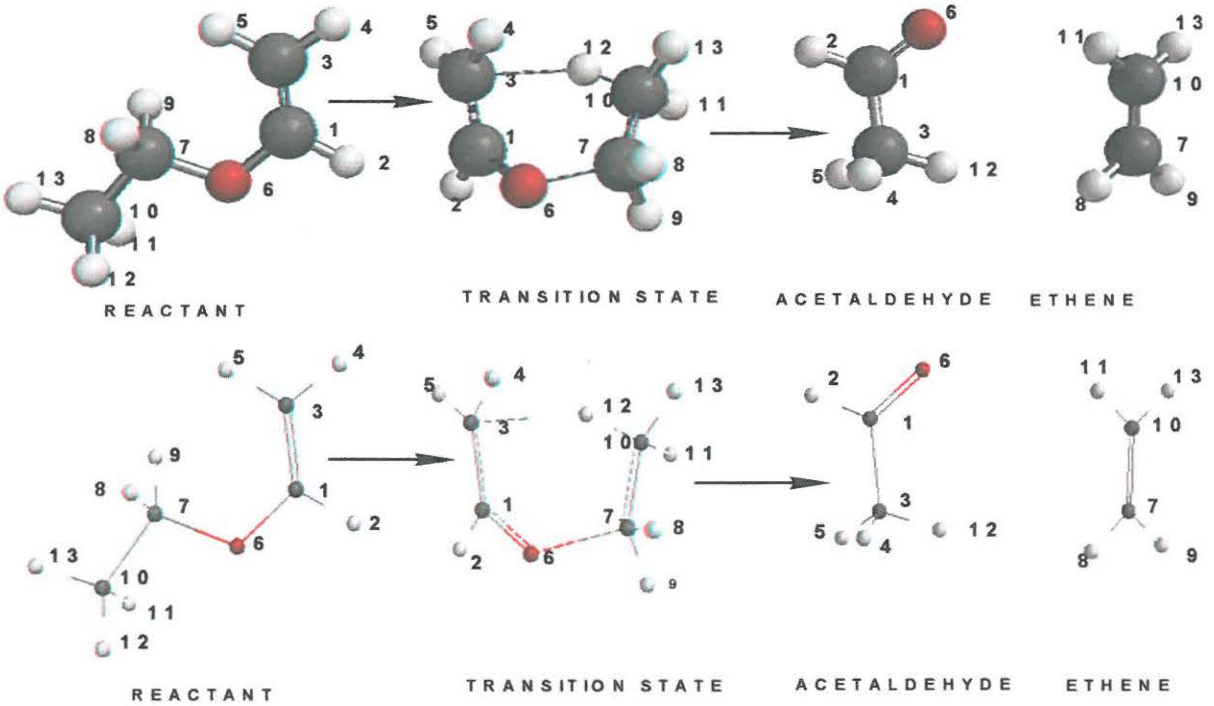
Energy = 25.189 **kJ/Mol**

HOF = -131.069 kJ/mol

Energy = 31.414 **kJ/Mol**

HOF = -133.733 kJ/mol

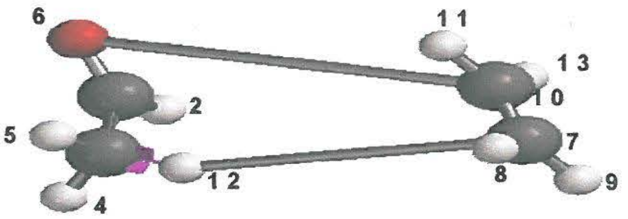
In the structure below H_{12} is the β -H atom to be eliminated from the alkyl part and the dihedral 6-7- 10-12(-59.91°) is acute negative.



Scheme 1: REACTION SCHEME

Reaction Path Study

Reaction path calculations were performed on the optimized geometry of each of the alkyl vinyl ether under study using $H_{12} - C_3$ as the reaction coordinate. The internal coordinate was varied from its initial distance in the stable reactants form to its value in the product molecule. For example, for ethyl vinyl ether, the initial distance between H_{12} and C_3 is 4.723Angstroms. This inter atomic distance is slowly altered throughout the reaction path calculation taking the value from 4.723 (initial value) to 1.09 Angstroms its approximate value in the stable product molecule in 20 steps. As reported in previous work, (McIver, 1971) instead of the energy to pass smoothly through a maximum rose to a very high value and the geometry suddenly drop to a product with a drop in the heat of formation with the values approximately the same as the sum of the expected products (acetaldehyde and ethylene) as shown in figure 2 below:



REACTION PATH STUDY (ETHYL VINYL ETHER)

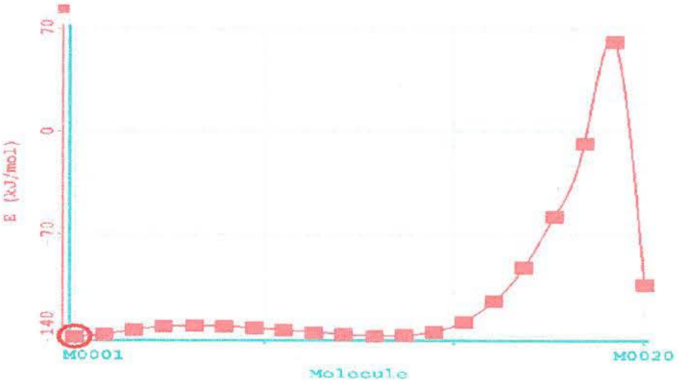


Fig 2: A PLOT OF ENERGY AGAINST THE NUMBER OF MOLECULES TO DEPICT THE REACTION PATH STUDIES

Transition State structure

Potential energy surfaces provide a basis for understanding the relationship between molecular structure and stability. Stable molecules correspond to energy minima along the reaction coordinate. Transition states correspond to the energy maxima. The problem is that the diagram cannot be constructed that is cannot bevisualized. However, the underlying principle is that stable molecules (energy minima) will be interconnected by smooth pathway passing through well – defined transition state remain the same. The only problem is to identify this special point (stable molecules/transition state).

Using the guess-transition state in Spartan on the suggested mechanism of the transition state structure was optimized and was subjected to the two tests needs to be performed in order to verify that a practical geometry corresponds to a saddle point (transition structure) and that this saddle point corresponds to the reactants and products. The tests are:

That the Hessian matrix of second – energy derivations with respect to coordinates yields one and only one imaginary frequency which will be in the range of 400-2000 cm^{-1} and the normal coordinates corresponds to the imaginary frequency smoothly corrects reactants and products. This could be achieved by animating the normal coordinate.

Intrinsic reaction Coordinate

The intrinsic reaction coordinates method was also used by optimizing the molecule subject to a fixed position along the reaction coordinate (Warren Hehre, 2003). The transition state was confirmed using the IRC method. Two IRC calculations were performed. The first one a positive perturbation was done by an initial perturbation on the atomic coordinates in the direction of the single negative frequency while the other one a negative perturbation performed along the same normal coordinates.

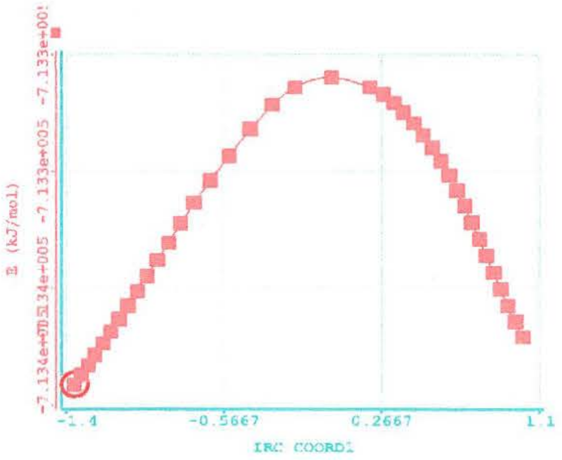
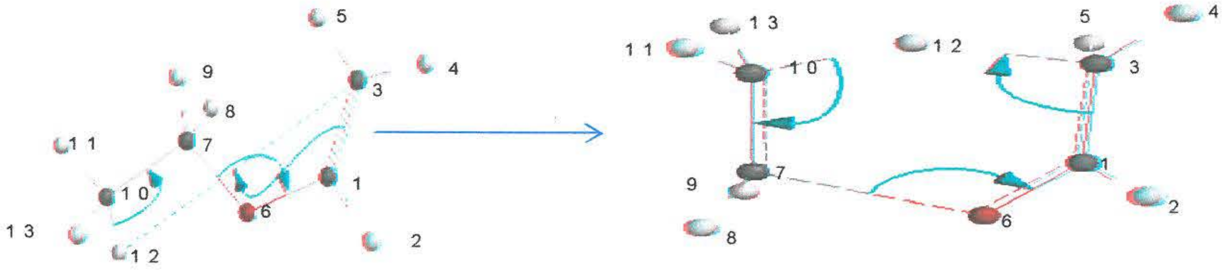


Fig 3: **A PLOT TO SHOW THE INTRINSIC REACTION COORDINATE**

Mechanismof decomposition of Alkyl Vinyl Ethers.

There are various studies on the thermal decomposition of aliphatic ethers in the gas phase but there are very few examples in the studies of vinyl ether with substituents on the vinyl carbon. (Flowers et al 1981 and Awan et al 1988) reported that the thermal decomposition of aliphatic ethers proceeds through a retro –ene molecular mechanism through a six – membered cyclic transition state in which the $\beta - H$ atom, attracting the terminal vinyl carbon atoms is part of the six member cyclic transition state which involves a C-H bond making, C-H and C-O bond breaking and according to experimental evidence, the C-O bond breaking is the rate-determining step (J.W. McIver Jr. and A. Kormonicki,1972)

In the kinetics study of the thermal gas phase decomposition of 2- butoxypropene at temperature range 640- 680K (Awan and Mahmood, 1999) states that acetone and 1-butene were the only products. Acetaldehyde and 1-butene were the only products in the pyrolysis of ethyl vinyl ether and the reaction proceeds through a six – membered cyclic transition state in which the $\beta - H$ atom, attracting the terminal vinyl carbon atoms is part of the six member cyclic transition state.



REACTANT TRANSITION STATE

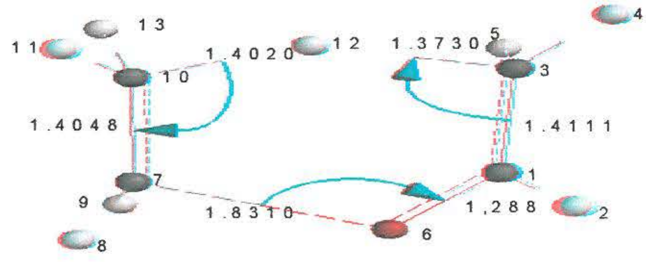


Fig 4: Reaction Mechanism

CALCULATION

The thermodynamic calculations were obtained for ethyl vinyl ether through calculation on the ground state GS, Transition state, TS and the product. The statistical mechanically calculated enthalpy and entropy was used which is not the true representative of the total energy of the molecule, knowing that the large portion of the enthalpy in a molecule is contained in its bonds and physical conformation hence the sum of the ground state energy (GSE) and the statistical mechanically calculated enthalpy are used to arrive at a closer approximation of the true energy of the molecule. With the said modified version of the heat of reaction the equation is given as shown below [Spartan guide]. The enthalpy of a species will be defined as:

$$\mathrm{H_i} = \mathrm{GSE}_i + \mathrm{H_i}^{\mathrm{sm}}$$

Where the superscript 'sm' is the statistical mechanically calculated enthalpy. Substitute this into the initial definition of the heat of reaction we have:

$$\Delta \mathrm{H_{Rxn}} = \left(\mathrm{GSE_{product}} + \mathrm{H^{sm}_{Product}}\right) - \left(\mathrm{GSE_{reactant}} + \mathrm{H^{sm}_{reactants}}\right)$$

The enthalpy of reaction was calculated at 624K.

Activation energy (Ea) was calculated according to the transition state theory for a unimolecular reaction at 624K.

$$\mathrm{Ea} = \Delta \mathrm{H} + \mathrm{RT}$$

The entropy of the reaction was calculated by taking the difference of product and reactant entropies that is

$$\Delta \mathrm{S_{reaction}} = \mathrm{S_{Product}} - \mathrm{S_{reactants}}$$

$$\text{And } \Delta S \text{ activated} = \mathrm{S_{transition}} - \mathrm{S_{reactant}}$$

The Gibbs free energy was calculated using the modified version of the heat of reaction equation. Knowing that $\mathrm{G = H - TS}$

$$\Delta \mathrm{G}^* = \Delta \mathrm{H}^* - \mathrm{T}\Delta \mathrm{S}.$$

The first order coefficient K (T) was calculated using transition State theory (TST) (Benson, 1960) assuming that the transition coefficient is unity as shown in the following equation

$$\mathrm{K(T)} = \frac{\mathrm{K'T}}{\mathrm{h}} \exp\left[\frac{-\Delta \mathrm{G}^*}{\mathrm{RT}}\right]$$

Where ΔG^* is the Gibbs free energy change between the reactant and the transition state and $K'$and h are the Boltzmann and Planck constants respectively.

Pre –exponential factor is given as $\mathrm{A} = \frac{\mathrm{K_B T}}{\mathrm{h}} \exp\left[\frac{-\Delta \mathrm{S}}{\mathrm{R}}\right]$

Arrhenius rate was obtained using the rate equation

$$K(T) = A \exp\left[\frac{-Ea}{RT}\right] \qquad [4]$$

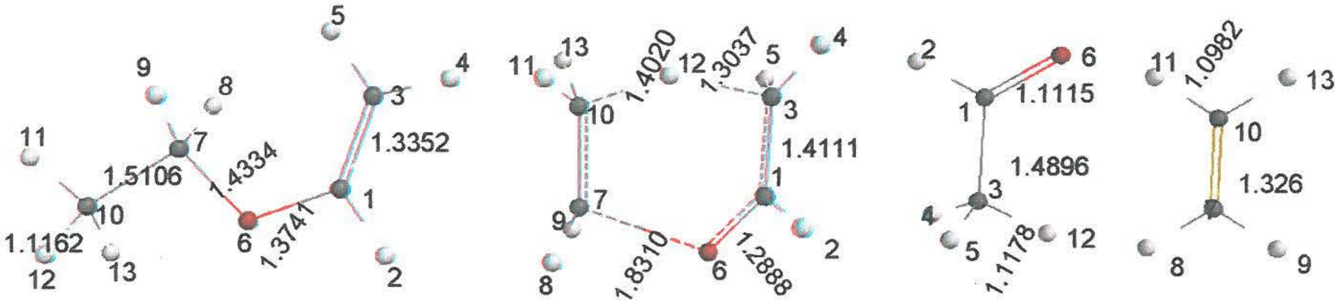
RESULTS AND DISCUSSION

The pyrolysis of ethyl vinyl ether gives acetaldehyde CH_3CHO and ethylene C_2H_4 in the structure (fig 1) H_{12} is the hydrogen attached to the β - carbon that is hydrogen eliminated from the alkyl group. The bond between C_3 and H_{12} is stretched with the bond length of 1.3730 (AM1), 1.4280 (RM1), 1.3910 (PM3), 1.2110 (MNDO) for semi empirical and the pyrolysis of ethyl vinyl ether gives acetaldehyde CH_3CHO and ethylene C_2H_4. The decomposition proceeds through a retro ene molecular mechanism through a six membered cyclic transition state as shown in fig (1) below which involves C – H bond making, C – H and C – O bond breaking as shown in fig 1 below. In the structure, $H_{12}$is the β – hydrogen to be eliminated from the alkyl group. In the transition state there is a stretch between $C_{10} - H_{12}$ bond with bond length 1.402 (AM1) 1.092 (RM1), 1.420 (PM3), 1.701 (MNDO) 1.400 (HF321G), 2.204 (HF631G*) 1.0761 (HF 631G**) and 1.0909 (DFT/B3LYP/631G*) as against the bond length of 1.1164 (AM1), 1.099 (RM1), 1.098 (PM3) 1.108 (MNDO), 1.082 (HF 321G), 1.0839 (HF 631G*), 1.0841 HF(631G*) and 1.095 (DFTB3LYP/631G*) at the ground state from the table 1 below, it is shown that both semi – empirical and ab initio method could predict the bond length effectively except for RM1 and DFT which has values lower compare with others. From the Table the (2) dotted lines shows the point where cleavage occurs that is between $O_6 - C_7$ also with a long stretch in the bond length in the transition state for all the methods and between $C_{10} - H_{12}$ while a bond is formed between $C_3 - H_{12}$ and also from the table, at the ground state the bond length is in the range of 4.7 to 4.9 transition state, in the range of 1.0 to 1.4 against the stable product bond length in the range of 1.07 to 1.09. The bond angles and dihedrals are shown in tables 1b and 1c below.

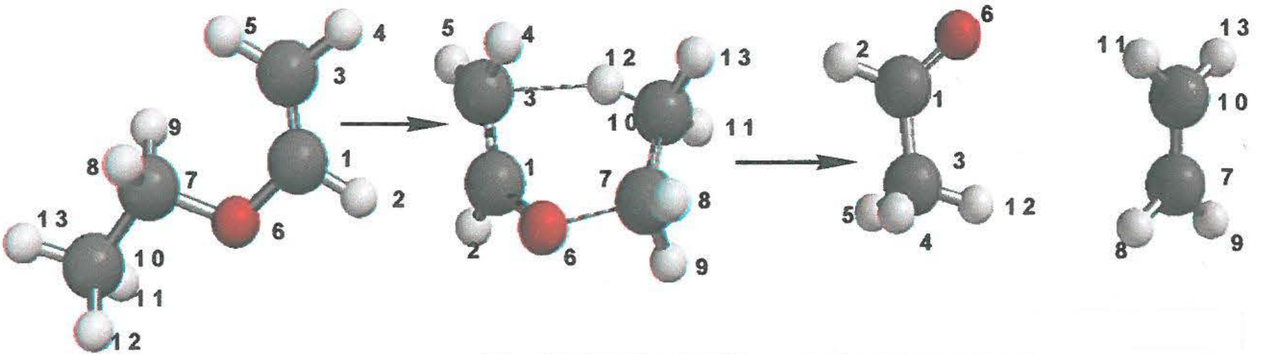
Atomic charges are shown in Mulliken. The Mullikencharges arepreferred because it gives simple and reasonable estimates of atomic charges. (Spartan guide). The formal charges in the TS: (table 1), show that H_{12} has the largest charge development while C_7 has the least (Lee et al 1987). The polarization of the $C_7 - O_6$ and $C_{10} - H_{12}$ bond cases positive charges on the carbon atoms C_1 and C_7 to increase and the C_{10} atom to become more negative (table 1d). the increase in the negative charge on C_{10} being much greater, cases much bond polarization of the $C_{10} - H_{12}$

places – considerable positive charge on the H_{12} atom, such that the positive charge is delocalized over the entire $O_6 - C_1 - C_3$ frame in the TS. In the TS, the $C_7 - C_{10} - H_{13}$ is electron demand and supply within the GS of ethyl vinyl ether, the vinyl carbon becomes (C_3) quite highly negative and β – Hydrogen, H_{12} becomes quite acidic, so that a fast proton transfer equilibrium takes place. The formation of an intermediate in which there is attack from the vinyl carbon on the β – Hydrogen, H_{12} takes place as a fast step followed by the rate determining step.

There is an assumption that the interaction and charge transmission C_7 and C_{10} is not efficient so that a sizable change on C_{10} is not efficiently transmitted to the electron deficient C_7, hence a double bond formation between C_7 and C_{10} takes place slowly. (Lee et al, 1987).



REACTANT TRANSITION STATE ACETALDEHYDE ETHYLENE



REACTANT TRANSITION STATE ACETALDEHYDE ETHENE

Table 1: BOND LENGTH FOR PYROLYSIS OF ETHYL VINYL ETHER

BOND		AMI	RMI	PM3	MNDO	HF/ 3-21G	HF/ 6-31G*	HF/ 6-31G**	DFT/ B3LYP 631G*
C_1-H_2	GS	1.1048	1.0965	1.0944	1.1013	1.0708	1.0743	1.0751	1.0871
	TS	1.1080	1.1016	1.0987	1.0990	1.0822	1.0940	1.0960	1.1065
	Prd	1.1142	1.1065	1.1024	1.1116	1.0868	1.0952	1.0971	1.1143
	Δd(TS-GS)	+0.0032	+0.0051	+0.0043	-0.0023	+0.0114	+0.0197	+0.0209	+0.0194
C_1-C_3	GS	1.3352	1.3310	1.3334	1.3486	1.3160	1.3206	1.3204	1.3371
	TS	1.4111	1.4000	1.4110	1.4525	1.3885	1.4990	1.4972	1.4010
	Prd	1.4896	1.5001	1.4985	1.5167	1.5070	1.5041	1.5030	1.5083
	Δd (TS-GS)	+0.0759	+0.069	+0.0776	+0.1039	+0.0725	+0.1784	+0.1768	+0.0639
C_1-O_6	GS	1.3741	1.3575	1.3619	1.3586	1.3693	1.3407	1.3406	1.3570
	TS	1.2888	1.2801	1.2737	1.3043	1.2721	1.1880	1.1880	1.2675
	Prd	1.1115	1.2146	1.2097	1.2214	1.2086	1.1876	1.1877	1.2105
	Δd (TS-GS)	-0.0853	-0.0774	-0.0882	-0.0543	-0.0972	-0.1527	-0.1526	-0.0895
C_3-H_4	GS	1.0958	1.0840	1.0846	1.0881	1.0705	1.0731	1.0733	1.0839
	TS	1.1018	1.0883	1.0887	1.1019	1.0733	1.0810	1.0821	1.0879
	Prd	1.1178	1.0997	1.0979	1.1090	1.0857	1.0866	1.0867	1.0924
	Δd (TS-GS)	+0.0060	+0.0043	+0.0041	+0.0138	+0.0028	+0.0079	+0.0088	+0.004
C_3-H_5	GS	1.0949	1.0821	1.0856	1.0860	1.0706	1.0729	1.0730	1.0836
	TS	1.1071	1.0903	1.0918	1.1065	1.0768	1.0830	1.0824	1.0883
	Prd	1.1169	1.0997	1.0979	1.1090	1.0857	1.0866	1.0867	1.0980
	Δd (TS-GS)	+0.0122	+0.0082	+0.0062	+0.0205	+0.0062	+0.0101	+0.0094	-0.0047
O_6-C_7	GS	1.4334	1.4133	1.4269	1.4056	1.4426	1.4059	1.4062	1.4275
	TS	1.8310	1.8880	1.8280	1.5060	1.9780	2.3670	2.3680	2.0600
	Prd	-	-	-	-	-	-	-	-
	Δd (TS-GS)	+0.3976	0.04747	+0.0401	+0.1004	+0.5354	+0.9611	+0.9618	+0.6325
C_7-H_8	GS	1.1221	1.1137	1.1071	1.1223	1.0833	1.0859	1.0869	1.0996
	TS	1.1037	1.0943	1.0949	1.1175	1.0694	1.0730	1.0736	1.0832
	Prd	1.0982	1.0858	1.0861	1.0891	1.0737	1.0761	1.0764	1.0876
	Δd (TS-GS)	0.01827	-0.0194	-0.0122	-0.0048	-0.0139	-0.0129	-0.0133	-0.0164
C_7-H_9	GS	1.1221	1.1137	1.1071	1.1223	1.0833	1.0859	1.0869	1.0996
	TS	1.1044	1.0941	1.0943	1.1166	1.0682	1.0710	1.0722	1.0827
	Prd	1.0982	1.0858	1.0861	1.0891	1.0737	1.0761	1.0764	1.0876
	Δd (TS-GS)	-0.0177	-0.0196	-0.0123	-0.0057	-0.0151	-0.0149	-0.0147	-0.0169
C_7-C_{10}	GS	1.5106	1.5247	1.5163	1.5406	1.5234	1.5150	1.5143	1.5186
	TS	1.4048	1.4164	1.4054	1.4521	1.3927	1.3140	1.3131	1.4055
	Prd	1.3260	1.3222	1.3220	1.3347	1.3151	1.3171	1.3165	1.3308
	Δd (TS-GS)	-0.1058	-0.1083	-0.1109	-0.0885	0.1307	-0.201	-0.2012	-0.1131
$C_{10}-H_{11}$	GS	1.1162	1.0994	1.0979	1.1081	1.0819	1.0839	1.0841	1.0946
	TS	1.1058	1.0926	1.0892	1.1089	1.0773	1.0760	1.0770	1.0760
	Prd	1.0982	1.0858	1.0861	1.0891	1.0737	1.0761	1.0767	1.0876
	Δd (TS-GS)	-0.0104	-0.0068	-0.0087	-0.0191	-0.0046	-0.0079	-0.0071	-0.0186
$C_{10}-H_{12}$	GS	1.1162	1.0994	1.0979	1.1081	1.0819	1.0839	1.0841	1.0946
	TS	1.4020	1.0926	1.4200	1.7010	1.4000	2.2040	1.0767	1.0909
	Prd	-	-	-	-	-	-	-	-
	Δd (TS-GS)	+0.2858	-0.0068	+0.3221	+0.5929	+0.3181	+1.1209	-0.0074	-0.0046
$C_{10}-H_{13}$	GS	1.1158	1.0989	1.0973	1.1095	1.0836	1.0854	1.0855	1.0955
	TS	1.1051	1.10927	1.0891	1.0883	1.0768	1.0750	1.0754	1.0906
	Prd	1.0982	1.0858	1.0861	1.0891	1.0737	1.0761	1.0767	1.0876
	Δd (TS-GS)	-0.0107	-0.0062	-0.0082	-0.0212	-0.0068	-0.0104	-0.0101	-0.0049
C_3-H_{12}	GS	4.7230	4.7400	4.7750	4.9130	4.7510	4.7360	4.7350	4.7630
	TS	1.3730	1.4280	1.3910	1.2110	1.4410	1.0770	1.0790	1.4980
	Prd	1.1178	1.0997	1.0977	1.1074	1.0804	1.0815	1.0816	1.0981
	Δd (TS-GS)	-3.3500	-3.3120	-3.3840	-3.7020	-3.310	-3.659	-3.6560	-3.2650

