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of Science Frontier Research: B

Chemistry

Solid State Reactions

Designed to Bind Herbicides

Highlights

Novel Calix[4] Arene

Aqueous DMSO Medium

Discovering Thoughts, Inventing Future

VOLUME 15 ISSUE 4 VERSION 1.0

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Phytochemical Evaluation of Phytochemicals of *Cassia Podocarpa*

By Adewole E
AFE Babalola University, ADO-EKITI (ABUAD), Nigeria

Abstract- The usefulness of *cassia podocarpa* as locally antifungal agent necessitated the qualitative and quantitative determination of the phytochemicals present.The screening of the leaf and flower showed the presence of flavonoid, tannin, saponin, alkaloid and glycoside. The quantitative analysis showed that the flavonoid in the leaf (6.73 mg/g)was more than that of the flower (5.83mg/g). Also, the tannin in the leaf (10.11mg/g) doubled that of the flower (5.24mg/g).The saponin content in the leaf (27.36mg/g) was higher than that of the flower (13.91mg/g). The alkaloid content in the leaf (19.70mg/g) was more than that of the flower (6.59mg/g). However the glycoside of leaf (7.10mg/g) was just little bit higher than that of flower (6.32mg/g). From the quantitative evaluation of the leaf and flower of this plant, this has really confirmed the local use in the treatment of eczema in human body when the liquid is being extracted and the plant is a reservoir of many novel compounds which can be of immense use to the pharmaceutical world.

Keywords: *cassia podocarpa, qualitative, quantitative, reservoir.*

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Phytochemical Evaluation of Phytochemicals of *Cassia Podocarpa*

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Keywords: cassia podocarpa, qualitative, quantitative, reservoir.

I. Introduction

The pharmacological usefulness of plants are known to us all because the variety of plants is a treasure house of potential drugs and in the recent years, researchers have beam their search light on plants that have medicinal activities. Medicinal plants contain some organic compounds that have pharmaceutical benefits to human being and these compounds include flavonoids, tannin, saponin, alkaloids (Edoga, 2005 and Mann, 1978) and host of others. A large number of phytochemicals that belong to different chemical classes have been shown to have inhibitory effects on all types of microorganisms in vitro (Cowan, 1999).

Products from plants have been part of phytomedicines since and this can be obtained from barks, leaves, flowers, roots, fruits, seed (Criag, 2001). Knowledge of the chemical contents of plants is desirable because such useful information will be valuable for the synthesis of novel compounds.

In this research work, both qualitative and quantitative phytochemical analysis were carried out on cassia podocarpa collected at the back of a house in Ajilosun area of Ado-Ekiti, Nigeria.

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II. Methodology

a) Phytochemical screening

i. *Test for saponins*

Crude extract was mixed with 5ml of distilled water in a test tube and it was shaken vigorously. The formation of stable foam was taken as an indication for the presence of saponins.

ii. *Test for glycosides*

Keller-kilani test

Crude extract was mixed with 2ml of glacial acetic acid containing 1-2 drops of 2% solution of $FeCl_3$. The mixture was then poured into another test tube containing 2ml of concentrated H_2SO_4. A brown ring at the interphase indicated the presence of cardiac glycosides.

iii. *Test for alkaloids*

Crude extract was mixed with 2ml of 1% HCl and heated gently. Mayer's And Wagner's reagents were then added to the mixture. Turbidity of the resulting precipitate was taken as evidence for the presence of alkaloids.

iv. *Test for flavonoids*

Alkaline reagent test

Crude extract was mixed with 2ml of 2% solution of NaOH. An intense yellow colour was formed which turned colourless on addition of few drops of diluted acid which indicated the presence of flavonoids.

v. *Test for tannins*

Crude extract was mixed with 2ml of 2% solution of $FeCl_3$. A blue-green or black coloration indicated the presence of tannins.