Table 2: SELECTED BOND ANGLE (0°) FOR ETHYL VINYL ETHER

BOND		AMI	RMI	PM3	MNDO	HF/ 3-21G	HF/ 6 31G*	HF/ 6-31G**	DFT/ B3LYP 631G*
$C_1 - C_3 - H_4$	GS	120.773	121.252	121.936	120.358	119.515	118.854	118.732	118.925
	TS	117.832	119.630	118.869	114.460	119.173	112.060	112.045	119.582
	Prd	109.531	110.919	110.065	109.575	109.888	109.807	109.713	110.499
$H_2 - C_1 - C_3$	GS	124.992	125.433	125.694	121.378	121.978	121.243	121.152	121.841
	TS	120.613	121.316	121.604	121.584	118.233	116.600	116.543	118.032
	Prd	115.258	115.910	116.637	114.022	114.306	115.317	115.295	114.800
$H_2 - C_1 - O_6$	GS	107.902	107.027	105.862	109.374	109.925	110.055	110.187	109.542
	TS	118.259	118.542	117.077	117.434	118.962	120.011	120.039	118.743
	Prd	121.214	122.101	119.944	121.016	120.897	120.281	120.325	120.495
$C_3 - C_1 - O_6$	GS	127.106	127.540	128.445	129.248	128.097	128.702	128.662	128.616
	TS	120.226	119.649	120.710	120.410	121.218	123.311	123.325	121.745
	Prd	123.528	121.990	123.419	124.962	124.796	121.805	124.380	124.705
$H_4 - C_3 - H_5$	GS	115.376	112.201	114.198	113.495	116.911	117.243	117.417	117.298
	TS	113.475	111.922	112.217	109.672	116.121	110.500	110.623	116.123
	Prd	108.508	107.112	107.544	108.185	107.632	107.199	107.194	109.999
$C_7 - C_{10} - H_{11}$	GS	110.473	112.205	111.976	111.976	109.617	109.671	110.539	110.699
	TS	117.456	118.035	119.714	119.714	117.922	117.922	121.860	121.933
	Prd	122.720	123.700	123.191	123.191	121.896	121.896	121.746	117.250
$C_7 - C_{10} - H_{13}$	GS	109.182	110.845	110.108	108.968	110.574	117.243	110.165	110.048
	TS	117.414	117.873	118.668	119.758	117.904	121.940	121.644	117.192
	Prd	122.720	123.700	113.805	123.191	121.896	121.805	121.746	121.933
$H_8 - C_7 - H_9$	GS	109.235	106.715	107.499	108.552	108.552	110.215	107.902	107.700
	TS	115.632	113.649	113.247	115.262	115.262	121.720	115.956	115.451
	Prd	114.560	112.599	123.098	116.208	116.208	121.805	116.538	116.134
$C_{10} - C_7 - H_8$	GS	111.351	111.296	111.437	111.283	111.283	110.926	110.897	111.171
	TS	119.661	120.127	119.063	120.523	120.580	122.030	122.056	121.032
	Prd	122.720	123.700	123.098	121.896	121.896	121.805	121.731	121.933
$C_7 - C_{10} - H_9$	GS	111.351	111.296	111.437	109.234	111.283	110.926	110.897	111.171
	TS	119.552	120.127	110.065	113.765	120.523	122.030	121.986	120.868
	Prd	122.720	123.700	123.098	123.191	121.890	121.805	121.731	121.933
$H_{11} - C_{10} - C_{13}$	GS	109.190	107.279	107.600	107.815	109.176	108.599	108.572	108.483
	TS	113.956	111.378	112.677	114.975	114.838	121.940	1116.501	116.134
	Prd	114.560	112.599	113.805	113.619	116.208	116.390	116.508	113.876
$C_1 - C_3 - H_5$	GS	123.851	126.547	124.866	126.147	123.574	123.903	123.851	123.777
	TS	118.385	121.016	119.869	116.745	117.632	112.060	110.494	118.421
	Prd	109.531	110.919	110.065	109.575	109.888	109.807	109.713	109.796

Table 3: SELECTED BOND DIHEDRALS OF ETHYL VINYL ETHERS

BOND		AMI	RMI	PM3	MNDO	HF/ 3-21G	HF/ 6-31G*	HF/ 6-31G**	DFT/ B3LYP 6 31G*
$H_2–C_1 – C_3 –H_4$	GS	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000
	TS	7.894	7.043	7.976	0.041	11.120	22.630	22.903	11.099
	Prd	59.448	-59.452	-59.182	-59.277	-59.129	-58.815	-58.756	180.000
$H_2–C_1 – C_3 –H_5$	GS	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000
	TS	150.786	154.514	151.290	130.001	160.592	146.290	146.754	163.093
	Prd	-59.448	59.452	59.182	59.277	59.129	58.815	58.756	-58.492
$H_4–C_3 – C_1 –O_6$	GS	180.000	180.000	180.000	180.000	180.000	180.000	180.000	180.000
	TS	176.837	178.869	178.763	171.059	176.604	-160.800	-160.625	177.042
	Prd	-120.552	120.548	120.818	120.723	120.871	121.185	121.244	-0.000
$H_5–C_3 – C_1 –O_6$	GS	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000	-0.000
	TS	-40.290	-33.660	-37.923	-58.898	-33.924	-37.140	-36.774	-30.965
	Prd	120.552	-120.548	120.723	120.723	120.871	-121.19	-121.244	121.508
$H_8–C_7 – C_{10} –H_{11}$	GS	-59.00	-60.466	-59.657	-60.993	-59.844	-60.024	-60.062	-59.922
	TS	-6.217	-5.452	-1.054	13.628	-5.488	-0.180	-0.200	180.00
	Prd	-0.000	-0.000	180.000	-0.000	-0.000	-0.000	-0.000	-0.000
$H_8–C_7 – C_{10} –H_{13}$	GS	61.090	-59.449	-60.040	58.187	60.605	59.981	59.933	59.988
	TS	-147.933	-143.938	-144.334	-138.782	-150.431	-179.680	-179.694	-150.154
	Prd	180.000	180.000	-180.000	180.000	180.000	180.000	180.000	180.000
$H_9–C_7 – C_{10} –H_{13}$	GS	-61.090	-59.449	-60.040	-58.187	-60.605	-59.981	-59.953	-59.988
	TS	5.594	6.842	1.518	-13.808	7.065	0.700	0.755	10.561
	Prd	-0.000	-0.000	180.000	-0.000	180.000	-0.000	-0.000	-0.000
$H_9–C_7 – C_{10} –H_{11}$	GS	178.820	-179.365	-179.736	-177.368	-178.946	-179.986	-179.927	179.898
	TS	147.309	144.799	144.799	138.602	152.008	-179.800	-179.760	151.500
	Prd	180.000	180.000	-0.000	-0.000	180.000	180.000	180.000	-0.000

Table 4: ATOMIC CHARGES (MULLIKEN) OF ETHYL VINYL ETHER

ATOMS		AMI	RMI	PM3	MNDO	HF/ 3-21G	HF/ 6 31G*	HF/ 6-31G**	DFT/ B3LYP 6 31G*
C_1	GS	-0.006	+0.068	+0.045	+0.099	+0.179	+0.216	+0.262	+0.158
	TS	+0.079	+0.170	+0.178	+0.097	+0.301	+0.301	+0.371	+0.227
	Prd	+0.180	+0.249	+0.278	+0.242	+0.340	+0.332	+0.379	+0.261
	Δq (TS-GS)	+0.073	+0.102	+0.133	-0.002	+0.122	+0.085	+0.109	+0.069
H_2	GS	+0.157	+0.127	+0.133	+0.081	+0.247	+0.194	+0.143	+0.140
	TS	+0.101	+0.075	+0.066	+0.063	+0.193	+0.301	+0.095	+0.097
	Prd	+0.083	+0.062	+0.041	+0.013	+0.183	+0.332	+0.090	+0.102
	Δq (TS-GS)	-0.056	-0.052	-0.047	-0.018	-0.054	-0.030	-0.048	-0.043
C_3	GS	-0.341	-0.345	-0.303	-0.186	-0.539	-0.505	-0.391	-0.402
	TS	-0.352	-0.404	-0.323	-0.047	-0.700	-0.597	-0.415	-0.456
	Prd	-0.289	-0.292	-0.196	-0.025	-0.726	-0.586	-0.434	-0.517
	Δq (TS-GS)	-0.011	-0.059	-0.020	-0.139	-0.161	-0.092	-0.024	-0.054
H_4	GS	+0.127	+0.111	+0.099	+0.053	+0.216	+0.180	+0.129	+0.140
	TS	+0.105	+0.099	+0.081	+0.021	+0.212	+0.176	+0.120	+0.147
	Prd	+0.103	+0.092	+0.062	+0.016	+0.234	+0.188	+0.140	+0.182
	Δq (TS-GS)	-0.022	-0.012	-0.018	-0.032	-0.004	-0.004	-0.009	+0.007
H_5	GS	+0.120	+0.111	+0.100	+0.050	+0.213	+0.179	+0.126	+0.140
	TS	+0.124	+0.118	+0.100	+0.038	+0.258	+0.219	+0.155	+0.180
	Prd	+0.103	+0.092	+0.062	+0.016	+0.234	+0.188	+0.140	+0.173
	Δq (TS-GS)	-0.004	+0.007	+0.000	-0.012	+0.045	+0.040	+0.029	+0.04
O_6	GS	-0.226	-0.246	-0.204	-0.288	-0.685	-0.606	-0.619	-0.445
	TS	-0.323	-0.377	-0.340	-0.258	-0.597	-0.604	-0.480	-0.458
	Prd	-0.287	-0.301	-0.315	-0.280	-0.516	-0.466	-0.475	-0.374
	Δq (TS-GS)	-0.097	-0.131	-0.136	+0.030	+0.088	+0.002	+0.139	-0.013
C_7	GS	-0.27	+0.040	+0.051	+0.166	-0.082	+0.001	+0.103	-0.029
	TS	-0.020	+0.111	+0.090	+0.172	-0.254	-0.292	-0.190	-0.160

	Prd	-0.218	-0.175	-0.153	-0.080	-0.425	-0.353	-0.254	-0.285
	Δq (TS-GS)	+0.007	+0.071	+0.039	+0.006	-0.172	-0.293	-0.293	-0.131
H_8	GS	+0.076	+0.054	+0.038	-0.006	+0.205	+0.158	+0.158	+0.141
	TS	+0.113	+0.082	+0.065	+0.018	+0.252	+0.212	+0.212	+0.183
	Prd	+0.109	+0.087	+0.076	+0.040	+0.213	+0.176	+0.176	+0.143
	Δq (TS-GS)	+0.037	+0.028	+0.027	+0.024	+0.047	+0.054	+0.022	+0.042
H_9	GS	+0.076	+0.054	+0.038	-0.006	+0.205	+0.158	+0.111	+0.141
	TS	+0.112	+0.090	+0.072	+0.021	+0.261	+0.212	+0.144	+0.184
	Prd	+0.109	+0.087	+0.076	+0.040	+0.213	+0.176	+0.127	+0.143
	Δq (TS-GS)	+0.046	+0.036	+0.034	+0.027	+0.056	+0.059	+0.033	+0.143
C_{10}	GS	-0.217	-0.191	-0.120	+0.024	-0.605	-0.492	-0.348	-0.456
	TS	-0.376	-0.394	-0.346	-0.075	-0.715	-0.606	-0.331	-0.471
	Prd	-0.218	-0.175	-0.153	-0.080	+0.425	-0.353	-0.254	-0.285
	Δq (TS-GS)	-0.159	-0.203	-0.226	-0.299	-0.110	-0.114	+0.017	-0.015
H_{11}	GS	+0.089	+0.075	+0.050	+0.009	+0.224	+0.177	+0.130	+0.162
	TS	+0.108	+0.103	+0.084	+0.037	+0.234	+0.245	+0.163	+0.184
	Prd	+0.109	+0.087	+0.076	+0.040	+0.213	+0.176	+0.127	+0.143
	Δq (TS-GS)	+0.019	+0.028	+0.034	+0.028	+0.010	+0.068	+0.033	+0.022
H_{12}	GS	+0.089	+0.075	+0.050	+0.009	+0.224	+0.177	+0.130	+0.162
	TS	+0.207	+0.221	+0.184	+0.071	+0.319	+0.185	+0.114	+0.171
	Prd	+0.107	+0.099	+0.067	+0.024	+0.250	+0.208	+0.160	+0.173
	Δq (TS-GS)	+0.118	+0.146	+0.134	+0.062	-0. 095	+0.008	-0. 016	+0.009
H_{13}	GS	+0.082	+0.075	+0.044	+0.003	+0.197	+0.161	+0.113	+0.148
	TS	+0.112	+0.106	+0.087	+0.042	+0.236	+0.188	+0.122	+0.173
	Prd	+0.109	+0.087	+0.076	+0.040	+0.213	+0.176	+0.127	+0.143
	Δq (TS-GS)	+0.030	+0.031	+0.043	+0.039	+0.039	+0.027	+0.009	+0.025

The calculated Arrhenius parameters as shown in table 5 below is in good agreement with the experimental value for instance ΔH calculated for AM1 (191.15), RM1 (191.21), PM3 (188.35). MNDO(193.94), HF/3 21G (190.55), HF/6 31G* (188.14), HF/ 6 31G**(194.56) and DFT/B3LYP 6 31G* (188.89) at 773K compare well with experimental data. Activation energy,Ea, log A and rate, k calculated are in perfect agreement with experimental data.

Table 5: ARRHENIUS PARAMETERS (624K)

	HOR	ΔS $Jmol^{-1}K^{-1}$	ΔG $Jmol^{-1}$	ΔH $kJmol^{-1}$	E_a $kJmol^{-1}$	log A	$k(s^{-1})$
EXPERIMENTAL	-	-	-	177.80 180.81 176.68	183.00 186.01 182.11	11.4 11.6 11.5	$1.3 X 10^{-4}$ (72) $1.1 X 10^{-4}$ (73) $1.7 X 10^{-4}$ (74)
AM1	31.30	11.29	-82.26	190.85	196.04	13.7	$2.0 X 10^{-3}$
RM1	31.01	11.79	-82.55	190.58	195.77	13.7	$2.2 X 10^{-3}$
PM3	33.99	14.49	-78.32	187.88	193.07	13.8	$5.2 X 10^{-3}$
MNDO	33.76	6.43	-81.81	193.13	198.33	13.5	$7.2 X 10^{-4}$
HF/3-21G	30.09	10.79	-64.22	190.05	195.24	13.7	$2.2 X 10^{-3}$
HF/6-21G*	29.62	13.46	-80.98	187.55	192.74	13.8	$4.9 X 10^{-3}$
HF/6-31G**	29.71	13.08	-87.60	189.25	194.44	13.8	$3.3 X 10^{-3}$
DFT/ B3LYP/6-31G*	32.45	13.88	-79.87	188.56	193.75	13.8	$3.9 X 10^{-3}$

The variation of rate, k with temperature from 498 to 773K at 25K interval as shown in table 6 shows that as the temperature increase, the rate of reaction also increases and at very high temperature the rate is at the maximum which in agreement with the Arrhenius theory(Bahl et al, 2004).

Table 6: Variation of Rate of Reaction (S^{-1}) with Temperature (K)

Temp (K)	AMI	RM1	PM3	MNDO	HF 3 21G	HF/6 31G*	HF/6 31G**	DFT
498	8.3x10^{-8}	9.1 X 10^{-8}	2.4 X 10^{-7}	2.9 X 10^{-8}	1.1 X 10^{-7}	2.61 X 10^{-7}	3.0 X 10^{-7}	1.84 X 10^{-7}
523	8.5 X 10^{-7}	9.3 X 10^{-7}	2.4 X 10^{-6}	3.1 X 10^{-7}	1.1 X 10^{-6}	2.58 X 10^{-6}	3.0 X 10^{-6}	1.85 X 10^{-6}
548	7.1 X 10^{-6}	7.8 X 10^{-6}	1.9 X 10^{-5}	2.6 X 10^{-6}	9.2 X 10^{-6}	2.07 X 10^{-5}	2.5 X 10^{-5}	1.51 X 10^{-5}
573	4.7 X 10^{-5}	5.4 X 10^{-5}	1.3 X 10^{-4}	1.8 X 10^{-5}	6.1 X 10^{-5}	1.39 X 10^{-4}	1.7 X 10^{-4}	1.01 X 10^{-4}
598	2.9 X 10^{-4}	3.2 X 10^{-4}	7.6 X 10^{-4}	1.1 X 10^{-4}	3.6 X 10^{-4}	8.39 X 10^{-4}	9.6 X 10^{-4}	6.06 X 10^{-4}
623	1.4 X 10^{-3}	1.6 X 10^{-3}	3.7 X 10^{-3}	5.9 X 10^{-4}	1.8 X 10^{-3}	4.02 X 10^{-3}	4.8 X 10^{-3}	2.95 X 10^{-3}
648	6.0 X 10^{-3}	7.4 X 10^{-3}	1.6 X 10^{-2}	2.8 X 10^{-3}	8.2 X 10^{-3}	1.78 X 10^{-2}	1.1 X 10^{-2}	1.32 X 10^{-2}
673	2.7 X 10^{-2}	2.9 X 10^{-2}	6.7 X 10^{-2}	1.1 X 10^{-2}	3.3 X 10^{-2}	7.10 X 10^{-2}	6.3 X 10^{-2}	5.22 X 10^{-2}
698	1.0 X 10^{-1}	1.1 X 10^{-1}	2.4 X 10^{-1}	4.3 X 10^{-2}	1.2 X 10^{-1}	2.55 X 10^{-1}	3.0 X 10^{-2}	1.89 X 10^{-1}
723	3.4 X 10^{-1}	3.6 X 10^{-1}	7.9 X 10^{-1}	1.4 X 10^{-1}	4.1 X 10^{-1}	8.39 X 10^{-1}	9.8 X 10^{-1}	6.23 X 10^{-1}
748	1.06	1.14	2.45	4.6 X10^{-1}	1.27	2.559	3.164	1.942
773	3.04	3.32	6.95	1.35	3.63	7.239	8.399	5.541

TABLE 7 : INFRA RED (CM^{-1})

	EXPERIMENTAL	AM1	RM1	PM3	MNDO	HF/ 321G	HF/ 6 31G*	HF/ 6 31G**	DFT/ B3LYP 631G*
REACTANT									
V(C-H)$_{BEND}$	N/A	1051 – 1393	1017 – 1357	1039 -1921	1068 - 1560	1038 – 1701	1069 – 1680	1066 – 1630	1066 – 1554
V(C=C) str	1660 -1675	1863	1822	1842	1849	1830	1862	1858	1715
V(C-O) str	1120	1411	1457	1274 - 1370	1560	1346	1372	1368	1254
V(C-H) str sp3	2870	3028 – 3162	2898 - 3087	2927 – 3090	3173 – 3448	3205 – 3292	3205 – 3294	3179 – 3276	3019 – 3140
V(C-H) str sp2	2975 - 3080	3179 - 3233	3119 - 15142	3152 – 3162	3355- 3448	3351 - 3430	3361 - 3442	3340 – 3427	3193 – 3278
PRODUCT1(Aldehyde)									
V(C-H)Bend	N/A	1036 – 1427	1061 – 1342	1053 -1401	1045 – 1481	1222 – 1646	1231 – 1616	1255 – 1600	1136 – 1500
V(C=O) str	1740 - 1690	2060	1947	.1985	2128	1925	2033	2031	1843
V(C-H) str	3100 - 3010	3058 – 3154	3026 – 3083	3082 – 3181	3245 – 3349	3157 - 3305	3206 – 3321	3185 – 3304	3043 – 3163
V(C-H) str (Aldehyde)	2720 - 2820		2922	2936			3151	3117	2900
PRODUCT 2(Ethene)									
V(C-H) $_{BEND}$	N/A	1056 – 1413	1035-1296	1054 – 1328	1099 – 1466	1115 – 1640	1095 – 1610	1093 – 1598	1068 – 1497
V(C=C) str	1680 – 1620	1827	1748	1829	1783	1842	1850	1852	1721
V(C-H) sp2	1470 -2925	3153 – 3217	3083 -3114	3128	3380 - 3433	3305 - 3402	3320 – 3420	3296 - 3400	3152 – 3247

SPECTRA OF ETHYL VINYL ETHER WITH AMI

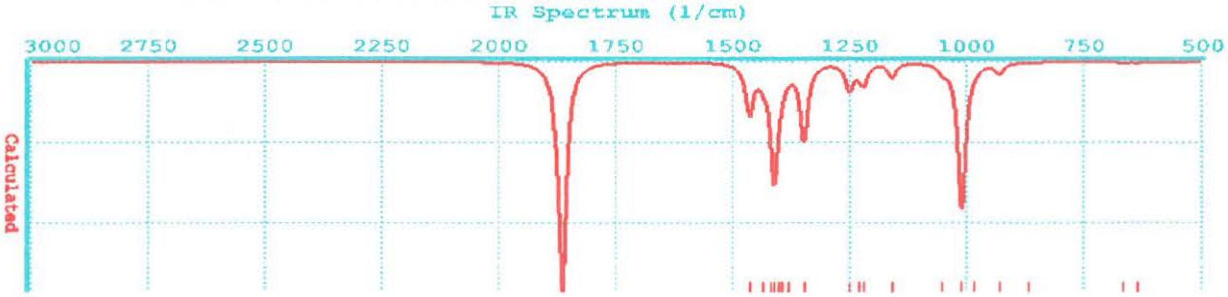


Fig 1: Ground state structure.

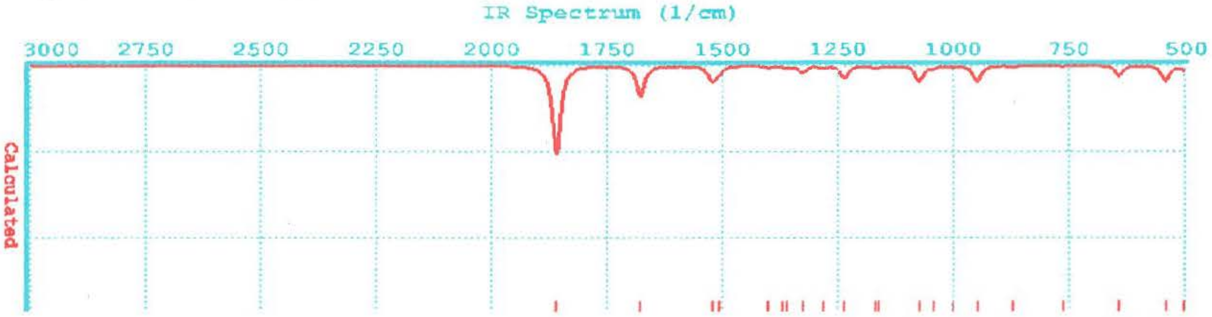


Fig 2: Transition State Structure.

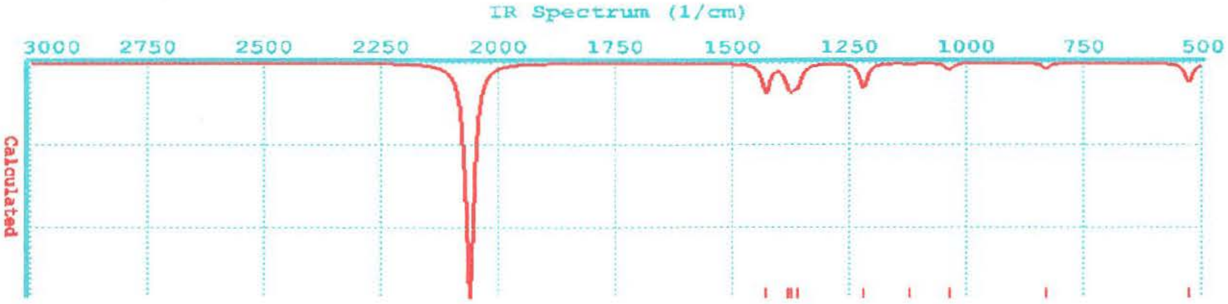


Fig 3: Product 1 (Acetaldehyde)

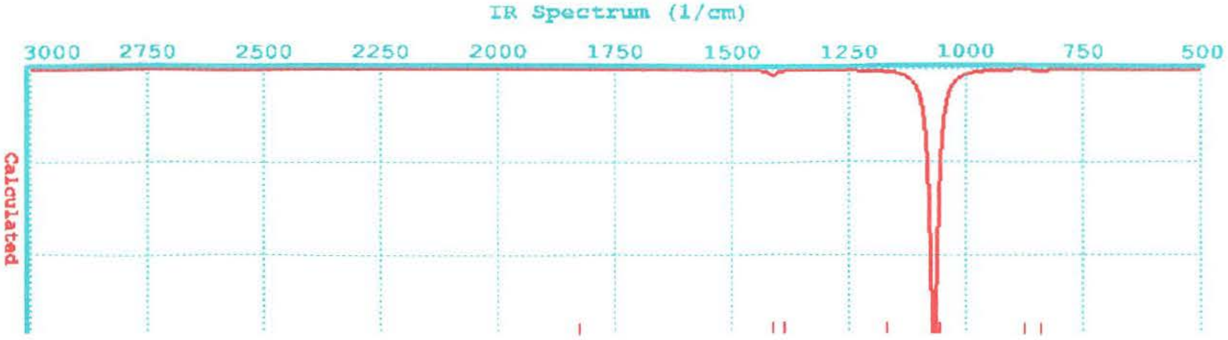
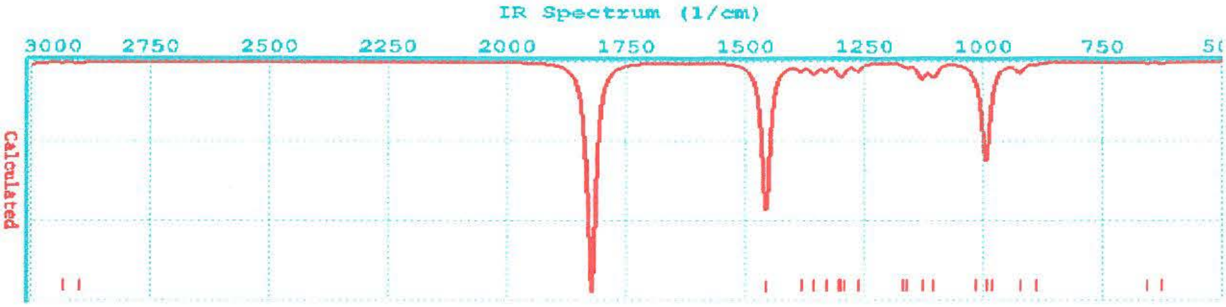


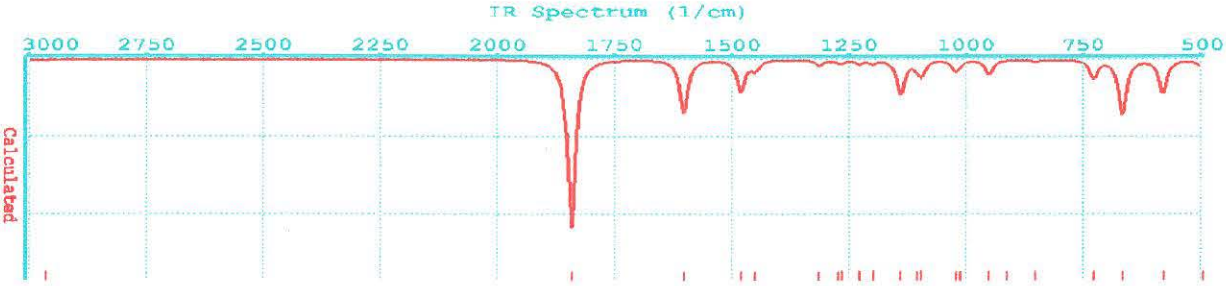
Fig 4 Product 2 (Ethene)

SPECTRA OF ETHYL VINYL ETHER WITH RMI

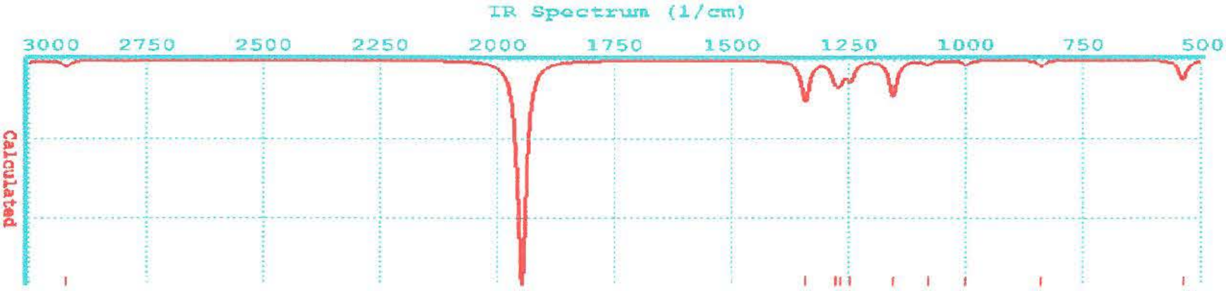
GROUND STATE SPECTRA



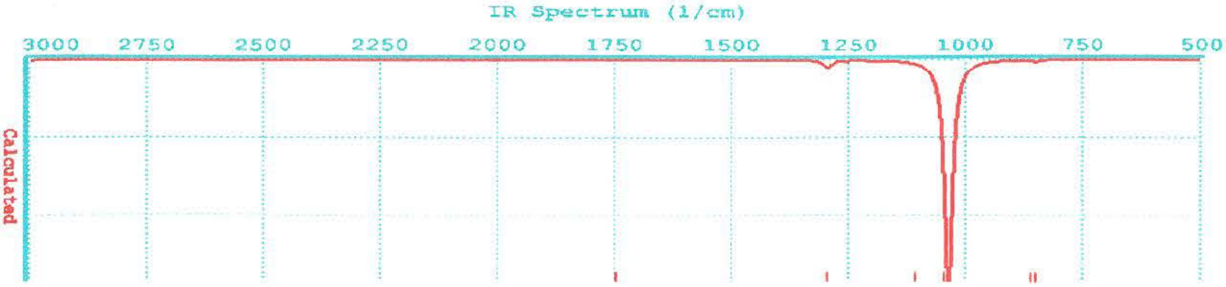
TRANSITION STATE



PRODUCT I (ACETALDEHYDE)

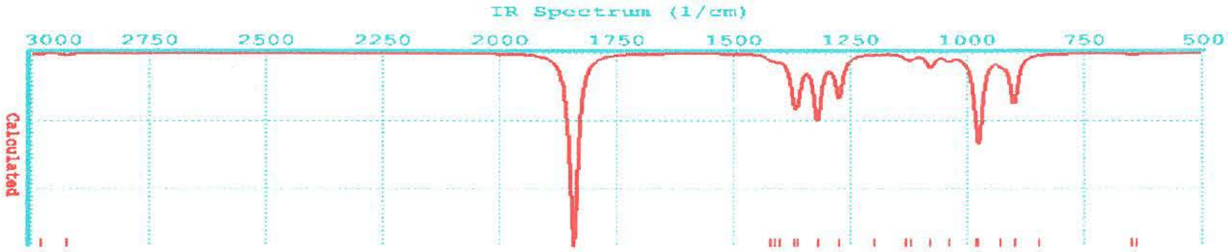


PRODUCT2 (ETHENE)

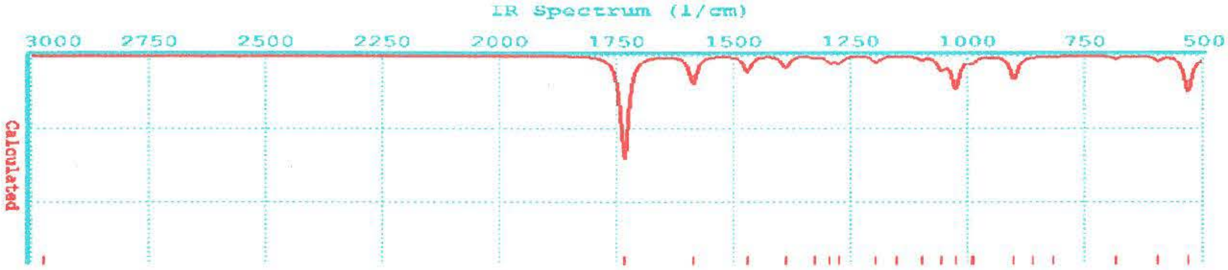


SPECTRA OF ETHYL VINYL ETHER WITH WITH PM3

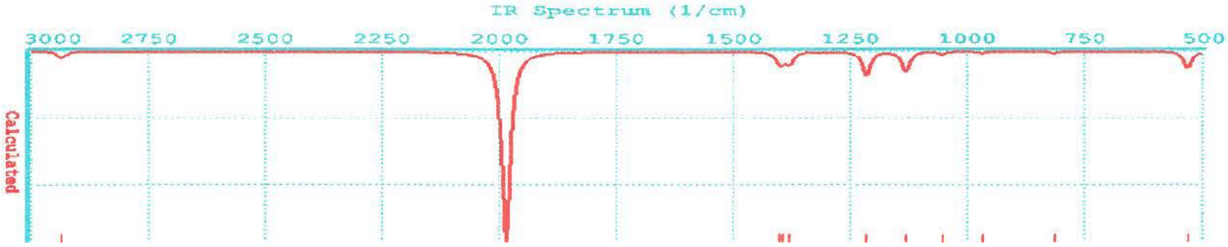
GROUND STATE SPECTRA



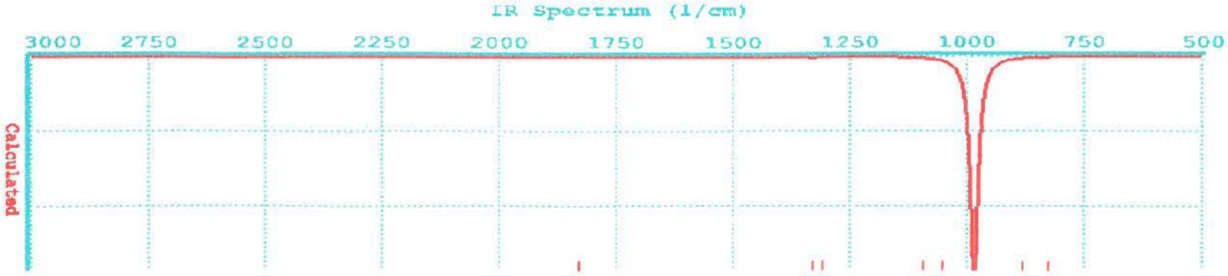
TRANSITION STATE



PRODUCT 1(PM3)

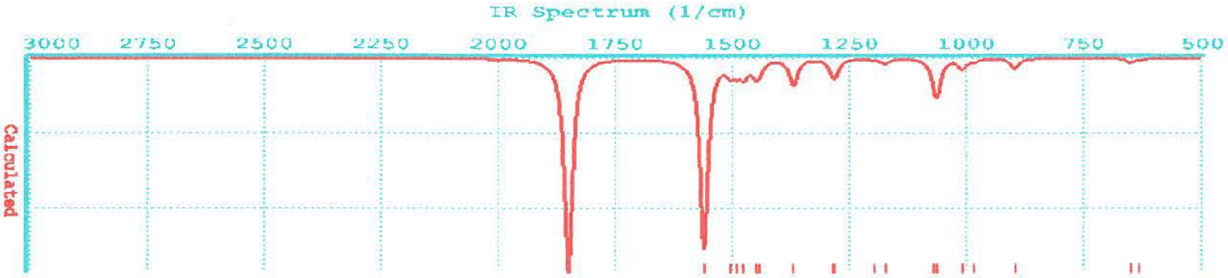


PRODUCT 2 (PM3)

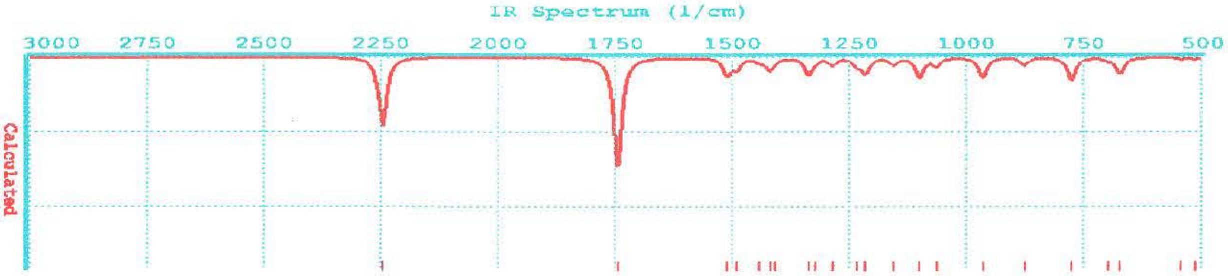


SPECTRA OF ETHYL VINYL ETHER WITH MNDO

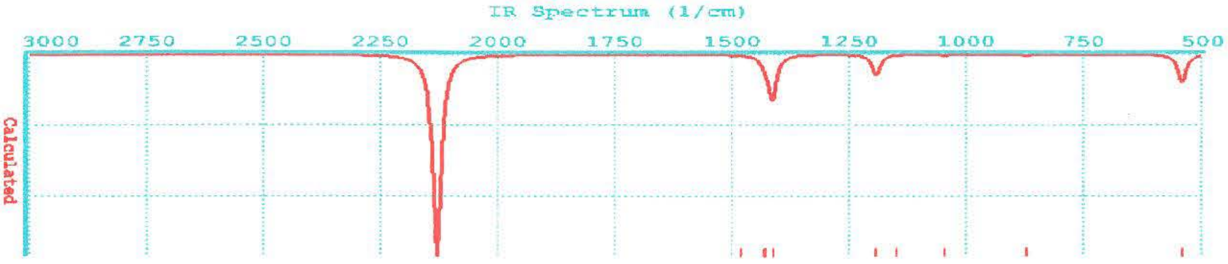
GROUND STATE SPECTRA



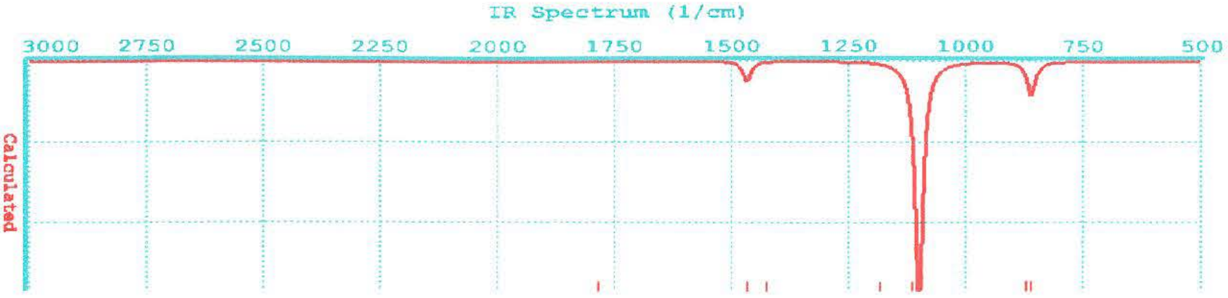
TRANSITION STATE WT (MNDO)



PRODUCT 1 MNDO



PRODUCT 2 MNDO



CONCLUSION

In conclusion, it is observed that both semi-empirical and ab-intio method in Spartan could be used effectively to study the kinetics, mechanism , thermodynamic and vibrational spectrosopy of ethyl vinyl ether.

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FLUORIDE REMOVAL USING ACTIVATED ALUMINA: A CASE STUDY OF BHOOMA CHOTA WATER

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ABSTRACT

The adsorption of fluoride, from a fluoride contaminated ground water sample from the village, Bhooma Chota, District Sikar, in the Sate of Rajasthan, India has been studied using activated alumina grade DF-101. The fluoride absorption capacity (q_t) *has been fitted into the psuedo first order adsorption, pseudo second order adsorption, Elovich and intraparticle diffusion models. It has been found that the kinetic data fits best in the pseudo second order rate equation giving very high correlation coefficient* (R^2= 0.991). *The modelled fluoride absorption capacity* (q_t) *has been calculated from the various equations using the constants derived from the least square regression plots. The calculated* q_t *values, model the experimental data very well, for the pseudo second order and Elovich equations, as is evident from the sum of square error calculations. Fluoride removal is through a combination of surface absorption and intraparticle diffusion. A study of fluoride removal process with increasing dosage of activated alumina reveal that though the percentage of fluoride removal increases with activated alumina, the adsorption capacity at equilibrium decreases. The minimum dosage of activated alumina which causes the maximum percentage removal of fluoride from water, while at the same time brings forth its highest equilibrium absorption capacity has been determined.*

KEYWORDS: **Activated alumina, fluoride adsorption**

RESUMO

A adsorção de fluoreto a partir de água contaminada do villarejo Bhooma Chota, Distrito de Sikar, Estado de Rajasthan, Índia foi estudada usando alumina ativada, grau DF-101. A capacidade de absorção do fluoreto (q_t) *foi analizada com vários modelos. Os resultados experimentais concordaram melhor com a equação de pseudo-segunda ordem* (R^2=0.991). *A remoção do fluoreto acontece através de uma combinação de absorção na superfície e difusão intraparticular. A dosagem mínima de alumina ativada para a melhor remoção de fluoreto foi determinada.*

PALAVRAS CHAVE: **Alumina ativada, Adsorção de fluoreto**

INTRODUCTION

Ground water is the major source of drinking water in India [1]. In most cases particularly in rural areas it is not treated before being used for drinking purposes. Fluoride is a major contaminant of ground water in India, particularly in the western desert state of Rajasthan [2]. Drinking water containing fluoride beyond the permissible limit of 1.5 ppm for prolonged periods causes Fluorosis [3]. The first signs of Fluorosis are yellowing and damage to the tooth enamel, followed by pain in knees, ankles and other joints. People afflicted with Fluorosis are unable to bend and do physical labour as it effects the muscles also [3]. It has been reported earlier that the ground water of the Sikar District of Rajasthan contains fluoride beyond permissible limits [4 (a-c)]. Children with mottled teeth, the first signs of Fluorosis are a common sight. There are unusually high incidences of the middle age population suffer from pains in joints, and stiffening of spine [5].

Activated alumina is known to absorb fluoride from water [6(a-l)]. Different grades of activated alumina are available from different manufactures [6f]. Domestic Defluoridation units have been distributed in Rajasthan India [7], using indigenously manufactured activated alumina grade DF-101 [8 (a-c)].

In the process of designing and fabricating simple domestic defluoridation filters of our own design, we decided at first to test the efficacy of DF-101 grade activated alumina to remove fluoride from locally available fluoride contaminated ground water and in this paper we report the case study of kinetics of fluoride adsorption from the ground water of a nearby village called Bhooma Chota in the Lakshmangarh Tehsil of Sikar District in Rajasthan, India.

EXPERIMENTAL

Fluoride was measured using a Fluoride ion meter and Fluoride combination electrode (Orion-Thermo Scientific, USA) using TISAB buffer. Activated alumina grade DF-101 was procured from M/S Bhargava Industries, Surat, Gujrat, India. All shaker experiments were done in duplicate. 100 ml of Bhooma Chota Middle tube Well water was shaken with fixed quantity of Activated alumina grade DF-101 at 180 rpm, at ambient temperature (20 deg °C) for a specified times. The activated alumina was filtered from water using a Whatman 42 filter paper and the residual fluoride was measured immediately.

RESULTS AND DISCUSSION

Bhooma Chota (Lat. 27.78 Long. 74.93 and altitude 354 m from msl,) is a big village with an area 1,089 hectares and population of 1,600 (2001 census). It has a dry, extreme climate (max. summer temp 48°C and minimum winter temp of 0°C) with an average annual rainfall 494 mm. The area has no mentionable natural resources. The region is arid, semi desert like with coarse sandy soil and little or no moisture content. There are frequent dust storms in summer. There are three deep tube wells (originally dug wells) which supply piped water supply to all houses. Of these, the tube well located at the centre of the village meets the domestic and drinking water needs of two third of the households. All people from the village are show signs of dental Fluorosis (fig. 1).

Water samples were collected on 15th January 2011 from the tubewell located at the centre of the village in Bhooma Chota (depth 102 m) and analyzed using standard procedures and the results of the analysis are as follows pH 8.9, TDS 1500 ppm (TDS meter), chloride 298 ppm (argentometric), carbonate 90 ppm, bicarbonate 1784 ppm (titrimetric H_2SO_4), Ca hardness 14 ppm (EDTA, P and R indicator), Mg hardness 43 ppm (EDTA, difference), sulphate 1.5 ppm (colorimetric), nitrate 100 ppm (phenol disulphonic acid), Na^+ 350 ppm (flame photometer), K^+ 13 ppm (flame photometer), fluoride 2.41 ppm (ISE). Notice the particularly high concentration of bicarbonates which are known to interfere with the fluoride adsorption capacity of activated alumina [6b,] [9].

The manufacturer's specifications for activated alumina (DF-101) balls are given in table 1.

The absorption capacities at equilibrium and at time t, q_e and q_t (mg/gm) are defined as $q_e = \frac{(C_0 - Ce)V}{W}$ (1)

and

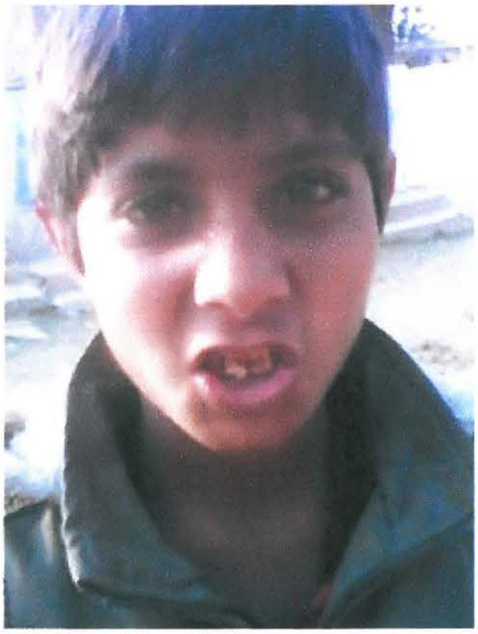

Fig. 1. Photograph of a Boy from village Bhooma Chota Showing Symptoms of Dental Fluorosis.

Table 1. Characteristics of Activated Alumina (DF-101) Balls (Manufactures Specifications)

a) Physical Properties

Parameters	**Values**
Sizes	0.40 -1.2 mm
Surface Area, m^2/g	360
Total Pore Volume, cc/g	0.50
Packed Bulk Density, gm/cc	0.769
Abrasion loss, wt %	0.5
Static Adsorption @60% R.H at 30^0C	22
LOI (250-1000°C)	6.5

b) Chemical Properties

Constituents	% Wt
Al_2O_3	92.5
SiO_2	0.025
Fe_2O_3	0.025
Na_2O	0.30

$$q_t = \frac{(C_0\text{-}C_t)V}{W} \qquad (2)$$

$$\%removal = \frac{(C_0 - C_t)}{C_i} \times 100 \qquad (3)$$

Where

C_o = initial concentration of fluoride in water (mg/l)

C_e= equilibrium concentration of fluoride in water (mg/l)

C_t= concentration of fluoride in water (mg/l) at time t

V = volume of solution (L)

W= weight of Activated Alumina used (g)

Taking C_o=2.41 ppm and C_e= 0.27 ppm yields q_e = 0.214 mg/gm.