III. Quantitative Analysis

a) Tannin determination

0.2g of finely ground sample was weighed into a 50ml sample bottle. 10ml of 70% aqueous acetone was added and properly covered. The bottle were put in an ice bath shaker and shaken for 2hours at 30^0C .Each solution was then centrifuge and the supernatant store in ice. 0.2ml of each solution was pipetted into the test tube and 0.8ml of distilled water was added. Standard tannin acid solutions were prepared from a 0.5mg/ml of the stock and the solution made up to 1ml with distilled water. 0.5ml of Folinciocateau reagent was added to both sample and standard followed by 2.5ml of 20%

Na_2CO_3 the solution were then vortexed and allow to incubate for 40minutes at room temperature, its absorbance was read at 725nm against a reagent blank concentration of the same solution from a standard tannic acid curve was prepared (Makkar and Goodchild. 1996).

b) Saponin determination

The spectrophotometric method of Brunner (1994) will used for Saponindetermination. 2g of the finely grinded sample was weighed into a 250ml beaker and 100ml of Isobutyl alcohol was added. Shaker was used to shake the mixture for 5hours to ensure uniform mixing. The mixture was filtered with No 1 Whatman filter paper into 100ml beaker containing 20ml of 40% saturated solution of magnesium carbonate ($MgCO_3$). The mixture obtain again was filter though No 1 Whatman filter paper to obtain a clean colourless solution. 1ml of the colourless solution was taken into 50ml volumetric flask using pipette, 2ml of 5% iron (iii) chloride ($FeCl_3$) solution was added and made up to the mark with distill water. It was allowed to stand for 30minutes for the colour to develop. The absorbance was read against the blank at 380nm.

c) Alkaloid determination

5g of the sample was weighed into a 250ml beaker and 200ml of 10% acetic acid in ethanol was added and allowed to stand for 4min. This was filtered and extract was concentrated on a water bath to one quarter of the original volume. Concentrated ammonium hydroxide added drop wise to the extract until the precipitation was completed. The whole solution was allowed to settle and the precipitated was collected and washed with dilute ammonium hydroxide and then filtered. The residue is then alkaloid which was dried and weighed. Harbone(1973).

$$\%alkaloid = \frac{W_3 - W_2}{W_1} \times 100$$

d) Cardiac glycoside determination

The procedure described by Sofowora (1995) was used 10ml the extract pipetted into a 250ml conical flask. 50ml chloroform was added and shaken on vortex mixer for 1hour. The mixture was filtered into 100ml conical flask. 10ml of pyridine and 2ml of 29% of sodium nitroprusside were added and shaken thoroughly for 10min. 3ml of 20% NaOH was added to develop a brownish yellow colour. Glycosides standard (Digitoxin). A concentration which range from 0 – 50mg/ml were prepared from stock solution the absorbance was read at 510nm.

e) Total flavonoid content

Aluminium chloride colorimetric method was used with some modifications to determine flavonoid content. 1ml of sample plant extract was mixed with 3ml of methanol, 0.2ml of 10% aluminium chloride, 0.2ml of 1M potassium acetate and 5.6ml of distilled water and remains at room temperature for 30 minutes. The absorbance was measured at 420nm. Quercetin was used as standard (1mg/ml). All the tests were performed in triplicates. Flavonoid contents were determined from the standard curve and were expressed as quercetin equivalent (mg/g of extracted compound) (Aiyegroro, 2010).

IV. Results

Table 1: showing phytochemical screening of *cassia podocarpa*

Part of the plant	Flavonoid	Alkaloid	Saponin	Tannin	Cardiac Glycoside
Leaf	+	+	+	+	+
Flower	+	+	+	+	+

V. Statistical Analysis

This was done using T-test (Package =R studio)

Data 1: FLAVONOID (Leaf)and FLAVONOID (Flower)
t –test = 11.9333, degree of freedom = 1, probability -value = 0.05322
Alternative hypothesis: True Difference in Means is not equal to 0
95 percent confidence interval: -0.05796536(leaf) : 1.847965369 (flower)
Sample Estimates:
Mean (leaf) : mean (flower) : 6.730mg/g : 5.835mg/g

Data 2: TANIN (Leaf) and TANIN (Flower)
t-test = 235.4743, degree of freedom = 1.145, probability -value = 0.001266
Alternative Hypothesis: True Difference in means is not equal to 0
95 percent confidence interval: 4.682361(leaf): 5.074509 (flower)
Sample Estimates:
Mean (leaf): Mean (flower): 10.11843mg/g: 5.24000mg/g