The time profile of percentage removal of fluoride from ground water has been determined from the average of two experiments is shown in Fig. (2). A plot of the fluoride removal versus time plot is smooth and continuous leading to saturation indicating the possible monolayer coverage of fluoride ions on the surface of the activated alumina. Fluoride removal is 88% at saturation level.

The kinetics of fluoride adsorption from ground water on AA has been analyzed by using different kinetic adsorption models and is discussed below.

Pseudo First Order Rate Equation

The experimental data has been fitted into the Lagergen's [10] pseudo first order rate equation

$$\log(q_e - q_t) = \log q_e - \frac{K}{2.303}t \qquad (4)$$

where K, is the pseudo first order rate constant (min^{-1})

If the adsorption process is to follow the Lagergen's equation, a plot of $\log(q_e\text{-}q_t)$ vs. t should yield a straight line. We find that a linear plot is obtained (fig.3) (R^2=0.9547). Notice however that there is considerable deviation of the experimental data from the best fit regression line. We obtained the value of pseudo first order rate constant K= 0.029 min^{-1} and thereby calculated the theoretical value of q_e= 0.1557 mg/gm which considerably differs from the experimental value mentioned above.

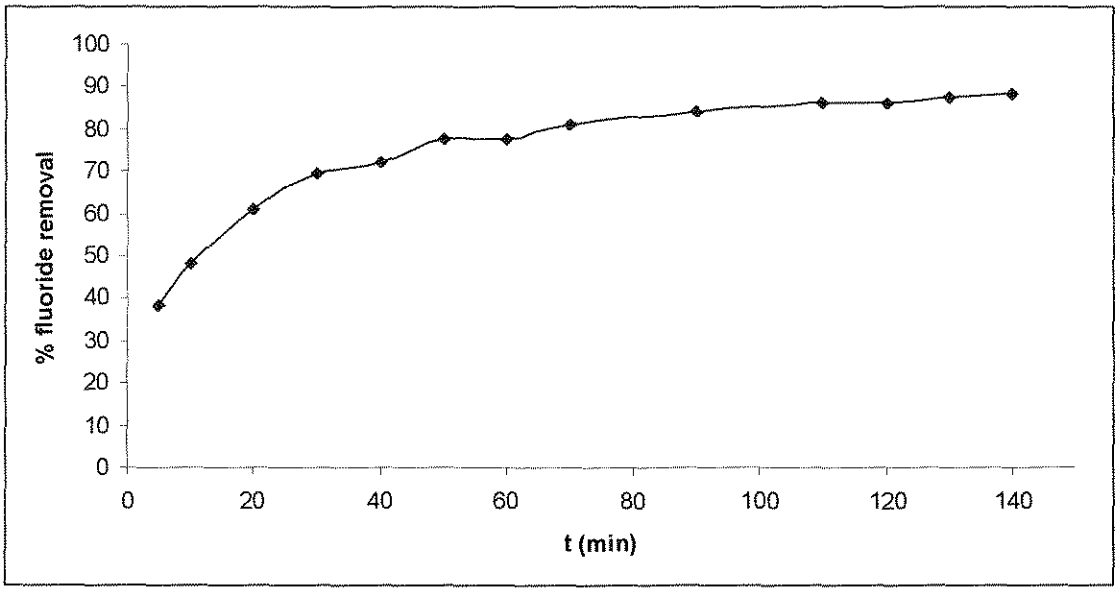

Fig.2.Experimental time profile of percentage removal of fluoride by AA from ground water.

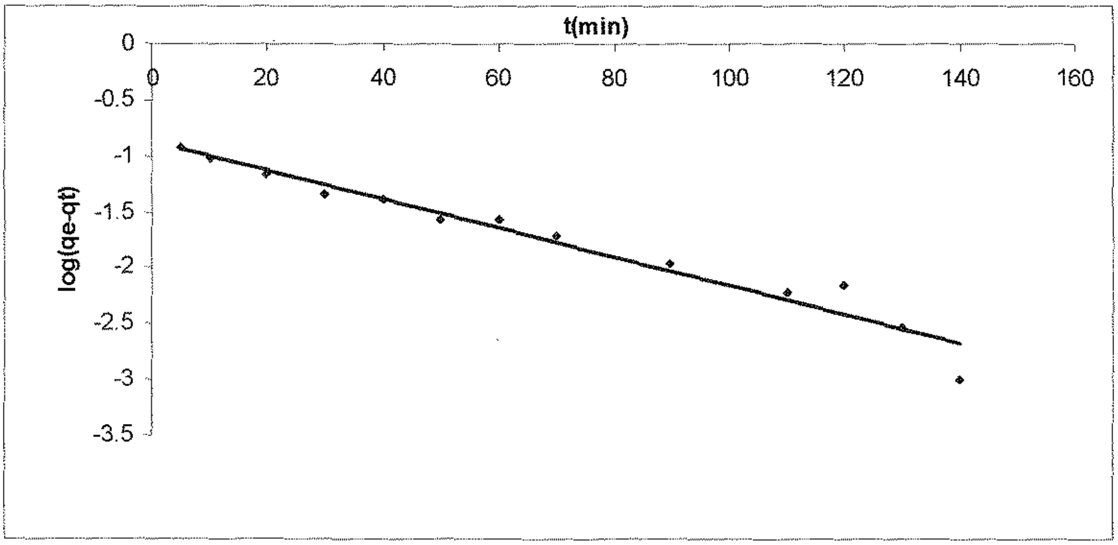

Fig. 3. Pseudo first order adsorption kinetics of fluoride on AA from ground water.

Pseudo Second Order Rate Equation

We tested experimental data with the Ho [11a,b] second order rate equation

$$\frac{t}{q_t}=\frac{1}{h}+\frac{t}{q_e} \qquad (5)$$

Where $h=K(q_e)^2$ (6)

If the adsorption process is to follow the pseudo second order rate equation, a plot of t/q_t vs. t should yield a straight line. We find that a linear plot is obtained (fig. 4) (R^2=0.9991). Notice that the t/q_t vs. t plot shows an excellent agreement with experimental data. The pseudo second order rate constant was found to be K= 0.4305 gm mg^{-1} min^{-1}. The calculated q_e = 0.226 mg/gm value agrees well the experimental value obtained.

Elovich Equation

The Elovich equation [12] as simplified by Chien and Clayton [13] and with the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ [14] is

$$q_t=\frac{1}{\beta}(\ln\alpha\beta)+\frac{1}{\beta}(\ln t) \qquad (7)$$

where α and β are constants. While α is the initial adsorption rate, β is related to the extent of surface coverage and the activation energy for chemisorption. This equation was used to fit the experimental data and if the equation is valid then a plot of q_t vs. lnt should yield a straight line. It was found that the straight line (fig. 5) had a R^2 = 0.9887. The Elovich constants α and β values were found to be 0.102 mg g^{-1} min^{-1} and 27.77 g/mg. The R^2 values are lower than pseudo second order model discussed earlier.

Weber and Morris Intraparticle Diffusion Model

A simplified form of Weber and Morris Intraparticle Diffusion Model [15] requires that

$$q_t=Kt^{0.5} \qquad (8)$$

where K is the intraparticle diffusion rate constant (mg g^{-1} $min^{-1/2}$) .

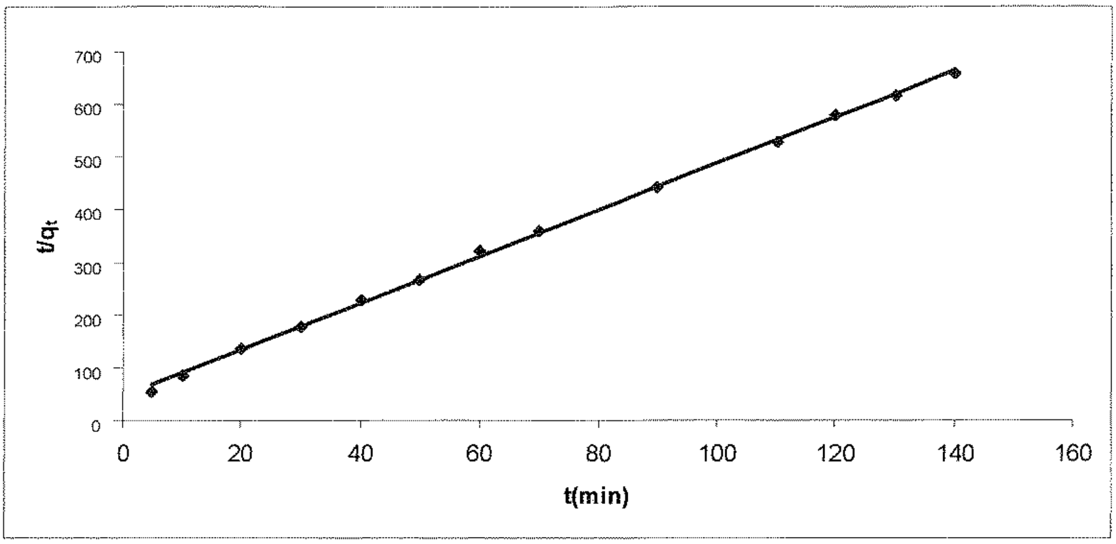

Fig. 4. Pseudo second order adsorption kinetics of fluoride on AA from ground water.

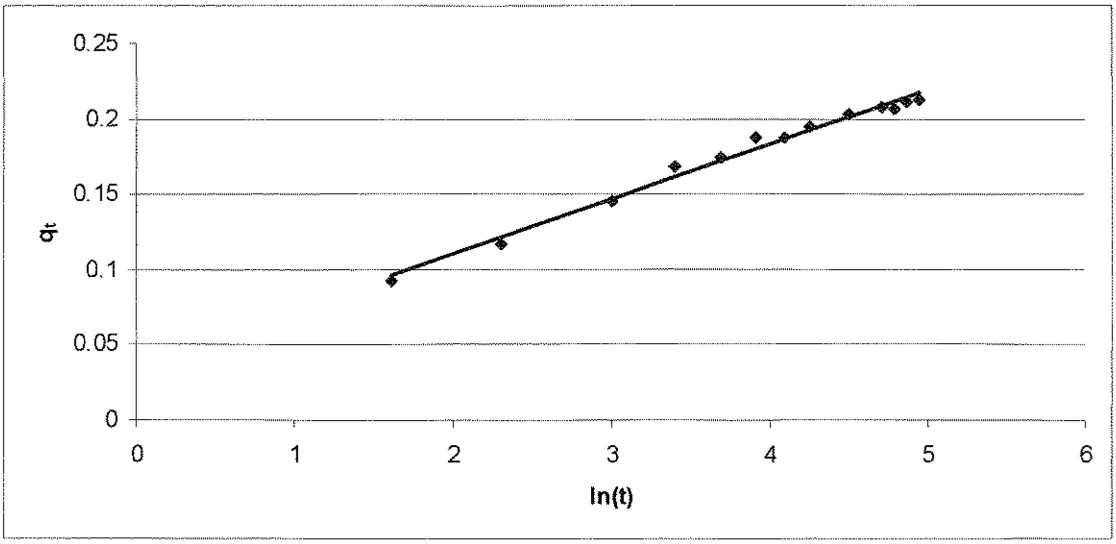

Fig. 5. Elovich adsorption kinetics of fluoride on AA from ground water.

If a plot of q_t vs. $t^{0.5}$ should pass through the origin then intraparticle diffusion is the only rate limiting step. Larger the values of C intercept, greater the contribution of the surface adsorption in the rate controlling step. On plotting the experimental data it was observed that (fig. 6) there are three distinct regions in the plot. There is a linear portion region, followed by a curved potion and finally the plateau like equilibrium portion. Notice that the linear portion starts from 5 to 30 min. Before this period nearly 40% of the fluoride is adsorbed (fig. 2). This is when the fluoride ions gets adsorbed on the most readily available adsorption sites on AA. The second stage (linear portion of the curve) is intraparticle diffusion rate controlled. The R^2 value for the initial linear portion of the curve (5 to 35 min) is 0.9986, C intercept is 0.0428 mg gm^{-1} and the intra particle rate constant value is 0.023 mg $gm^{-1/2}$ $min^{-1/2}$ (fig. 7). Though we obtain a linear relationship, the fact that the line does not pass through the origin indicates that intraparticle diffusion is not the sole mechanism contributing to the rate determining step during the time period of 5min to 30 min. In the equilibrium portion of the curve intraparticle diffusion is very slow because of the low equilibrium concentration of fluoride remaining in the solute. Such multistage adsorption phenomena with lines of different slopes have been earlier observed [6k, 16].

Modelling of Experimental q_t

The time profile of fluoride adsorption capacity of AA from ground water has been modelled using the constants determined from the four different models and the results are shown in fig. (8). A sum of squared errors (eqn. 8)

$$SSE = \sum (qt(\exp) - qt(calc))^2 \qquad (8)$$

has been calculated for q_t of all the models (Table 2). Notice that the modelled q_t values obtained from the Elovich Equation (R^2=0.9887) has the least value of the sum of square errors, (0.000372). However, the pseudo second order kinetic model (R^2=0.9991) has a SSE= 0.00048. The difference between the squared sum of errors between the two models is marginal. On the basis of R^2 values the pseudo second order kinetic model is the most applicable to describe the kinetic behaviour the adsorption process during the

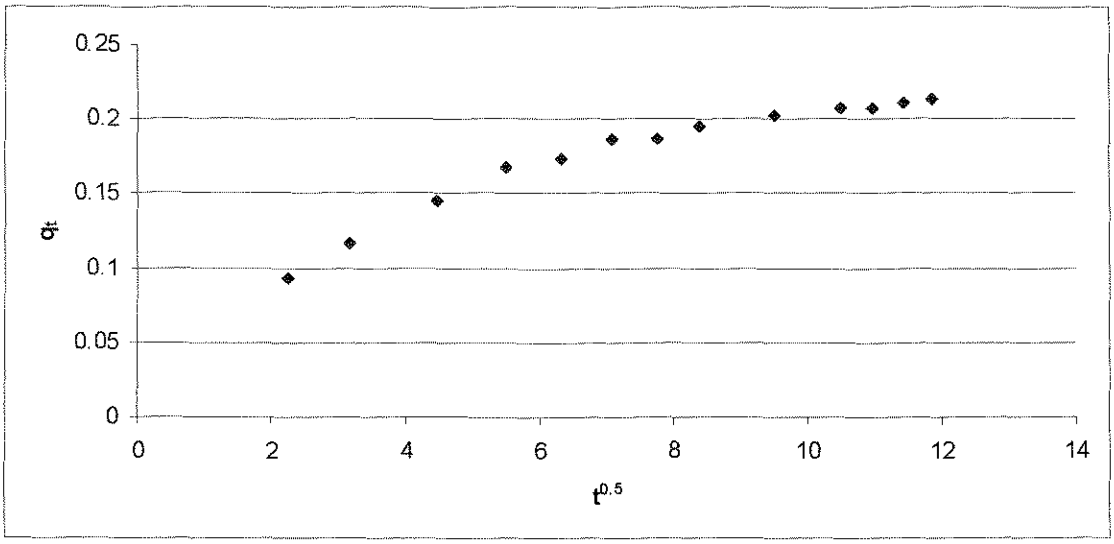

Fig. 6. Weber and Morris adsorption kinetics of fluoride on AA from ground water

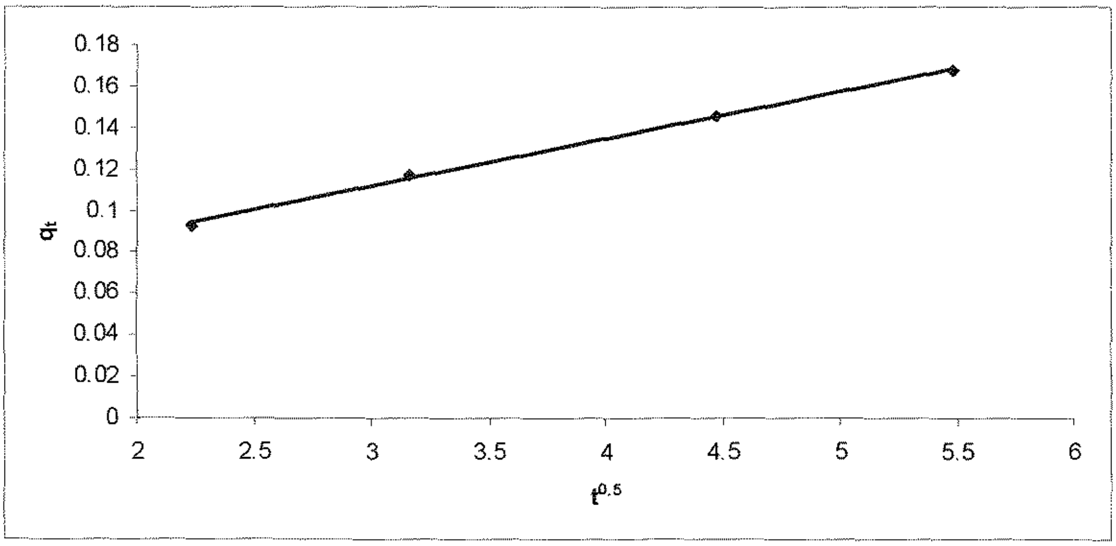

Fig. 7. Intraparticle adsorption kinetics of fluoride on AA from ground water (initial part of Weber and Morris Plot.

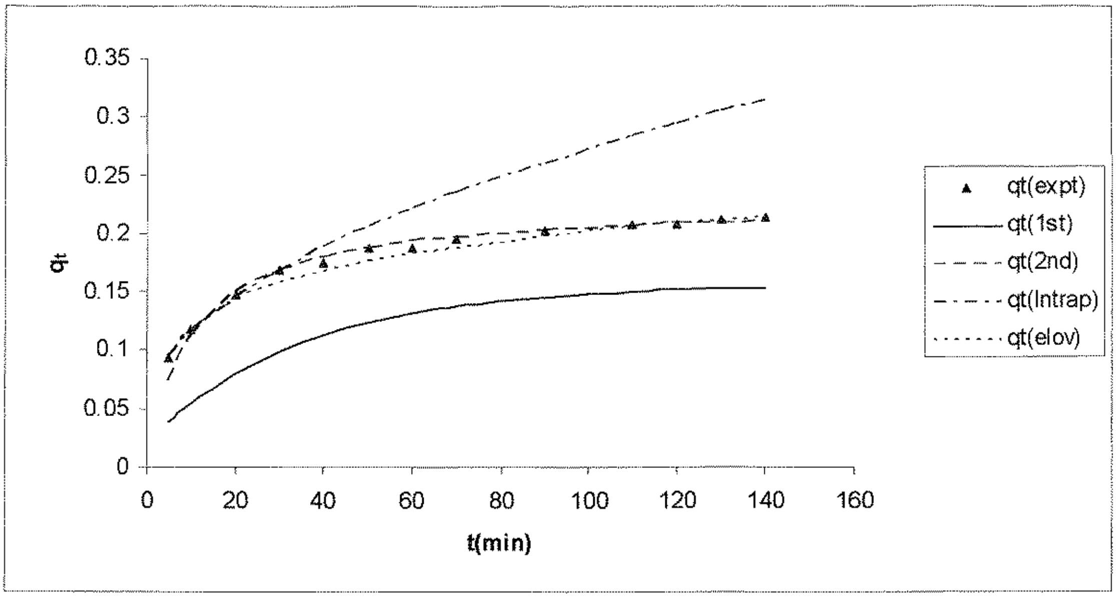

Fig. 8.Modelled and Experimental time profiles of adsorption capacity of AA for fluoride from ground water.

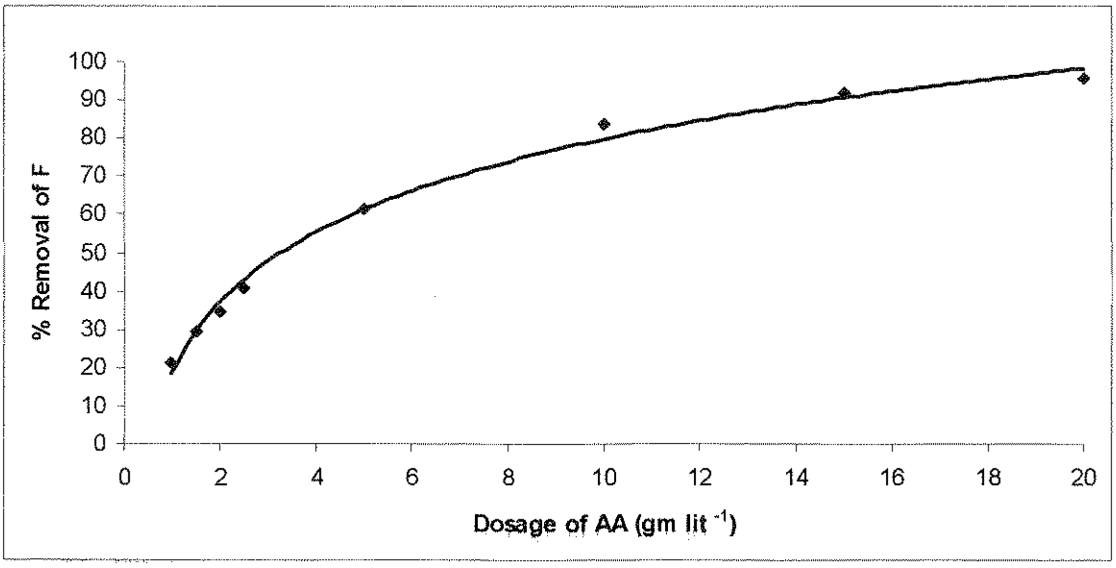

Fig. 9. Variation of percentage removal of fluoride with increasing dosage of AA.

Table 2. Sum of Square Errors of Modelled Data from Experimental Data

Model	Sum of Square Errors
Ist Order	0.04691
2nd Order	0.00048
Intraparticle Diffusion	0.03886
Elovich Equation	0.00037

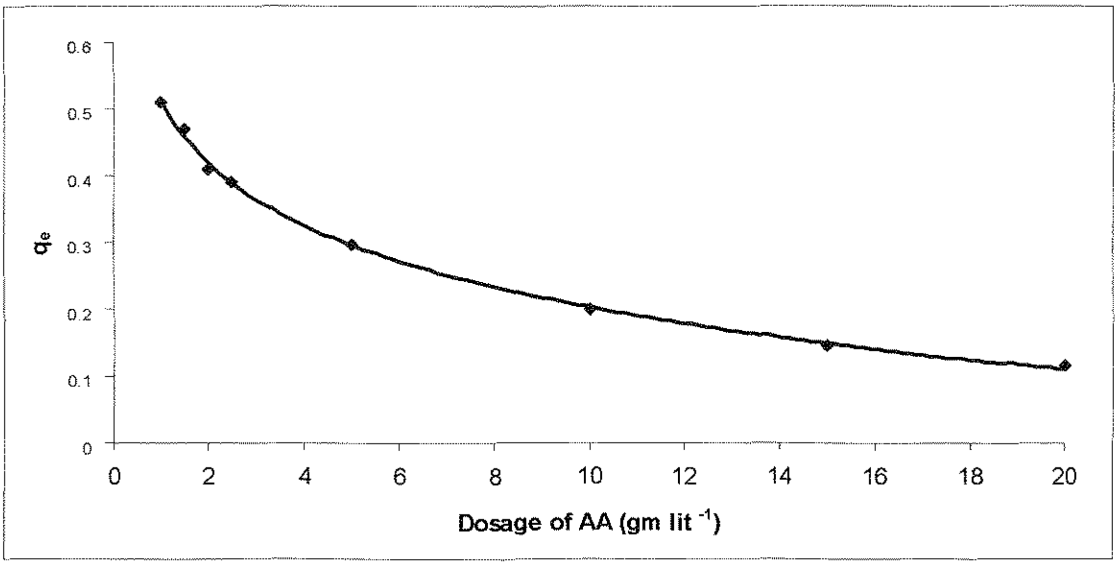

Fig. 10. Variation of equilibrium absorption capacities of AA with increasing dosage of AA.

whole adsorption process. Notice that the intraprticle diffusion model closely describes the adsorption process at the initial 5 to 30 min. (fig 8).

In order to test the effect of increasing dosage of activated alumina on fluoride removal ground water was equilibrated with increasing quantities (1-20 gm/lit) of AA. It was found that as dosage of activated alumina was increased, percentage removal of fluoride removal increased logarithmically ($R^2 = 0.9932$) (fig. 9).

This is attributed to increase in number of available active sites for fluoride adsorption. However, as dosage of AA is increased, adsorption capacity q_e decreases logarithmically ($R^2 = 0.9982$) (fig. 10). The minimum dosage of activated alumina which causes the maximum percentage removal of fluoride from water, while at the same time brings forth its highest equilibrium absorption capacity can be determined by solving the equations of the fitted lines simultaneously. A value of 0.5 gm lit^{-1} of AA has been obtained in this case. It is postulated that with increase in adsorbent dose fluoride ions are not able to saturate the active sites and consequently there is lowering of the adsorption capacity. Alternatively, adsorbent particles may agglomerate at higher adsorbent does, which would lead to decrease in surface area available for adsorption. This would in turn result in increase of diffusional path length for fluoride ions resulting in lowering of adsorption equilibrium capacity.

CONCLUSION

From the kinetic analysis of fluoride removal process it is concluded that the adsorption process of fluoride on AA DF-101 from natural water tested follows an overall pseudo second order kinetics. Good correlation coefficient values are obtained from Elovich equation also. Sum of square error calculations also supports the above findings. Intraparticle diffusion is the significant mechanism of fluoride adsorption from 5 to 30 min though it is not the sole adsorption mechanism as the plot of q_t vs. $t^{0.5}$ does not pass through the origin. In all probability the fluoride removal is through a combination of intraparticle diffusion and surface adsorption. On increasing the dosage of AA its adsorption capacity to remove fluoride decreases. This is attributed to unsaturation of the active sites and agglomeration of AA particles at higher dosages.

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TESTING OF A DEFLUORIDATING FILTER USING MgO-CaO-$CaCl_2$ FOR USE IN RURAL RAJASTHAN

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ABSTRACT

A Magnesium Oxide based defluoridation technique using MgO–CaO-Calcium Chloride and pH adjustment by Sodium Bisulphate has been suitably modified for use with fluoride contaminated local groundwater having high alkalinity. Taking into consideration the high bicarbonate concentration in raw ground water the proportion of the lime has been changed. It was found that sodium bisulphate was not suitable for pH adjustment due to high concentration of sulphate in the pH adjusted water. Therefore dilute HCl was used instead. Six trials of the adapted defluoridation technique have been carried out in the laboratory successfully at 50 liter scale.

KEY WORDS: Defluoridation, Defluoridating Filter, MgO, CaO, Calcium Chloride

RESUMO

Uma técnica de defluoretação usando MgO-CaO-Cloreto de Cálcio e ajuste de pH com bisulfato de sódio foi modificada com éxito para água contaminada com fluoreto e com alcalinidade elevada. Considerando a alta concentração de bicarbonato na água natural, a proporção de CaO foi modificada, O bisulfato de sódio não foi adequado para ajuste do pH devido à alta concentração resultante de sulfato. Consequentemente, HCl diluído foi usado. Os resultdos experimentais com amostras de 50 litros de água foram satisfatórios para remover o fluoreto.

PALAVRAS CHAVE: Defluoretação, Filtro para Remoção de Fluoreto, MgO, CaO, Cloreto de Cálcio

INTRODUCTION

The desert state of Rajasthan in India primarily depends upon groundwater for meeting its drinking water requirements. The groundwater in Rajasthan[1] has fluoride in excess of the permissible limit set by WHO of 1.5 ppm[2]. Flouride is known to be beneficial if present in the desirable concentration of 1 ppm and has adverse impacts on human health if present in excess[3 4]

Magnesium Oxide is known to remove fluoride from water since 1940's[5]. Since then various researchers have studied this process[6 7 8 9 10 11]. MgO being non-toxic, relatively easily available and cheap is a suitable adsorbent for F^- removal.

A new method of defluoridation based on MgO-CaO-$CaCl_2$ and pH adjustment using $NaHSO_4$ has recently been reported from the Indian Institute of Science, Bangalore, India[12 13 14]. The ratio of various chemicals used depends on fluoride concentration and bicarbonate concentration in the raw water. The ground water in Rajasthan has very high concentration of bicarbonates. A project supported by the Water Technology Initiative of the Department of Science and Technology, Govt. of India, New Delhi involves the testing and field trials of this filter in the fluoride affected Lakshmangarh Tehsil (subdivision), in the Sikar District of Rajasthan. Due to higher alkalinity of the local fluoride contaminated ground water, the defluoridation technique had to suitably be modified, and in this paper we report the preliminary findings of our study.

MATERIALS AND METHODS

Fabrication and Testing of the Filter

Food grade drums (50 liters capacity) were purchased from Time Technoplast (New Delhi). Plastic taps were fixed 2.5cm above the base of the containers Fig. 1. Calcium oxide (Mahalaxmi Traders, Ajmer) was purchased locally from Laxmangarh in 5 kg plastic sacks.

Fig. 1 Photograph of Testing of the Fluoride Filter in Laboratory.

Technical grade magnesium oxide, (light) was purchased from R/S Enteprises, Jaipur. Calcium Chloride Dihydrate (AR), conc. HCl (AR) was purchased from CDH (India) and Rankem (India), respectively.

Fluoride contaminated ground water was brought from village Shola 30km away from the Institute in mini water tankers and transferred to 500 liter drums in the laboratory.

Fixed volumes of 7.5% $CaCl_2$ solution in demineralised water was added to 50 liters fluoride contaminated water and stirred using plastic PVC pipes. Weighed amounts of MgO and CaO were added to it, and the water stirred vigorously using a PVC plastic pipe. The water was left overnight undisturbed. MgO and $Ca(OH)_2$ flocks settled down to the bottom of the container in form of white sludge. The supernatant water was filtered through six layers of cotton cloth tied to the mouth of the tap into another food grade container fitted with plastic tap Fig. 1. Hydrochloric acid (0.38 N) in demineralised water was added with constant stirring to the filtered water till the pH of the treated water was in between 6.5 to 8.5, and fit for the human consumption.

Water Testing

Fluoride was measured by using a Fluoride Ion Selective Electrode (Orion Thermo Scientific) using TISAB Buffer. Total Hardness, Calcium Hardness was determined by EDTA method. Carbonate and Bicarbonate was determined by titrating with H_2SO_4. For chloride, titration with silver nitrate was used. Duly calibrated pH, TDS meter was used for determining pH and TDS. Sodium and Potassium was determined by Flame Photometer (ESICO). Nitrate was measured by measuring the absorbance at 220nm and 270nm. Sulfate was determined by turbidity method using a colorimeter.

RESULTS AND DISCUSSION

MgO hydrates in water to form $Mg(OH)_2$[6 13]

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad \text{(eq.1)}$$

Since the ionic radii of fluoride and hydroxide are similar, OH^- ions in the crystal lattice $Mg(OH)_2$ gets substituted by F^- [15,11,12].

$$Mg(OH)_2 + F^- \rightarrow Mg(OH)_{2-y}F_y \qquad \text{(eq.2)}$$

For defluoridation using $MgO\text{-}CaO\text{-}CaCl_2\text{-}NaHSO_4$ [12,13], the concentration of bicarbonate in raw water is the critical parameter. A preliminary sampling of the ground water of village Shola, a fluorosis affected village in Lakshmangarh indicated a very high HCO_3^- concentration of 937 ppm and high fluoride concentration of 2.15 ppm (Table 1). The ratio derived for $MgO\text{-}CaO\text{–}CaCl_2$ treatment method as given in the application notes[16] are only up to 700ppm HCO_3^{2-} concentration. Since the bicarbonate concentration in raw water sample was very high, we increased the lime dosage from the maximum dosage of 0.5 gm to 0.75 gm (Table 1). This is to ensure the presence of enough Ca^{2+} ions in the solution, as in the basic medium Ca^{+2} ions react with HCO_3^- ions to form $CaCO_3$ as precipitate .

$$HCO_3^{-1} + Ca^{2+} + OH^{-1} \rightarrow CaCO_3\downarrow + H_2O \qquad \text{(eq.3)}$$

The concentration of bicarbonate ions has to be low in the raw water to be treated by this process, otherwise it will get converted to carbonate ions when a mixture of $MgO\text{-}CaO\text{-}CaCl_2$ is added and the pH of water become basic

$$HCO_3^- + OH^{-1} \rightarrow CO_3^- + H_2O \qquad \text{(eq.4)}$$

Moreover in the pH adjustment step by 5% $NaHSO_4$ solution, one equivalent more of $NaHSO_4$ would be consumed by the CO_3^{2-} ions that are generated above.

$$CO_3^{2-} + HSO_4^{-1} \rightarrow HCO_3^- + SO_4^{2-} \qquad \text{(eq.5)}$$

The MgO dosage was kept at minimum (1.0 gm/lit) since the F^- concentration in the raw water as not very high (MgO dosage 1.0 →1.5 for F^- concentration 1.5 to 7 ppm).

In a preliminary experiment, 1.0 liter sample was treated with 1.0 gm MgO, 0.75gm CaO, 4.0 ml of 7.5% of $CaCl_2$ (in demineralised water) and stirred for five minutes. The solution was left overnight undisturbed. Next day it was filtered through Whatman 42 filter paper, 500 ml of this filtered water required 6.0 ml of 5% $NaHSO_4$ (in demineralised water) for neutralization to

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Table 1 Analysis and Treatment of Water Sample of Village Shola (Pilaniyon Ki Dhani).

Date of Sampling 7th May 2012	Water 1 lit., MgO 1gm, CaO 0.75 gm, $CaCl_2$ (7.5 %) 4 ml				Sampling Site: Pilaniyon ki Dhani (Vill. Shola)	Date of Treatment 15th May 2012
S.No.	Parameter	Raw water	After 16 hrs.	After pH adjustment with 5% $NaHSO_4$	Desirable limits[17]	Permissible limits[17]
1	pH	8.53	11.02	7.45	6.5-8.5	No relaxation
2	TDS by meter	1527	1637	2109	500	2000
3	Chloride	262	393	399	250	1000
4	Carbonate	0	384	0	-	-
5	Bicarbonate	937	149	512		
6	Ca Hardness	19.3	1.594	2.561	75	200
7	Mg Hardness	20.2	2.903	3.241	30	100
8	Fluoride	2.15	0.472	0.432	1	1.5
9	Sulphate	61	64	425	200	400
10	Na^+	477	460	522		
11	K^+	4.5	5.8	5.92		
12	Total alkalinity ($CaCO_3$ eqv.)	750	426	410	200	600

pH 7.45 (Table 1). We found that the fluoride concentration reduced from 2.15 in raw water to 0.47 ppm in pH adjusted water (Table 1). To our expectation, we found that Total Alkalinity had decreased from 750 to 426 ppm (Table 1), as (HCO_3^{-1} had precipitated as $CaCO_3$).

However, it was observed that SO_4^{2-} concentration increased considerably from 61ppm in raw water to 425 ppm in pH adjusted water (Table 1), beyond the permissible limit of 400 ppm[17]. Therefore the pH adjustment with $NaHSO_4$ was not suitable. pH adjustment with H_2SO_4 was ruled out for the same reason (it would have increased the sulphate concentration).

Since nitrate concentration in raw water was found to be 161 ppm, one and half times the permissible limit of 100 ppm[17], pH adjustment with nitric acid would not be suitable. Therefore dilute HCl was tried for pH adjustment.

$$CO_3^{2-} + HCl \rightarrow HCO_3^{-} + Cl^{-} \qquad \text{(eq.6)}$$

Next, 1.0 liter raw water sample was treated with, 1.0 gm MgO, 0.75gm CaO, 4.0 ml $CaCl_2$ (in demineralised water) and left overnight. Next day this water was filtered and, 400 ml of the filtrate was titrated pH metrically to determine the volume of 0.38 N HCl required for neutralization. The variation of pH with volume of 0.38 N HCl added is shown in Fig. 2. Notice that the $CO_3^{2-} \leftrightarrow HCO_3 \leftrightarrow H_2CO_3$ equilibrium is apparent. We found 5.6 to 9.6 ml of 0.38 N HCl was required to reduce the pH between 8.5 to 6.5 (within the potable limits) at 927 ppm HCO_3^{-1} conc. in raw water. This translates to 630 to 1008 ml of 0.38 N HCl for 45 liters of filtered MgO-CaO-$CaCl_2$ treated water.

Dilute HCl of 0.38 normality was considered to be adequate for pH adjustment, as it would not be prudent to handle highly concentrated HCl solution when the filters are put to field trails and possible use in the villages. If too dilute HCl solution is used the volume of HCl required would be more. As 1 liter food grade plastic containers are easily available therefore this volume of HCl solution can be easily dispensed.

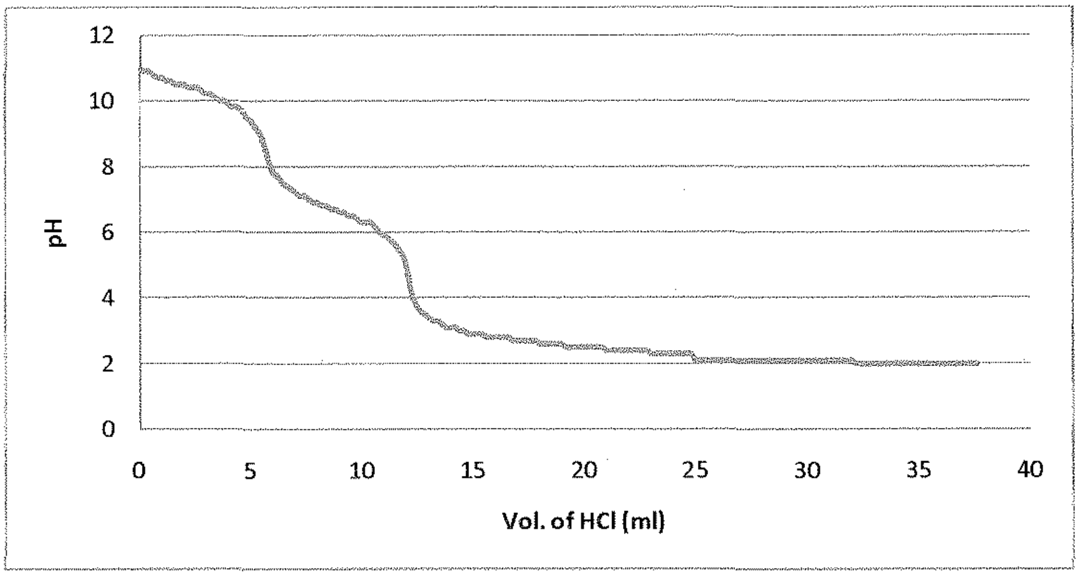

Fig. 2 Variation of pH of CaO-MgO-$CaCl_2$ treated water (400ml) from Pilaniyon ki Dhani (Village Shola) on addition of 0.38 N HCl

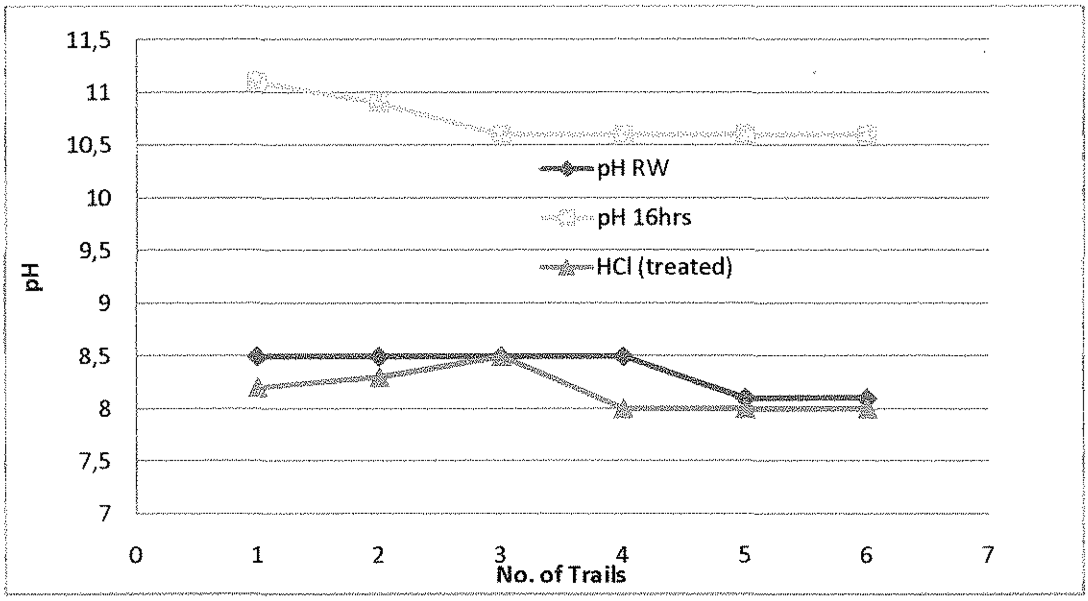

Fig.3 Variation of pH during six laboratory trails of the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

After pH adjustment by HCl, the pH of water was 8 to 8.5, (Fig. 3) with fluoride concentration ranging from 0.7 to 0.86 ppm with an initial fluoride in the raw water varying from 2.26 and 2.3 ppm (Fig. 4). The CO_3^{-2} in pH adjusted water varied from 30 to 34 ppm when the concentration varied from 30 to 42 ppm (Fig. 5). The bicarbonate concentration in pH adjusted water was 305 to 420 ppm, while it was 934 to 1150 ppm in raw water (Fig. 6). The sulphate concentration was found to be low 40-80ppm (Fig. 7) and chloride concentration 470-581 ppm well within the permisible limit of 1000 ppm (Fig. 8). Also notice, that the method produces water of nearby constant total alkalinity of approximately 400 ppm though the total alkalinity of raw water various from 840 to 1000 ppm (Fig. 9). Thus there is a reduction of total alkalinity by 400ppm. Notice that the TDS of treated water increased by 1200 to 1400 ppm (Fig. 10), in treated water as compared to raw water, but is still very much within the permissible limit of 2000 ppm[17].

As the solubility $Mg(OH)_2$ in water is low (5.0×10^{-12})[18], therefore Mg^{2+} concentration in raw water and treated water does not vary appreciably (average concentration 38 ppm) (Fig. 11). The Calcium added in form of CaO and $CaCl_2$, gets precipitated in form of $CaCO_3$, and the concentration of Ca^{2+} decrease from 15 ppm in raw water to 4 to 5ppm in pH adjusted water (Fig. 12). For the above reasons the Total Hardness was also found to decrease (Fig. 13).

There is no significant change in Na^+ and K^+ values in raw and treated water which average 300-500 ppm in the various samples. It was found using six layers of cloth for filtering and one tap as outlet it took on an average 2.5 hrs for 45 liter of $MgO\text{-}CaO\text{-}CaCl_2$ treated water to filter through and the filter cloth had to removed and cleaned twice to remove the fine particles of sludge. Hence two taps were fitted 6 inches apart, after which it took only 45 minutes for filtration. It was observed the filter cloth did not choke in the new arrangement. Notice that the volume of filtered water is 45 liter in the second container which increased to 45.6 liters on addition of 600 ml 0.38 N HCl.

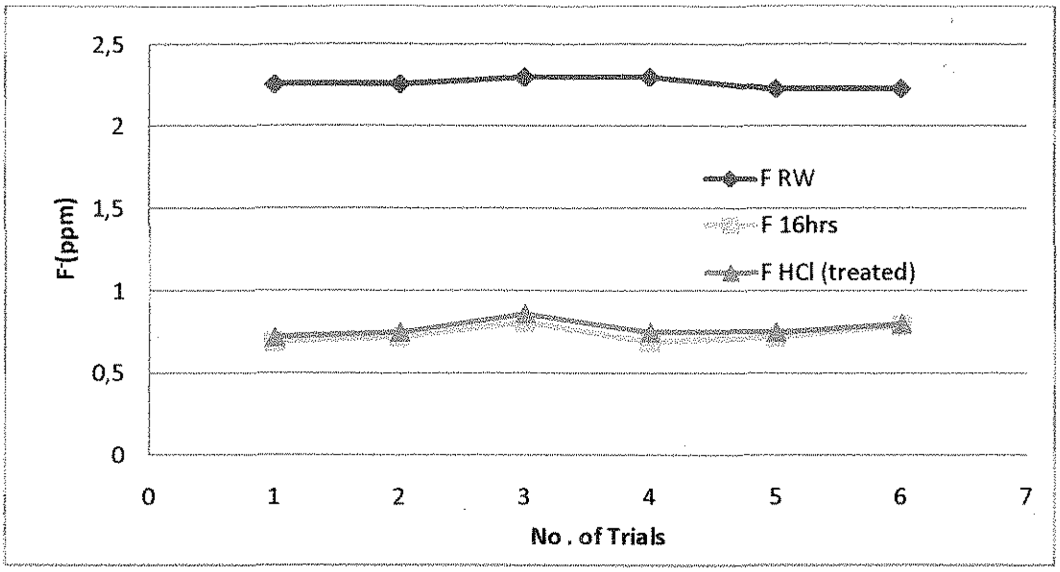

Fig.4 Variation of F^- during six laboratory trails of the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water Pilaniyon ki Dhani (Village Shola)

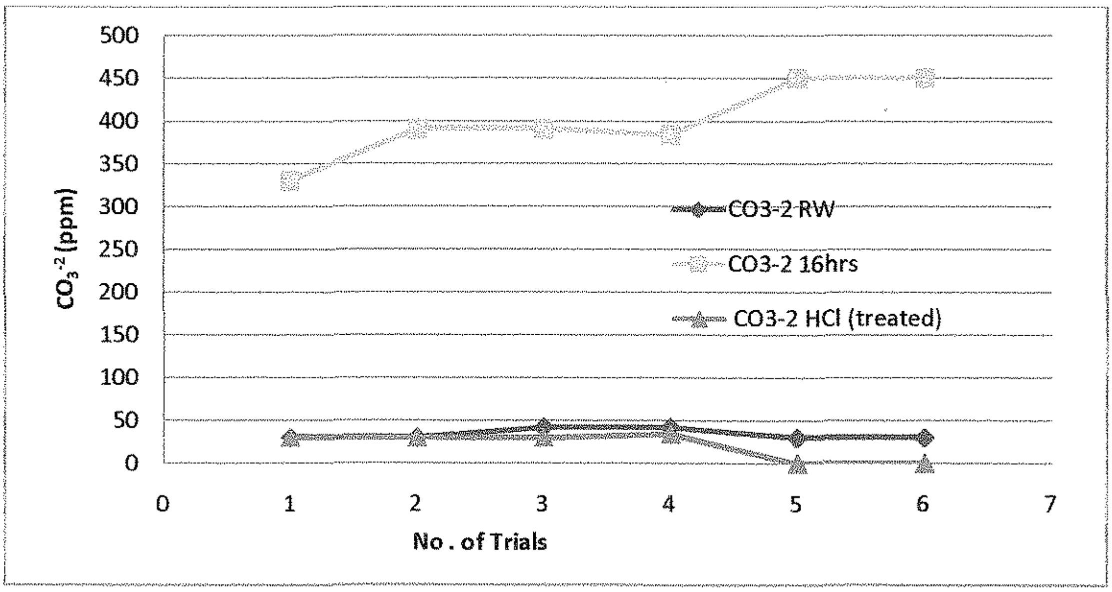

Fig.5 Variation of CO_3^{-2} during six laboratory trails of the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

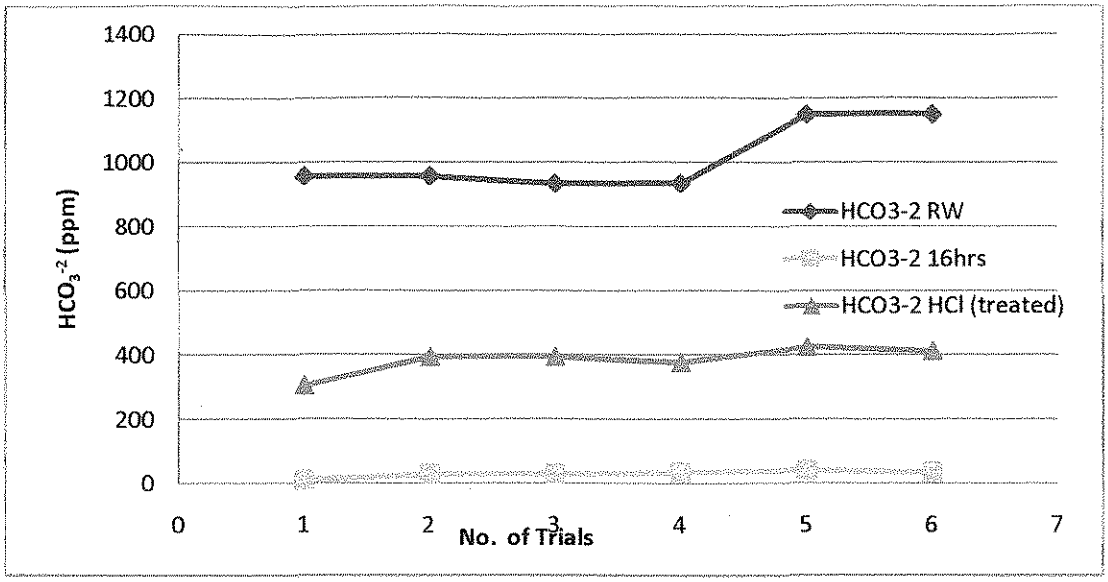

Fig.6 Variation of HCO_3^{-1}during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

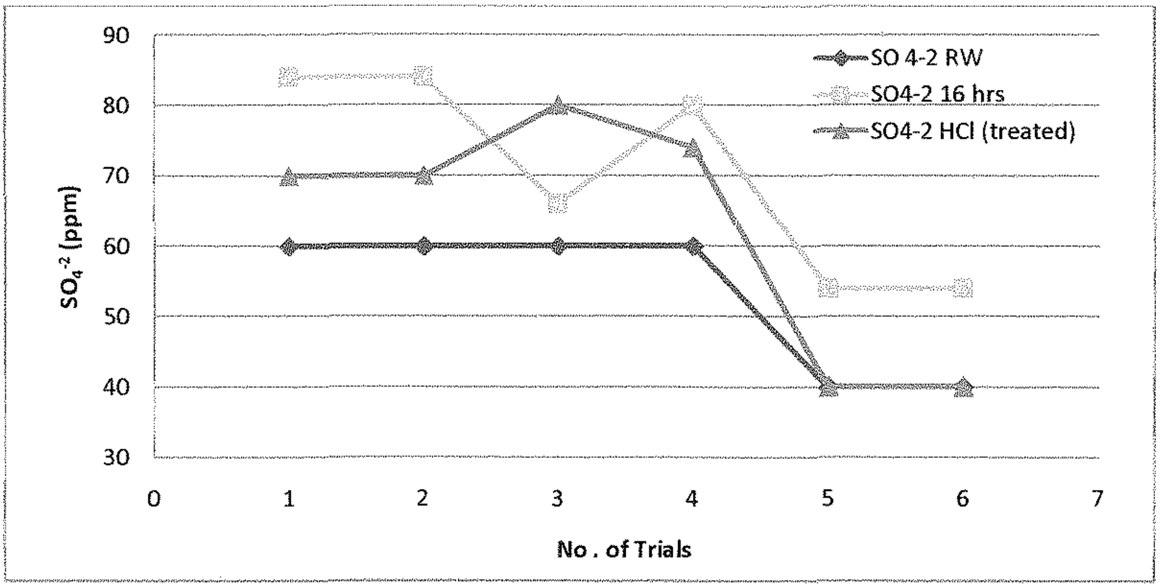

Fig.7 Variation of SO_4^{-2} during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water Pilaniyon ki Dhani (Village Shola)

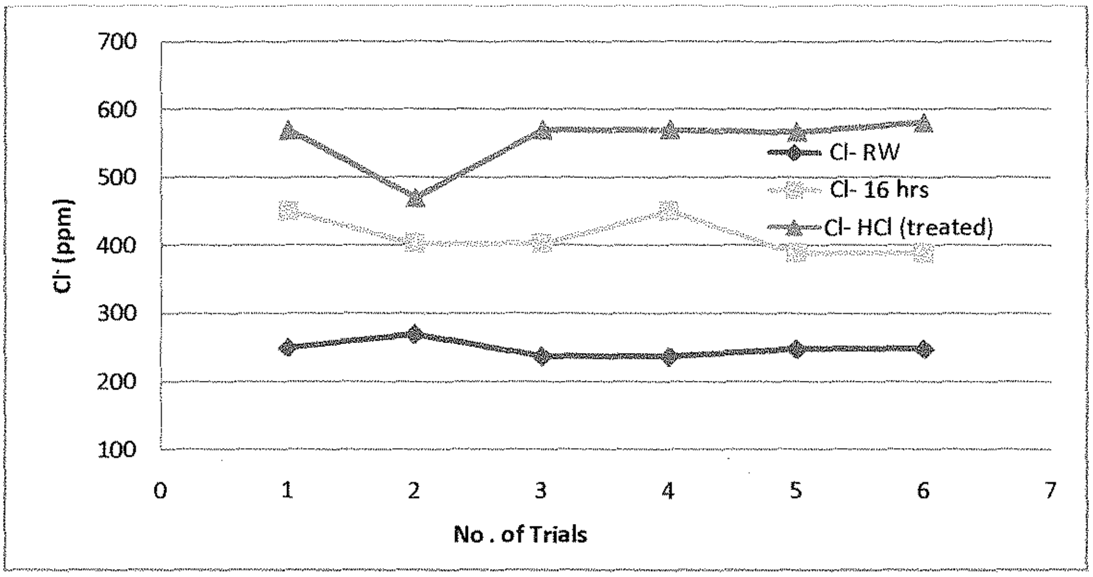

Fig.8 Variation of Cl^- during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

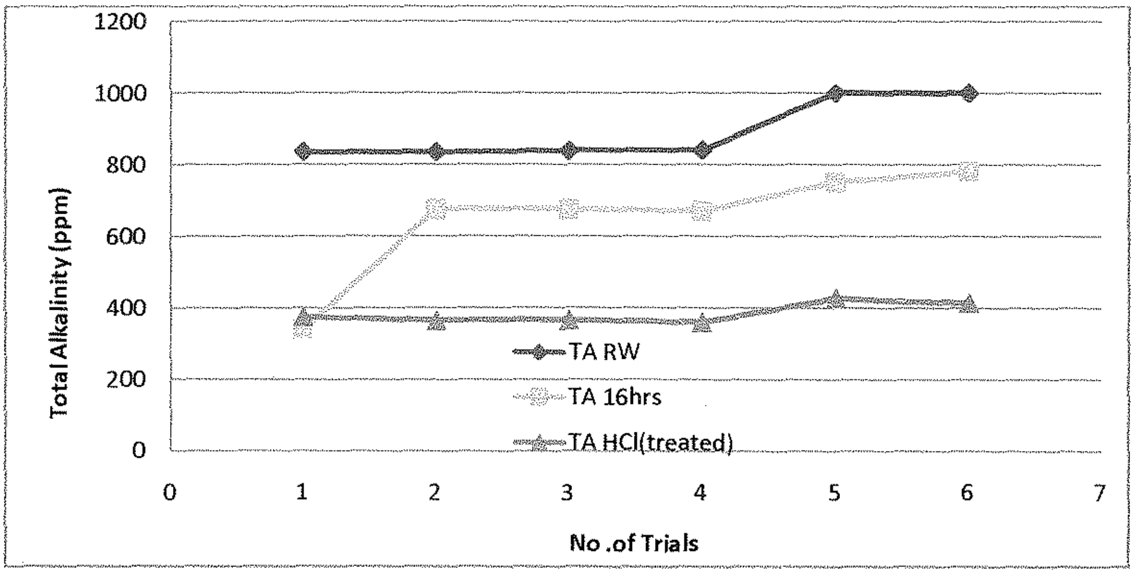

Fig.9 Variation of Total Alkalinity during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

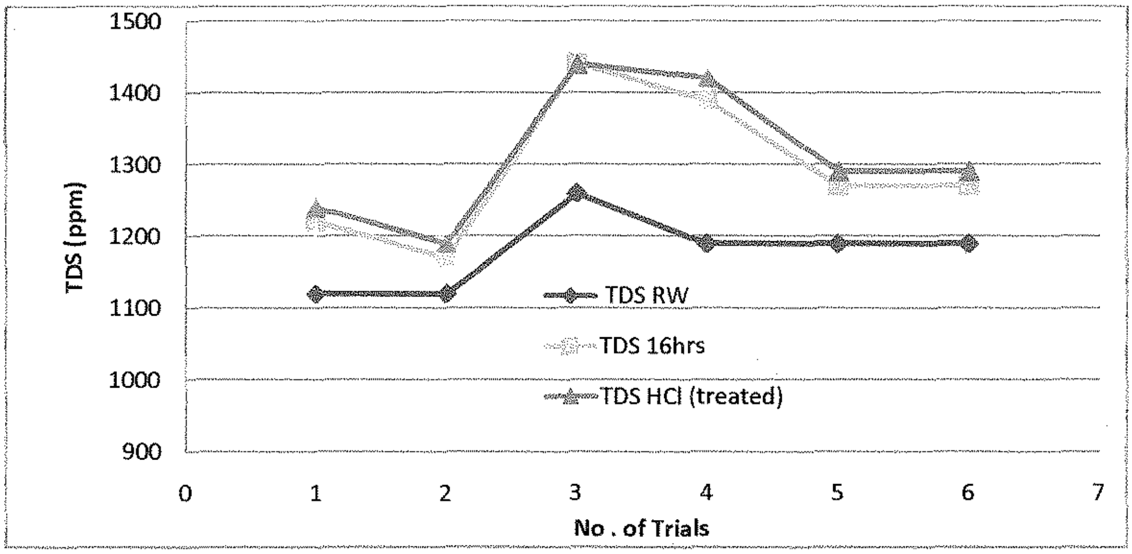

Fig.10 Variation of TDS during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

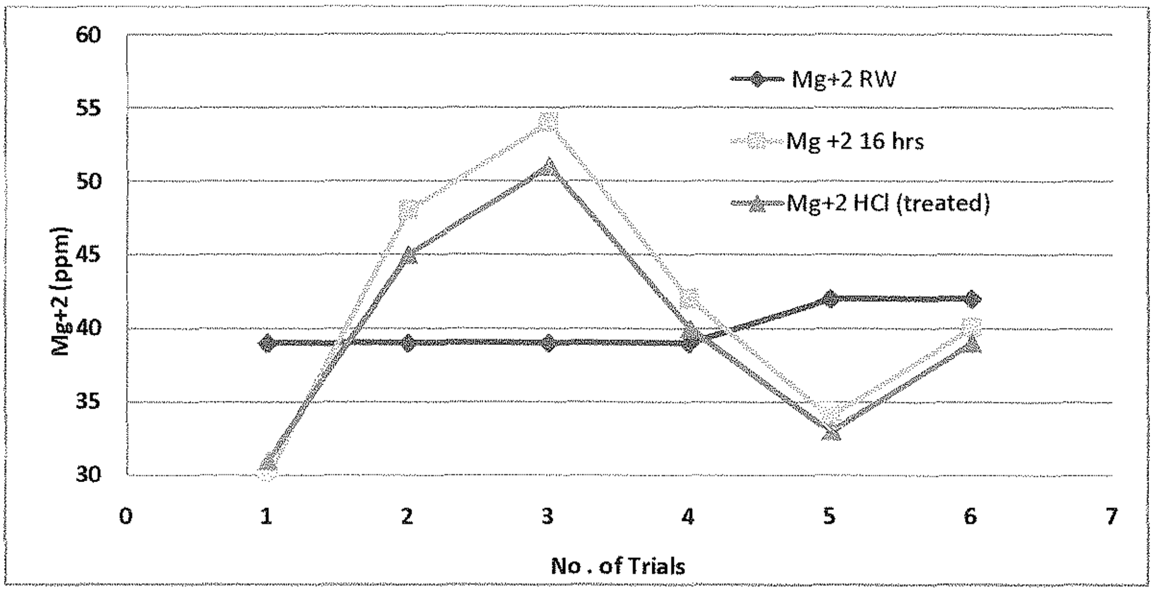

Fig.11 Variation of Mg^{+2} during six laboratory trails of on the process of MgO-CaO-$CaCl_2$-HCl treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

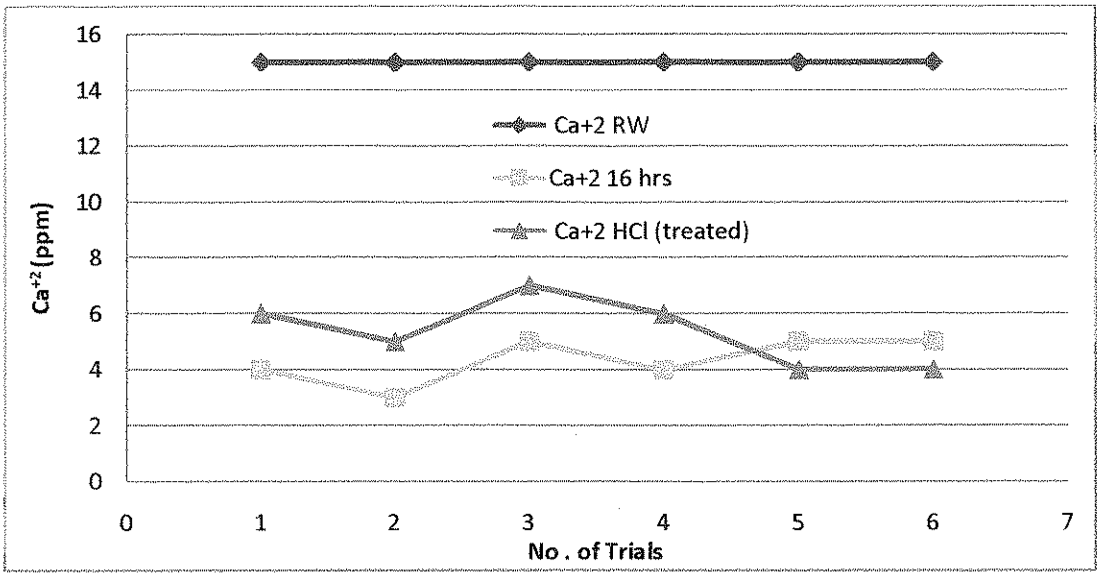

Fig.12 Variation of Ca^{+2} during six laboratory trails of on the process of $MgO-CaO-CaCl_2-HCl$ treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

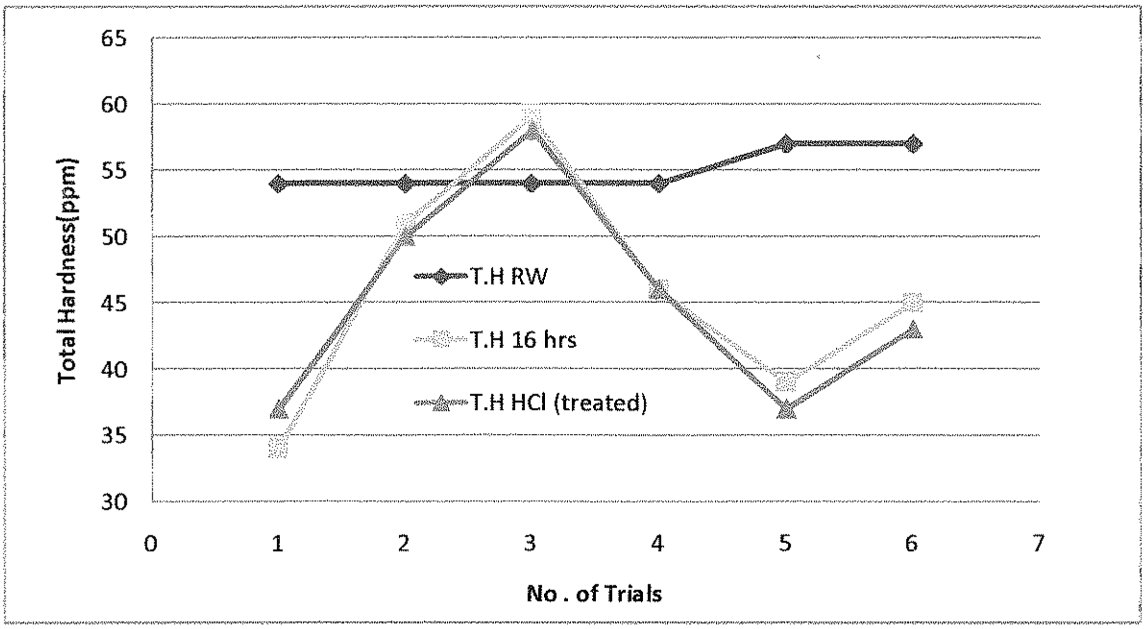

Fig.13 Variation of Total Hardness during six laboratory trails of the process of $MgO-CaO-CaCl_2-HCl$ treatment with 50 liter raw water from Pilaniyon ki Dhani (Village Shola)

CONCLUSION

We have determined that the MgO-CaO-$CaCl_2$ method of defluoridation can be adopted for water having high alkalinity. Since the local ground water contains high SO_4^{2-} concentration $NaHSO_4$ cannot be added for pH adjustment, instead 0.38 N HCl can be used . The final Cl^- concentration in treated water was found to be within the permissible limits, so were other parameters except nitrate which is very high in the raw water itself.

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY

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NEW 7-(2-(BENZOL[*d*]THIAZOL-2-YLAMINO)ETHOXY)-4-METHYL-2*H*-CHROMEN-2-ONE DERIVATIES WITH ATYPICAL ANTIPSYCHOTIC ACTIVITY

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ABSTRACT

A new series of 7-(2-(benzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one derivatives(4a-4k) was synthesized and evaluated for their D_2 and $5HT_2$ antagonistic activity as a measure of atypical antipsychotic property. Compounds 7-(2-(benzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one derivatives (4a-4k) was synthesized by refluxing 2-amino benzothiazoles substituted derivatives (3a-3k) and 7-(2-Chloroethoxy)-4-methyl-2H-chromen-2-one (2) in dry pyridine. The synthesized compounds were characterized with the help of spectral and analytical data. Most of these compounds showed dopamine D_2 receptor antagonistic activity from moderate to high potency along with serotonin 5-HT_2 receptor blockage activity: a property that has been suggested to be necessary for atypical nature of antipshycotic agents. The D_2 and 5-HT_2 receptor blockage activity was evaluated by inhibition of apomorphine-induced climbing behavior and 5HTP induced head twitches in mice respectively.

KEYWORDS: **Schizophrenia, Atypical Antipsychotics, Benzothiazole. Chromen-2-one**

RESUMO

*Uma nova série de derivados de **7-(2-benzo[d]tiazol-2-ilamino)etoxi-4-metil-2H-cromeno-2-ona** foram sintetizados e avaliados para suas propriedades D_2 e $5HT_2$ antagónicas e medida de propriedade antipsicótica. A maioria destes compostos mostraram atividade antagônica do receptor da dopamina e bloqueio da atividade do receptor 5-HT2 da serotonina, propriedades necessárias para a atividade atípica de agentes antipsicóticos. Os efeitos foram confirmados em camundongos.*

PALAVRAS CHAVE: **Esquizofrenia, Antipsicótico Atípico, Benzotiazol, Cromeno-2-ona**

Corresponding Author: Dr. Ashish A. Gawai, Associate Professor, Anuradha College of Pharmacy, Chikhli-443201, Dist-Buldana, M.S, India.

INTRODUCTION

A number of psychiatric disorders, including anxiety, depression, schizophrenia and neurodegenerative disorder like Parkinson's disease are known to involved defects in the function of neural pathways sustained by the neurotransmitters dopamine and serotonin[1, 2, 3]. Antipsychotic drugs antagonising central dopaminergic receptors have been used for several decades in the treatment of psychiatric disorder schizophrenia[4]. Although these drugs can reduce the positive symptoms of schizophrenia, they unfortunately often induce extapyramidal side effects and are furthermore often not able to control the negative symptoms. The antipsychotic action has been suggested due to a blockade of the mesocorticolimbic dopaminergic system[5, 6]. In accordance with this, the pharmacological potencies of classical antipsychotics correlate with their affinities for dopamine D_2 receptors[7]. The last decade has witnessed the discovery of the multiplicity of serotonin 5-HT receptors[8, 9, 10] and several 5-HT ligands have been studied with regard to their affinity, specificity and potential therapeutic application. The current status of antipsychotic agents and our previous works, synthesis and Pharmacological screening of new coumarinoacetamides[11], synthesis and neuroleptic activity of new **Coumarinoacetamides** with special reference to atypical antipsychotic activity[12] have led to the design and synthesis of new series of novel **2-(4-methyl-2-oxo-2*H*-chromen-7-yloxy)-N-(benzo[*d*]thiazol-2-yl) acetamide derivatives** (In Press). These compounds shown antipsychotic and analgesic activity assuming their interaction with serotoninergic 5HT and Dopaminergic D_2 receptor property. In an effort to increase such properties and gain access to new neuroleptic agents with or without reduced extrapyramidal side-effects, we have synthesized benzothiazole derivatives attached with Chromen-2-one moiety by ethoxy polar side chain linkage. Benzothiazole derivatives were reported to have 5HT antagonistic property[13] where as Chromen-2-one moiety was reported for their dopaminergic D_2 antagonistic activity[14]. The combination of these two antagonistic moieties could possibly lead to a new series of antipsychotic drugs with reduced CNS side-effects.

MATERIAL AND METHODS

Melting points were determined by open capillary method on Campbell electronic apparatus and are uncorrected. The purity of the synthesized compounds was checked by TLC using precoated silica G_{254} plates and visualized in iodine and UV light. The IR spectra of synthesized compounds were recorded by a Jasco-V-5300 FTIR in potassium bromide discs. The ^1H NMR was recorded on a 300 MHz JEOL spectrophotometer in DMSO and $CHCl_3$ using tetramethylsilane as internal standard.

EXPERIMENTAL METHODS

The general methods of synthesis exemplified are illustrated as below.

General method of synthesis of 7-hydroxy-4 methyl-2*H*-chromen-2-one (1)

(Scheme 1)

The method of Pechmann and Duisberg[15] was followed for the preparation of 7-hydroxy-4 methyl-2*H*-chromen-2-one (1). 100ml of conc. H_2SO_4 was kept in an ice-bath. When temperature fell below 10^0C, a solution of resorcinol (10gm, 0.091 moles) and ethylacetoacetate (13ml, 0.103 moles) was added with continuous stirring for 2hr. The temperature was maintained below 10^0C throughout the addition. The reaction mixture was kept at room temperature for 18 hr after which it was poured with vigorous stirring into the mixture of 200gm of crushed ice and 300ml of distilled water. Precipitate was collected by vacuum filtration and washed with cold water (325ml). The solid was dissolved in 150ml of 5% NaOH, filtered, and 2M H_2SO_4 (55ml) was added to it with vigorous stirring until the solution was acidic. The crude 7-hydroxy-4 methyl-2*H*-chromen-2-one (1) was collected by filtration at the pump, washed with cold water and dried. The product was recrystallized from ethanol.

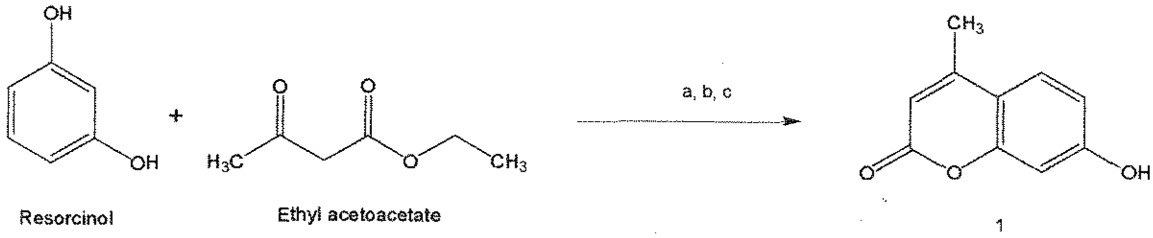
General method of synthesis of 7-(2-Chloroethoxy)-4-methyl-2*H*-chromen-2-one (2), (Scheme 2)

7-hydroxy-4-methyl-2H-chromen-2-one (1) (0.01 mol) was dissolved in 10ml acetonitrile with anhydrous K_2CO_3 (0.01 mol) was added to the solution. 1-Bromo 2-Chloroethane (0.01 mol) was added drop wise to the mixture in the round bottom flask over a period of 15 min. The reaction was refluxed for 18h. The filtrate was removed under vacuum using molecular distiller to afford dry solid. The solid obtained was dissolved in dichloromethane; the organic layer was washed with water and dried over anhydrous sodium sulfate. The organic layer was separated and evaporated to dryness to afford crude products **(2)** which was then recrystallized using ethanol.

General method of synthesis of 2-amino benzothiazoles substituted derivatives (3a-3k) (Scheme 3)

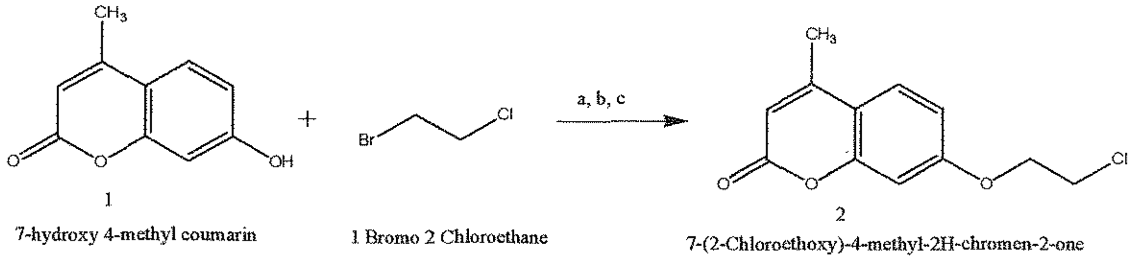
2-amino benzothiazole substituted derivatives was synthesis by following method[16]. To glacial acetic acid (20ml) precooled to 5^0C were added 8gm (0.08mol) of potassium thiocynate and 1.45gm (0.01mol) of substituted aniline. The mixture was placed in freezing mixture of ice and salt and mechanically stirred while 1.6ml of bromine in 6ml of glacial acetic acid was added from dropping funnel at such a rate that the temperature doesn't rise beyond 0^0C. After addition of bromine for 105 minutes, the solution was stirred for an additional 2 hours at 0^0C and at room temperature for 10 hour. It was then allowed to stand overnight during which period an orange precipitate was settled at the bottom where 6ml water was added quickly and slurry was heated at 85^0C on steam bath and filtered in hot condition. The orange residue was placed in a reaction flask and treated with 10ml of glacial acetic acid, heated again to 85^0 and filtered in hot state. The combined filtrate was cooled and neutralized with concentrated

Scheme 1: Synthesis of 7-hydroxy-4 methyl-2*H*-chromen-2-one (1)



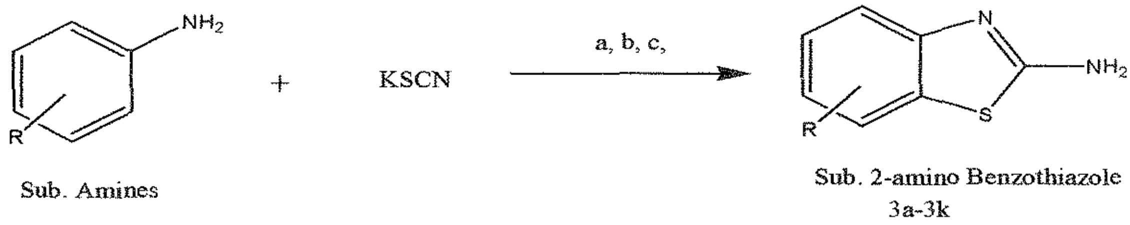
a. conc.H_2SO_4, b.5% NaOH, c.2M H_2SO_4,

Scheme 2: Synthesis of 7-(2-Chloroethoxy)-4-methyl-2*H*-chormen-2-one



a. Acetonitrile, b. anhydrousK_2CO_3, c. Dichloromethane

Scheme 3: Synthesis 2-amino Benzothiazole substituted derivatives (3a-3k)



a. Gl. Acetic Acid, b. Bromine, c. Benzene ammonia to pH 6 when dark yellow precipitate was collected and recrystallised from benzene.

General method of synthesis 7-(2-(benzo[*d*]thiazol-2-ylamino)ethoxy)-4-methyl-2*H*-chromen-2-one derivatives (4a-4k) (Scheme 4)

A mixture of **7-(2-Chloroethoxy)-4-methyl-2*H*-chromen-2-one (2)** with compounds **3a-3k** (0.01 mol) was added to the reaction flask and refluxed in dry pyridine for 24 hours. The solvent was distilled off. The mixture was collected and poured on to cursed ice. The solid product was filtered and recrystallised from ethanol.

Pharmacological Evaluation of Atypical Antipsychotics Activity:

Pharmacological evaluation of atypical antipsychotic activity was performed by testing their ability to inhibit apomorphine induced climbing behavior (Figure 1) and 5HTP induced head twitches in mice (Figure 2).

Animals: Albino Swiss male mice, 20-25 g were maintained on standard pallet diet and given tap water *ad libidum*. The experiments were performed in a quiet room with an ambient temperature of 22^{0+}-2^{0}C and between 12.00- 18.00 hrs each day to avoid behavioral changes resulting from circadian rhythm. The test compounds were suspended in 3% gum acacia in water for injection. All the injections were given intraperitoneally (i.p). The effects of the test compounds and vehicle control (3% gum acacia 5ml/Kg) on drug induced models were observed by injecting test compounds 30 minutes prior to the apomorphine and 5HTP.

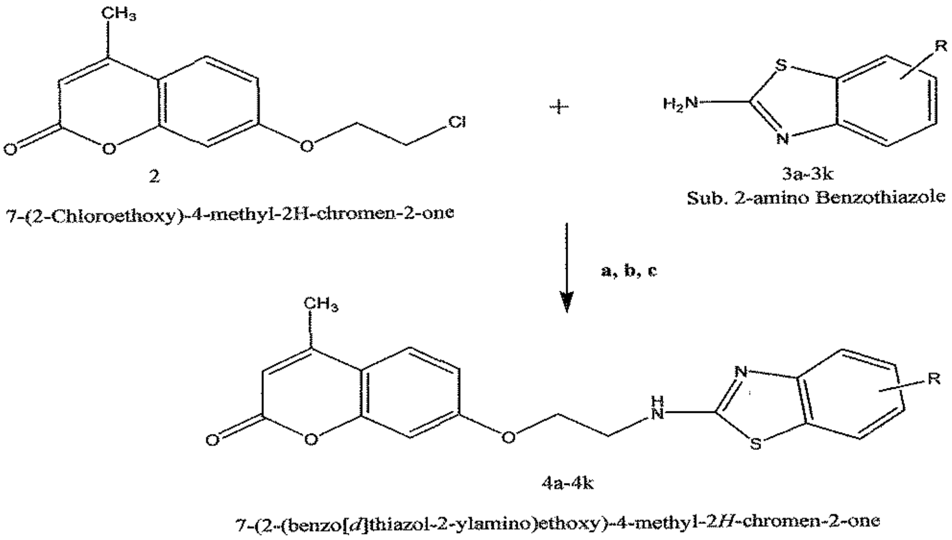
Apomorphine induced Climbing Behavior[17]

The animals were grouped randomly containing six animals in each group. The test groups received dose of test compounds 5 mg/kg body weight. The control and standard group received 3% gum acacia 5ml/kg and olanzepine 1mg/kg body weight respectively. Climbing behaviour was assessed in the animals by placing them individually in cylindrical wire mesh cage (height 18cm, diameter 14 cm) 5 minute after administration of apomorphine (1.0 mg/kg) The animals were kept in the cage, and observed at the interval of 10, 20, 30 minute after the administration of apomorphine. The following score was assigned to an individual animal: 0, when all four paws on the floor; 1, when two paws on the mesh; and 2, when all the four paws on the mesh. The score was summed up for each animal. Data were expressed as percentage of blockage of climbing relative to apomorphine-treated control mice.

5-HTP induced Head Twiches[18]

The mice were grouped and administered test compounds at 5 mg/kg and control group 3 % gum acacia but the standard group received olanzepine (1 mg/kg, b.w). The head twitches in mice were counted after 20 minutes of 5-HTP (100mg/kg) administration at an interval of 5 minutes and for a period of 1hour.

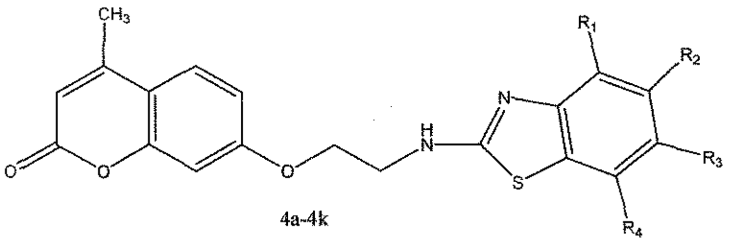
Scheme 4: Synthesis of 7-(2-(benzo[*d*]thiazol-2-ylamino)ethoxy)-4-methyl-2*H*-Chromen-2-one derivatives



a. dry pyridine, b. crushed ice, c. ethanol.

RESULTS AND DISCUSSION

Table-1. Physicochemical data of synthesized compounds **(4a-4k)**



4a-4k

Cmp	Mol. Formula	R1	R2	R3	Elemental Analysis (%) C	H	N	Yield (%)	m. p (^{0}C)◆	Rf*
4a	$C_{19}H_{16}N_2O_3S$	-	-	-	64.7	4.5	7.9	80	180-182	0.60
4b	$C_{19}H_{15}ClN_2O_3S$	-	-	Cl	58.9	3.9	7.2	53	130	0.35
4c	$C_{20}H_{18}N_2O_4S$	-	-	OCH_3	62.8	4.7	7.3	69	170	0.5
4d	$C_{19}H_{15}N_3O_5S$	-	-	NO_2	57.1	3.7	10.5	73	160-161	0.63
4e	$C_{19}H_{15}ClN_2O_3S$	Cl	-	-	58.9	3.9	7.2	75	152-153	0.59
4f	$C_{19}H_{15}FN_2O_3S$	-	-	F	61.6	4.1	7.5	63	174	0.32
4g	$C_{19}H_{14}ClFN_2O_3S$	-	Cl	F	56.4	3.4	7.0	68	130-131	0.38
4h	$C_{20}H_{18}N_2O_3S$	CH_3	-	-	65.6	5.0	7.7	55	168-169	0.44
4i	$C_{20}H_{18}N_2O_3S$	-	-	CH_3	65.6	5.0	7.7	68	154-155	0.60
4j	$C_{19}H_{15}ClN_2O_3S$	-	Cl	-	59.0	3.9	7.3	18	149	0.49
4k	$C_{19}H_{15}BrN_2O_3S$	Br	-	-	52.9	3.5	6.5	13	134	0.55

◆ Melting points were uncorrected
*Mobile phase for (4a-4k) [Benzene; Ethyl acetate : 4;1]

7-Hydroxy-4-methyl chromen-2-one (1)

The method of Pechman and Duisberg was followed for the synthesis of 7-Hydroxy-4-methyl chromen-2-one. **Yield**: 51%; **m.p.** 181-182; **Rf**: 0.45 [benzene; ethyl acetate: 4:1] **IR (KBr) cm^{-1}**: 3500(-OH), 2957(aromatic C-H), 1680(C=O), 1601-1452(C=C), 1336-1159(-C-CO-O), 1215(-C-O phenol) and 746(C-H out of plane). **^{1}H NMR (DMSO)**: 10.5(b,1H,-OH), 7.51-7.53(d,1H,C_5-H), 6.6-6.9(m,2H,C_6-H), 6.06(s,1H,C_3-H), 2.29(s,3H,C_4-CH_3).

7-(2-Chloroethoxy)-4-methyl-2H-chromen-2-one (2)

Yield: 59% ; **m.p.** 120-121; **Rf**: 0.65 [benzene; ethyl acetate: 4:1] **IR (KBr) cm^{-1}**: 2931.6(aromatic C-H) 1724(C=O streching), 1682(aromatic C=C streching), 1386-1201(-C-CO-O), 1240(-C-O phenol), 644(C-Cl stretching) and 746(C-H out of plane), **^{1}H NMR (DMSO)**: 7.51(d,1H,C_5-H), 6.6-6.9(m,2H,C_6-H and C_8-H), 6(s,1H,C_3-H), 2.15(s,3H,C_4-CH_3). 4.20(t, 2H, O-CH_2 linkage), 4.12(t, 2H, Cl-CH_2 linkage)

7-(2-(benzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one (4a)

IR (KBr): 3359.5(N-H stretching), 2990(Aromatic C-H stretching), 1688(C=O stretching), 1587-1440(C=C), 1248(C-N), 748(C-S stretching) **cm^{-1}**. **^{1}H NMR (δ, ppm, DMSO):** 8.6(t, 1H, N-H), 7.16(d,1H,C_5-H in Chromen-2-one), 6.6-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 5.90(s,1H,C_3-H in Chromen-2-one), 2.3(s,3H,C_4-CH_3 in Chromen-2-one), 4.24(t,2H,O-CH_2 linkage), 4.12(t,2H,N-CH_2 linkage), 7.47(m,2H, $C_{5'}$-H,&$C_{6'}$-H in Benzothiazole), 8.10(d,2H,$C_{4'}$-H&$C_{7'}$H in benzothiazole)

7-(2-(6-Chlorobenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one (4b)

IR (KBr): 3211(N-H stretching), 2966(C-H stretching), 1732(C=O stret), 1458-1365 (C=C), 1277(C-N), 1171(CO-O-C stert), 781(C-S stretching) **cm^{-1}**. **^{1}H NMR (δ, ppm, DMSO):** 9.11(t,1H,N-H), 7.23(d,1H,C_5-H in Chromen-2-one), 6.6-6.9 (d,2H,C_6-H and C_8-H in Chormen-2-one), 6.05(s,1H,C_3-H in Chromen-2-one), 2.0(s,3H,C_4-CH_3 in Chromen-2-one). 4.5(t, 2H, O-CH_2 linkage), 4.60(t, 2H, NH-CH_2 linkage), 7.60(d, 1H, $C_{5'}$-H in Benzothiazole), 8.15(d, 2H, $C_{4'}$-H&$C_{7'}$H in benzothiazole)

7-(2-(6-methoxybenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one (4c)

IR (KBr): 3410(N-H), 2854(C-H), 1715(C=O), 1452(C=C), 1264(C-N), 1134(CO-O-C), 747(C-S) **cm^{-1}**. **^{1}H NMR (δ, ppm, $CDCl_3$):** 8.1(t,1H,N-H), 7.4(d,1H,C_5-H in Chromen-2-one), 6.5-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 5.6(s,1H,C_3-H in Chromen-2-one), 2.1(s,3H,C_4-CH_3 in Chromen-2-one), 4.12(t,2H,O-CH_2 linkage), 4.0(t,2H,N-CH_2 linkage), 7.6(s,1H,$C_{7'}$-H in Benzothiazole), 8.1(d,1H,$C_{4'}$-H in benzothiazole), 7.1(d,1H,$C_{5'}$-H in benzothiazole), 3.7(S,3H,OCH_3 in benzothiazole)

7-(2-(6-nitrobenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one (4d)

IR (KBr): 3341(N-H), 1685(C=O), 1588(C=C), 1310(C-O-O stretching), 1266(C-N), 754(C-N) **cm^{-1}**. **^{1}H NMR (δ, ppm, $CDCl_3$):** 8.5(t,1H,N-H), 7.5(d,1H,C_5-H in Chromen-2-one), 6.5-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 6.2(s,1H,C_3-H in Chromen-2-one), 2.1(s,3H,C_4-CH_3 in Chromen-2-one). 4.0(t, 2H, O-CH_2 linkage), 4.2(t, 2H, N-CH_2 linkage), 8.47(m, 2H, $C_{4'}$-H & $C_{5'}$-H in Benzothiazole), 8.56 (s, 1H, $C_{7'}$-H in benzothiazole)

7-(2-(4-chlorobenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one **(4e)**
IR (KBr): 3310(N-H), 2920(C-H), 1734(C=O), 1504(C=C), 1140(C-O), 582(C-Cl), 781(C-S) **cm^{-1}**. **^{1}H NMR (δ, ppm, DMSO):** 9.1(t,1H,N-H), 7.20(d,1H,C_5-H in Chromen-2-one), 6.5-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 6.1(s,1H,C_3-H in Chromen-2-one), 2.4(s,3H,C_4-CH_3 in Chromen-2-one). 4.2(t, 2H, O-CH_2 linkage), 4.62(t, 2H, N-CH_2 linkage), 7.4-7.6(m, 2H, $C_{5'}$-H &$C_{6'}$-H in Benzothiazole), 8.1 (d, 1H, $C_{7'}$.H in benzothiazole)

7-(2-(6-fluorobenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one **(4f)**
IR (KBr): 3327(N-H), 2922(Ar C-H), 1703(C=O), 1596-1334(C=C), 1135(C-O), 929 (C-F), 751(C-S) **cm-1**. **^{1}H NMR (δ, ppm, DMSO):** 9.3(t,1H,N-H), 7.2(d,1H,C_5-H in Chromen-2-one), 6.4-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 6.20(s,1H,C_3-H in Chromen-2-one), 2.32(s,3H,C_4-CH_3 in Chromen-2-one). 4.11(t, 2H, O-CH_2 linkage), 4.32(t, 2H, N-CH_2 linkage), 7.2-7.8(m, 2H, $C_{5'}$-H & $C_{7'}$-H in Benzothiazole), 8.01(d, 2H, $C_{4'}$-H in benzothiazole)

7-(2-(5-chloro-6-fluorobenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one **(4g)**
IR (KBr): 3360(N-H), 2920(C-H), 1720(C=O), 1589-1365(C=C), 667(C-Cl), 931(C-F), 1153(CO-O-C stretching), 1253.9(C-O-O) **cm^{-1}**. **^{1}H NMR (δ, ppm, DMSO):** 9.6(t, 1H,N-H), 7.26(d,1H,C_5-H in Chromen-2-one), 6.5-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 6.13(s,1H,C_3-H in Chromen-2-one), 2.17(s,3H,C_4-CH_3 in Chromen-2-one), 4.34(t, 2H, O-CH_2 linkage), 4.48(t, 2H, N-CH_2 linkage), 7.89(s, 1H, $C_{7'}$-H in Benzothiazole), 8.30(s, 1H, $C_{4'}$-H in benzothiazole)

7-(2-(4-methylbenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one **(4h)**
IR (KBr): 3342(N-H), 2920(C-H), 1693(C=O), 1565(C=C), 1259(C-N), 841(C-H out of plane), 1174(CO-O-C), 743(C-S Stretching) **cm^{-1}**. **^{1}H NMR (δ, ppm, DMSO):** 8.3(t, 1H,N-H), 7.10(d,1H,C_5-H in Chromen-2-one), 6.6-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 5.90(s,1H,C_3-H in Chromen-2-one), 1.9(s,3H,C_4-CH_3 in Chromen-2-one) 4.3(t, 2H, O-CH_2 linkage), 4.10(t, 2H, N-CH_2 linkage), 7.3-7.4(m,2H,$C_{5'}$-H & $C_{6'}$-H in Benzothiazole), 8.0(d,1H,$C_{7'}$.H in benzothiazole), 2.35(s,3H,-CH_3 of Benzothiazole)

7-(2-(6-methylbenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one **(4i)**

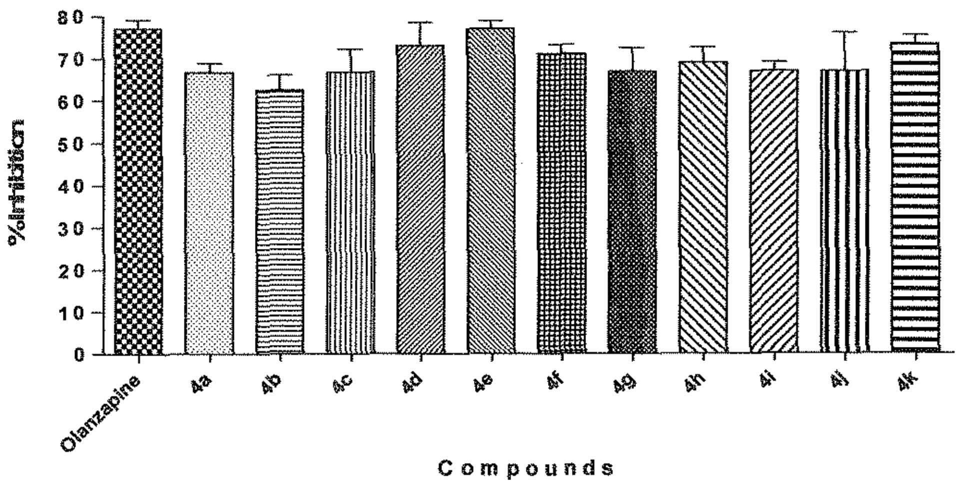
IR (KBr): 3095(N-H), 2991(C-H), 1611(C=O), 1428(C=C), 1282(C-N), 1184(CO-O-C), 851(C-H), 732(C-S stretching) **cm^{-1}**. **^{1}H NMR (δ, ppm, $CDCl_3$):** 8.1(t,1H,N-H), 6.96(d,1H,C_5-H in Chromen-2-one), 6.5-6.6(d,2H,C_6-H and C_8-H in Chormen-2-one), 6.0(s,1H,C_3-H in Chromen-2-one), 2.23(s,3H,C_4-CH_3 in Chromen-2-one). 4.34(t, 2H, O-CH_2 linkage), 4.17(t, 2H, N-CH_2 linkage), 7.9-8.1(m, 2H, $C_{4'}$-H & $C_{7'}$-H in benzothiazole), 7.4(d, 1H, $C_{5'}$-H in benzothiazole)

7-(2-(5-chlorobenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one **(4j)**
IR (KBr): 3089(N-H), 2972(C-H), 1708(C=O), 1555(C=C), 1246(C-N stretching), 1180(CO-O-C stretching), 816(C-H) **cm^{-1}**. **^{1}H NMR (δ, ppm, DMSO):** 8.6(t,1H,N-H), 7.16(d,1H,C_5-H in Chromen-2-one), 6.6-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 5.90(s,1H,C_3-H in Chromen-2-one), 2.3(s,3H,C_4-CH_3 in Chromen-2-one), 4.24(t, 2H, O-CH_2 linkage), 4.12(t, 2H, N-CH_2 linkage), 7.56(m, 1H, $C_{6'}$-H in Benzothiazole), 8-8.2(d, 2H, $C_{4'}$-H & $C_{7'}$.H in benzothiazole)

7-(2-(4-bromobenzo[d]thiazol-2-ylamino)ethoxy)-4-methyl-2H-chromen-2-one **(4k)**
IR (KBr): 3267(N-H), 2891(C-H), 1732(C=O), 1492(C=C), 1226(C-N), 1056(CO-O-C), 701(C-S), 631(C-Cl) **cm^{-1}**. **^{1}H NMR (δ, ppm, DMSO):** 8.4(t,1H,N-H), 7.20 (d,1H,C_5-H in Chromen-2-one), 6.6-6.9(d,2H,C_6-H and C_8-H in Chormen-2-one), 6.10 (s,1H,C_3-H in Chromen-2-one), 2.1(s,3H,C_4-CH_3 in Chromen-2-one). 4.11(t, 2H, O-CH_2 linkage), 4.18(t, 2H, N-CH_2 linkage), 7.72(m, 1H, $C_{5'}$-H in benzothiazole), 8.1-8.2 (d, 2H, $C_{4'}$-H & $C_{7'}$.H in benzothiazole)

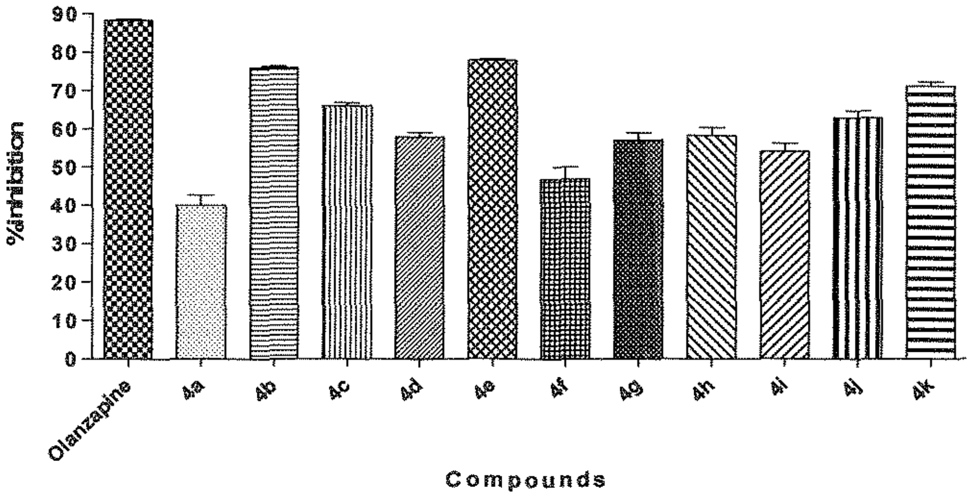
Pharmacological Results.

Figure 1. Percent Inhibition of apomorphine induced climbing behavior, at the dose of 5 mg/kg.



*n = 6, p < 0.05, $ Dose of Olanzapine was 1mg/kg, Apomorphine 1mg/kg

Figure 2. Percent Inhibition of 5-HT induced head twitches at the dose of 5 mg/kg.



*n = 6, p < 0.05, $ Dose of Olanzapine was 1mg/kg

CONCLUSIONS

Our study suggests that all the synthesized compounds provide a chemical class of compounds that showed significant antipsychotic activity in pharmacological model predictive of D_2 antagonist activity and also had significant antagonistic activity at 5-HT receptor, an index of hypothesized atypical antipsychotic profile. The compounds which were substituted with *chloro, bromo* at *ortho* position and nitro, methyl and *chloro* at *meta* position showed significant dopamine D_2 receptor antagonistic activity and the compounds which were substituted with *chloro, bromo* at ortho position and *chloro, fluoro* and *methoxy* at *meta* position showed significant 5HT receptor antagonistic activity.

From this data we can conclude that compounds 7-(2-(4-chlorobenzo[*d*]thiazol-2-ylamino)ethoxy)-4-methyl-2*H*-chromen-2-one (4e) and 7-(2-(6-methoxybenzo[*d*]thiazol-2-ylamino)ethoxy)-4-methyl-2*H*-chromen-2-one (4c) have better atypical antipsychotic profile. A detailed toxicity study is required for characterization of the compounds for the therapeutic utility.

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A BRIEF HISTORY OF MINERALOGY IN BRAZIL

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ABSTRACT

This article presents a brief history of mineralogy in Brazil. Special attention is given to the contribution of José Bonifácio de Andrada e Silva and also to the minerals that were first described in Brazil, the so-called "type –minerals" of Brazil.

KEYWORDS: **Mineralogy in Brazil, José Bonifácio de Andrada e Silva, Type Minerals of Brazil**

RESUMO

Este artigo apresenta um breve histórico sobre a mineralogia no Brasil. A contribuição de José Bonifácio de Andrada e Silva e os minerais que foram descritos pela primeira vez no Brasil, os chamados "minerais-tipo" brasileiros são tratados em detalhe.

PALAVRAS CHAVE: **Mineralogia no Brasil, José Bonifácio de Andrada e Silva, Minerais-tipo brasileiros**

INTRODUCTION

Brazil possesses a very wide mineralogical diversity. About 16% of the mineralogical species known world wide are present in Brazil and about 60 species are type minerals of Brazil. [1-14]

The use of minerals was relatively wide spread among the native Indian population before the discovery of our country by the Portuguese in 1500, as can be documented by the excellent cave paintings of Serra da Capivara , São Raimundo Nonato, Piauí and the large number of stone utensils made from minerals and their variety of rocks. In addition, minerals and rocks were widely used for adornment, religious objects and rituals. [15] Some of the minerals used included amazonite (a variety of microcline ($KAlSi_3O_8$), graphite (C), hematite (Fe_2O_3), jadeite ($NaAlSi_2O_6$), malachite ($Cu_2(CO_3)(OH)_2$), nephrite (a variety of actinolite, $Ca_2(Mg,Fe^{2+})_5Si_8O_{22}(OH)_2$), opal ($SiO_2.nH2O$), quartz ($SiO_2$) and its varieties, chalcedony, aventurite, hyaline, silex and jasper, sillimanite (Al_2SiO_5), amphibolite, basalt, diabase, diorite, steatite, phyllite, gabbro, gneiss, granite, quartzite schist and copal [15-16].

The oldest historical mineralogical record in Brazil is due to the Spaniard, Felipe de Guillén (born in Sevilla, 1487, died in Porto Seguro, 1571 ?) who suggested the occurrence of emerald (a variety of beryl. $Be_3Al_2Si_6O_{18}$) in the so-called Serra Resplandescente (Glowing Mountain) , a place full of emeralds. This was really a legendary geological formation, result of popular imagination, a place that was looked for by many explorers , but was never found or discovered. [16]

The first historian to describe expeditions in the Brazilian Highlands (Sertão) was the Portuguese Pêro de Magalhães Gândavo (born in Braga. 1540, died in Braga 1580). He talked about the occurrence of gold in the region corresponding to the present state of Minas Gerais.

Pêro de Magalhães Gândavo (1540-1580)

As mentioned by Cornejo and Bartorelli [16] the history and development of Brazilian mineralogy depended on a large number of factors and events. Some of them are the use of these substances for personal adornment, artifacts used in daily life and in rituals , the search for noble metals by the Portuguese Crown and by the scouts and explorers (bandeirantes), the discovery of large quantities of gold and diamond in Minas Gerais during the Colonial Period and the great scientific expeditions by European naturalists and travelers.

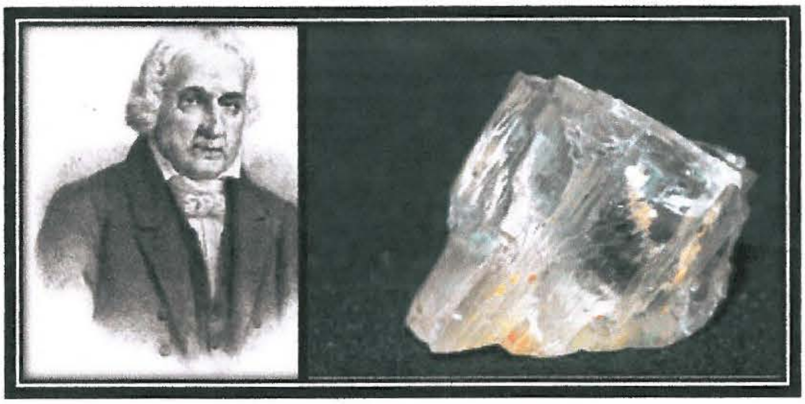
Other factors and events include the escape of the Portuguese Royal Family to Brazil , that eventually led to the founding of the Museu Nacional (National Museum) in Rio de Janeiro and the establishment of the Escola de Minas (School of Mines) in Ouro Preto , Minas Gerais.

The Portuguese Gabriel Soares de Souza (born in Portugal, 1540 and died in Bahia, 1591), in his work *"Tratado Descritivo do Brasil"*, published in 1587 made the first reports of the possible occurrence of gold, copper, iron, amethyst and garnet in the Sertão and in regions that correspond to the present State of Minas Gerais.

Father and son, both with the same name and residents of Santos (Afonso Sardinha "o Velho" , unknown date of birth and who died in 1616 and the son, called "o Moço", unknown date of birth and who died in 1604), who were experienced in mining discovered in 1589 the magnetite iron deposits in Morro de Araçoiaba, Ipanema (near present day Sorocaba in the State of São Paulo). They were also responsible for the first establishment of the first metallurgy plant in Brazil. The house of the "Sardinhas" is still preserved today and can be visited in the Parque Estadual do Pico do Jaraguá, São Paulo, a place known for gold prospecting[17].

JOSÉ BONIFÁCIO DE ANDRADA E SILVA

He is considered the "father of Brazilian mineralogy" and was born in Santos on July 13, 1763 and passed away on April 6, 1838 in Niteroi. He was the first Brazilian to describe a mineral species, petalite ($LiAlSi_4O_{10}$) while in Sweden.



José Bonifácio de Andrada e Silva (1763-1838) and a crystal of petalite

Besides being known as a notable statesman and industrial chemist he is also famous for describing three other minerals: spodumene, cryolite and scapolite . They form a group of minerals that constitute a solid solution series between marialite and meionite and were also described in Sweden.

The mineral andradite (nesosilicate) was named in his honor by the American mineralogist James Dwight Dana in 1868.

José Bonifácio, who originally studied at the University of Coimbra, Portugal, performed most of his scientific work in Europe. Upon his return to Brazil, he was mainly concerned with the governing of the country.

During his stay in Europe, he traveled widely and collaborated , worked and studied with many well known and renown scientists of the time. Among them we shall name Domenico Vandelli, Antoine François de Fourcroy, Jean-Pierre François Guillot Duhamel, René Just Haüy, Abraham Gottlob Werner, Friedrich Mohs, Friedrich Heinrich Alexander (Baron von Humboldt). Andrés Manuel Del Rio, Christian Leopold von Buch, Alessandro Volta, Peter Jacob Hjielm, Johann Gottlieb Gahn, Carl Axel Arrhenius, Peter Christian Abilgaard and Wilhelm von Eschwege. He consolidated his knwoldege in natural sciences and especially in mineralogy.[16] According to Figuerôa [18], José Bonifácio de Andrada may have not collaborated with F.H. Alexander and W. von Eschwege, for they may have not been present in Freiberg when he was there.

CONTEMPORARIES OF JOSÉ BONIFÁCIO

In 1789, the German geologists Abraham Gottlob Werner (born in Ozieczinica in 1749, died in Dresden in 1817) and Dietrich Ludwig Karsten (born in Bützow in 1768, died in Berlin in 1810) determined the first type mineral of Brazil, chrysoberyl ($BeAl_2O_4$), collected in alluvions of the region of Araçuai in Minas Gerais.

José Vieira Couto from Minas Gerais (born and died in Diamantina in 1752 and 1827, respectively) in 1798 indicated the possible occurrence of native lead, tin, diamond, copper, gold and platinum in Serro Frio, Abaeté, Diamantina (Arraial do Tijuco), Conceição do Mato Dentro and Ouro Preto (Vila Rica), all in Minas Gerais.

José de Sá Bettencourt Accioly (born in Caeté in 1754 or 1755 and died in Caeté in 1828) mentioned in 1822 the occurrence of niter (KNO_3) , specularite (a variety of hematite) and crocoite ($PbCrO_4$) in the region of Catas Altas in Minas Gerais.

The German naturalists Karl Friedrich Philipp von Martius (born in Erlangen in 1794 and died in Münich in 1868) and Johann Baptiste Ritter von Spix (born in Höchstadt an der Aisch in 1781 and died in München in 1826) related the presence of a variety of imperial topaz, ($Al_2SiO_4(F,OH)_2$)) in Vila Rica (actually Ouro Preto) in Minas Gerais and were the first scientists to visit the siderite meteorite (octahedrite I) Bendegó found in 1784 in Monte Santo, Sertão of Bahia and presently part of the municipality of Uauá. The voyage of the naturalists to Brazil was supported by the Academy of Sciences of Bavaria and had the purpose to establish botanical, zoological and mineralogical collections of the most important Mineralogical Provinces of our country. Their party was also present at the wedding of the Grand Duchess Leopoldina, who was also a very important amateur collector of minerals at the time.[19]

PERIOD AFTER JOSÉ BONIFÁCIO

Augustin Alexis Damour (born in Paris in 1808 and died also in Paris , probably in 1902) was a French mineralogist and described the second type mineral of Brazil, goyazite ($SrAl_3(PO_4)_2(OH,H_2O)_6$), found in 1894 in Lavra Ribeirão do Inferno, near Diamantina.

The Austrian petrologist, Eugen Hussak (born in Austria in 1856 and died in Caldas in 1911) with the English mineralogist George Thurland Prior (born in Oxford in 1862 and died in 1936) described in 1895 the type minerals derbylite ($Fe^{3+}Ti_3Sb^{3+}O_{13}(OH)$), tripuhyite ($Fe^{3+}Sb^{5+}O_4$), and florencite ($CeAl_3(PO_4)_2OH,H_2O)_6$), found in Tripui, Ouro Preto, Minas Gerais and senaite ($Pb(Ti,Fe,Mn)_{21}O_{3\ 8}$ found in Datas, Minas Gerais.

In 1906, E. Hussak described the type mineral of Brazil gorceixite, ($BaAl_3[PO_3(O,OH)]_2(OH)_6$), in honor of the French geologist Claude-Henri Gorceix (born and died in Saint Denis des Murs , 1842 and 1919, respectively) founder of the School of Mines and metallurgy in Ouro Preto, Minas Gerais. Besides being the first director, Gorceix also taught geology, mineralogy, chemistry and physics. His mortal remains were brought from France in 1973 and are resting in the yard of the Gorceix Museum of the Escola de Minas de Ouro Preto.

The first Brazilian to formulate a type mineral of Brazil was Professor Djalma Guimarães (born in Santa Luzia das Velhas in 1894 and died in Belo Horizonte in 1973) , who determined the mineral arrojadite in 1925, now arrojadite(KFe) ($(KNa)Fe^{2+}(Ca,Na_2)Fe^{2+})_{13}Al(PO_4)_{11}(PO_3OH)(OH)_2$), named in honor of Miguel Arrojado Ribeiro Lisboa (born in Rio de Janeiro in 1872 and died in the same city in 1932). He studied mining engineering and geology at the Escola de Minas de Ouro Preto , was General Inspector of Public Works against Drought (Inspetoria de Obras Contra as Secas-IOCS) established in 1909, studied the geology of North-Eastern Brazil as well as the geology of Western São Paulo and Eastern Mato Grosso and played an important role in the mining industry of Brazil.

During the last ten years (2003 to 2013), twenty three (23) type minerals from Brazil were approved by the *Commission on New Minerals, Nomenclature and Classification (CNMNC)* of the *International Mineralogical Association (IMA).* This corresponds to 2,2 minerals per year. From 1959 to 2002, seventeen (17) new minerals were approved, corresponding to 0,33 minerals per year. (See Table I).

The 23 new minerals are coutinhoite[20], lindbergite[21], atencioite[6], oxykinoshitalite[22], arrojadite (PbFe)[25], ruifrancoite[2], matioliite[24], menezesite[3], guimarãesite[26], brumadoite[4], qingheiite-(Fe^{2+})[9], bendadaite[7], manganoeudialyte[8], hidroxycalcioromeite[5], jacutingaite[11], uvite[10], carlosbarbosaite[27], **fluor-elbaite**[12], hydrokenomicrolite[13], fluorcalciomicrolite[14], pauloabibite[42] and almeidaite[42], **besides fluoronatromicrolite [28] that was approved in 1998, but published only in 2011.**

Other factors and events related to new minerals in Brazil happened during this period. In 2003 two new names for Brazilian minerals (waimirite and atroarite) were introduced in the literature without the approval of IMA[29]. The type mineral of Brazil arrojadite became a group of minerals in 2005[25].

The minerals giannettite and lewisite were officially discredited as being identical to hainite and romeite with Ti, respectively[30]. Recently, with the approval of IMA a new system of nomenclature was published for the super group of pyrochlore . Many species pertaining to this supergroup are presently under study[5].

Acoording to Smith[31], there are only three compilations about Brazilian minerals (Ferraz[32],Fróes Abreu[33] and Franco et al.[34]) and one about minerals from the State of São Paulo (Knecht)[35]. None of these has been updated.

TABLE I. LIST OF TYPE MINERALS FROM BRAZIL (1789-2013).

Year	Mineral	Author(s)
1789	Chrysoberyl	D. L. G. Karsten
1792	Euclase	R. J. Haüy
1803	Palladium	W. H. Wollaston
1853	Joseite	A. Kengott
1884	Goyazite	A. Damour
1895	Derbylite	E. Hussak; G. T. Prior
1897	Tripuhyite	E. Hussak; G. T. Prior
1898	Senaite	E. Hussak; G. T. Prior
1899	Florencite-(Ce)	E. Hussak; G. T. Prior
1906	Gorceixite	E. Hussak
1945	Brazilianite	F. H. Pough; E. P. Henderson
1947	Souzalite	W. T. Pecora; J. J. Fahey
1947	Scorzalite	W. T. Pecora; J. J. Fahey
1949	Frondelite	M. L. Lindberg
1953	Faheyite	M. L. Lindberg; K. J. Murata
1953	Moraesite	M. L. Lindberg; W. T. Pecora; A. L. Barbosa
1954	Barbosalite	M. L. Lindberg; W. T. Pecora
1954	Tavorite	M. L. Lindberg; W. T. Pecora
1955	Arsenopalladinite	F. A. Bannister; G. F. Claringbull; M. H. Hey
1974	Tantalaeschynite-(Y)	M. S. Adusumilli; C. Kieft; E. A. J. Burke
1974	Atheneite	A. M. Clark; A. J. Criddle; E. E. Fejer
1974	Isomertieite	A. M. Clark; A. J. Criddle; E. E. Fejer
1976	Bahianite	P. B. Moore; T. Iraki
1977	Palladseite	R. J. Davis; A. M. Clark; A. J. Criddle
1978	Whiteite-(CaFeMg)	P. B. Moore; J. Ito
1978	Whiteite-(MnFeMg)	P. B. Moore; J. Ito
1980	Lantanite-(Nd)	A. C. Roberts; G. Y. Chao; F. Cesbron
1986	Minasgeraisite-(Y)	E. E. Foord; R. V. Gaines; J. G. Crock; W. B. Simmons Jr.; C. P. Barbosa
1986	Parabariomicrolite	T. S. Ercit; F. C. Hawthorne; P. Cerny
1988	Lantanite-(La)	E. H. Nickel; J. A. Mandarino
1990	Arupite	V. F. Buchwald
1990	Zanazziite	P. B. Leavens; J. S. White; J. A. Nelen
1994	Yanomamite	N. F. Botelho; G. Roger; F.d'Yvoire; Y. Moëlo; M. Volfinger

1997	Quintinite	G. Y. Chao; R. A. Gault
2000	Dukeite	J. A. R. Stirling; A. C. Roberts; P. C. Burns; A. J. Criddle; M. N. Feinglos
2000	Serrabrancaite	Th. Witzke; R. Wegner; Th. Doering; H. Pöllmann; W. Schukmann
2004	Coutinhoite	D. Atencio; F. M. S. Carvalho; P. A. Matioli
2004	Lindbergite	D. Atencio; J. M. V. Coutinho; S. Graeser; P. A. Matioli; L. A. D. Menezes Filho
2005	Oxykinoshitalite	L. N. Kogarko; Yu. A. Uvarova; E. Sokolova; F. C. Hawthorne; L. Ottolini; J. D. Grice
2006	Atencioite	N. V. Chukanov; R. K. Rastsvetaeva; St. Möckel; A. E. Zadov; L. A. Levitskaya
2006	Kalungaite	N. F. Botelho; M. A. Moura; R. C. Peterson; C. J. Stanley; D. V. G. Silva
2006	Matioliite	D. Atencio; J. M. V. Coutinho; Y. P. Mascarenhas; J. A. Ellena
2006	Arrojadite-(PbFe)	C. Chopin; R. Oberti; F. Cámara.
2007	Guimarãesite	N. Chukanov; D. Atencio; A. E. Zadov; L. A. D. Menezes Filho; J. M. V. Coutinho
2007	Ruifrancoite	D. Atencio; N. V. Chukanov; J. M. V. Coutinho; L. A. D. Menezes Filho; V. T. Dubinchuk; St. Möckel
2008	Menezesite	D. Atencio; J. M. V. Coutinho; A. C. Doriguetto; Y. P. Mascarenhas; J. A. Ellena; V. C. Ferrari
2008	Brumadoite	D. Atencio; A. C. Roberts; P. A. Matioli; J. A. R. Stirling; K. E. Venance; W. Doherty; C. J. Stanley; R. Rowe; G. J. C. Carpenter; J. M. V. Coutinho
2010	Qingheite-(Fe^{2+})	F. Hatert; M. Baijot; S. Philippo; J. Wouters
2010	Bendadaite	U. Kolitsch; D. Atencio; N. V. Chukanov; N. V. Zubkova; L. A. D. Menezes Filho; J. M. V. Coutinho; W. D. Birch; J. Schlüter; D. Pohl; A. R. Kampf; I. M. Steele; G. Favreau; L. Nasdala; G. Giester; D. Yu. Pucharovsky

2010	Manganoeudialyte	S. F. Nomura; D. Atencio; N. V. Chukanov; R. K. Rastsvetaeva; J. M. V. Coutinho; T. K. Karipidis
2010	Uvite	C. M. Clark; F. C. Hawthorne; J. D. Grice
2010	Hydroxicalcioromeite	D. Atencio; M. B. Andrade; A. G. Christy; R. Gieré; P. M. Katarshov
2011	Carlos barbosalite	D. Atencio; A. C. Roberts; M. A. Cooper; L. A. de Menezes Filho; J. M. V. Coutinho; J. A. R. Stirling; N. A. Ball; E. Moffatt; M. L. S. C. Chaves; P. R. G. Brandão; A. W. Romano
2011	Jacutingaite	A. Vylamazová; F. Laufek; M. Drábek; A. R. Cabral; J. Haloda; T. Sidorinová; B. Lehmann; H. F. Galbiatti; J. Drahokoupil
2011	Fluornatromicrolite	Th. Witzke; M. Steins; T. Doering; W. Schukmann; R. Wegner; H. Pöllmann
2011	Fluorelbaite	F. Bosi; G. B. Andreozzi; H. Skogby; A. Lussier; N. A. Ball; F. C. Hawthorne
2012	Hydrokenomicrolite	F. C. Hawthorne
2012	Fluorcalciomicrolite	M. B. Andrade, D. Atencio, N. V. Chukanov, J. Ellena
2013	Pauloabibite	M. B. Andrade; D. Atencio; H. Yang; T. Downs; A. I. C Persiano; J. Ellena
2013	Almeidaite	D. Atencio

One can add some articles : Oliveira[36], Leonardos[1c] and Franco[14].

The book by Atencio represents an update of the subject[2a].

Before the establishment of the Commission for New Minerals and Names of Minerals (today CNMNC) of the International Mineralogical Association (IMA) in 1958, more than eighty names of new minerals were attributed to species from Brazil. Only nineteen (19) can really be considered type minerals from Brazil valid today, namely arsenopalladinite, barbosalite, brazilianite, chrysoberyl, derbylite, euclase, faheyite, florencite-(Ce), frondelite, gorceixite, goyazite, joseite, moraesite, palladium, scorzalite, senaite, souzalite, tavorite and tripuhyite.

After the establishment of CNMMN-IMA , the description of staringite, tantalaeschynite-(Y), atheneite, isomertieite, bahianite, palladseite, whiteite-(CaFeMg), whiteite-(MnFeMg), lantanite-(Nd), minasgeraisite-(Y), parabariomicrolite, zanazziite, arupite, yanomamite, quintinite, dukeite, serrabrancaite, fluornatromicrolite, coutinhoite, lindbergite, oxykinoshitalite, atencioite, kalungaite, matioliite. menezesite, arrojadite-(PbFe), ruifrancoite guimarãesite (new definition), bendadaite, qingheiite-(Fe^{2+}), brumadoite, manganoeudialyte, hydroxicalcioromeite, carlosbarbosaite, uvite, jacutingaite, fluorelbaite, hydrokenomicrolite and fluorcalciomicrolite were approved by the CNMMN-IMA. A redefinition of arsenopalladinite was published in 1974 With the approval of CNMMN-IMA, the mineral staringite was officially discredited in 1992.

The name lipscombite was first used for a synthetic material. The mineral, "lipscombite with Mn", described by Lindberg[37] in the Sapucaia pegmatite from Galileia, Minas Gerais and considered a type species, appears to be a different species with Mn or Fe^{3+} predominating over Fe^{2+}. X-ray diffraction patterns are practically identical, but the chemical results are very poor and an adequate formula can not be obtained. Today a lipscombite type is considered to be a material from the Otov pegmatite, near Domazlice, Bohemia, Czech Republic, described by Czech et al[38].

The name pseudorutile (1966) was introduced without official approval for a mineral that occurs in many places, including Brazil , was disaccredited and eventually officially revalidated in 1994 for a species from South Australia.

There is a large number of mineral species from Brazil that were introduced without official justification and include a wide variety of minerals

such as tantalaeschynite-(Ce) (1968), ferrohalotrichite (1969), trautite (1971) ibitiarite (1975), coutinhite (1981), neodymite (1981) and heitorite (1991).

Another example are the minerals of the pyrochlore group rijkeboerite (1963) and djalmaite (1939) that were scrutinized by Atencio et al[5].

The important minerals investigated and studied in Brazil are the type minerals listed in Table I. An important work "*Enciclopédia dos Minerais do Brasil*" by P.C.P. das Neves and D. Atencio was launched in 2013 (Reference 1f) and is highly recommended for those interested in Brazilian Mineralogy.

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