Data 3: SAPONIN (Leaf) and SAPONIN (Flower)
t-test = 35.0566, degree of freedom = 2, probability -value = 0.0008132
Alternative Hypothesis: True Difference in Means is not equal to 0
95 percent confidence interval: 11.80225(leaf): 15.10502 (flower)
Sample Estimates:

Mean (leaf): Mean (flower) 27.36364mg/g: 13.91000mg/g

Data 4: ALKALOID (Leaf) and ALKALOID (Flower)
t-test= 36.0159, degree of freedom = 1.162, probability -value = 0.01028
Alternative Hypothesis: True Difference in means is not equal to 0
95 percent confidence interval: 9.762957 (leaf): 16.457043 (flower)
sample estimates:
Mean (leaf): Mean (flower) 19.70mg/g : 6.59mg/g

Data 5: GLYCOSIDE (Leaf) and GLYCOSIDE (Flower)
t –test = 26.1119, degree of freedom = 1, probability -value = 0.02437
Alternative Hypothesis: True Difference in means is not equal to 0
95 percent confidence interval: 0.4021699(leaf): 1.1645421(flower)
Sample Estimates:
Mean (leaf): Mean (flower) 7.103356 mg/g: 6.320000mg/g

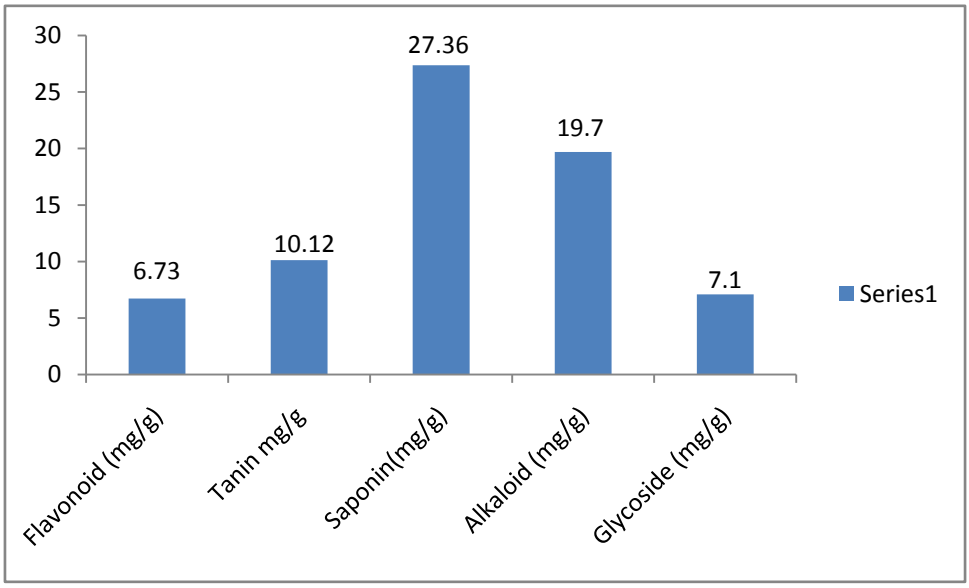

Figure 1 : showing graph of the mean values of phytochemicals of leaf

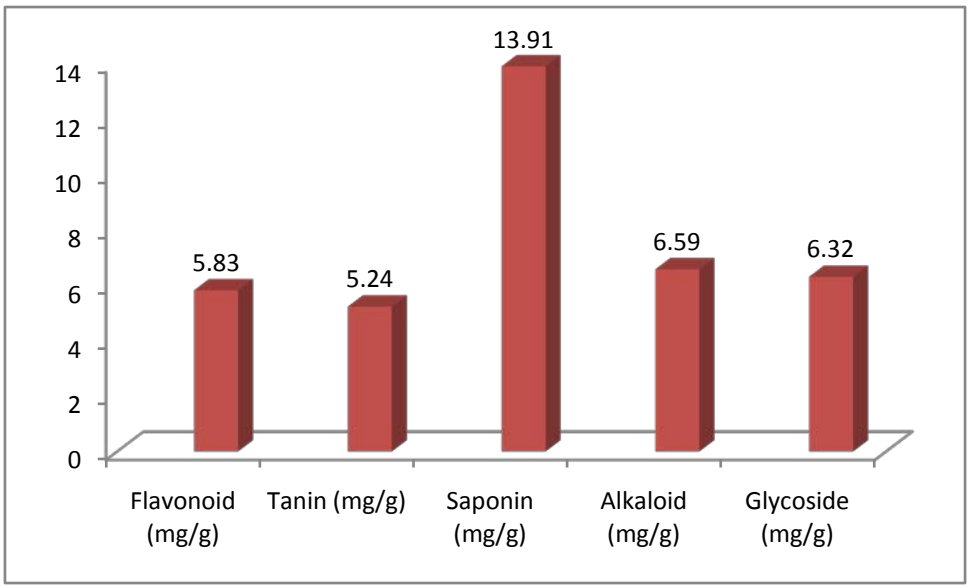

Figure 2 : showing graph of the mean values of phytochemicals of flower

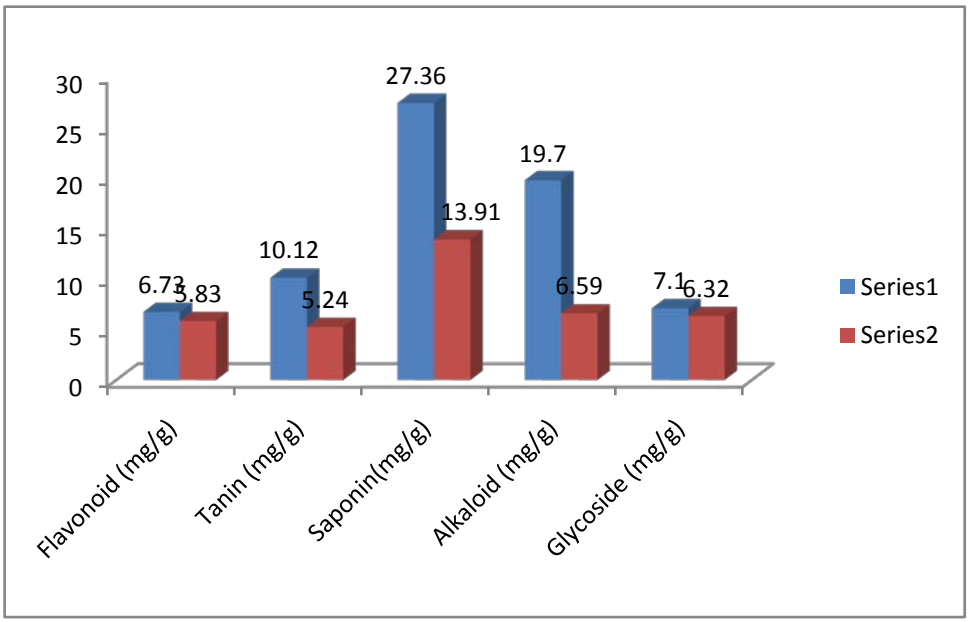

Figure 3 : showing comparisms of the mean of phytochemicals of leaf and flower

VI. Discussion

Phytochemical analysis carried out on the *cassia podocarpa* ethanolic extract showed presence of constituents; flavonoid, tannin, saponin, alkaloid and glycoside which are known to exhibit medicinal and pharmacological activities. From the analysis, it showed that flavonoid content in the leaf (6.73mg/g) was more than that of flower (5.83mg/g). Also, the leaf had more tannin (10.12mg/g) than the flower (5.24mg/g). The saponin content of the leaf (27.36mg/g) was more than the flower (13.91mg/g).Alkaloid content of the leaf (19.70mg/g) was higher than that of flower (6.59mg/g). The Cardiac glycoside in the leaf (7.10mg/g) was higher than the flower content (6.32mg/g). However, the presence of these metabolites is an indication that the plant both the leaf and the flower is a reservoir of novel and lead compounds. Tanninbind to proline rich protein and interfere with protein synthesis. Saponin was higher in the leaf, it has been reported that saponins are known to produce inhibitory effect on inflammation (Just *et al,* 1998). Saponin has the ability to precipitate and coagulate the red blood cells. Alkaloids have also been associated with medicinal uses and one of their common biological properties is cytotoxicity (Nobori *et al*, 1994). Many workers have reported the anagelsic (Antherden, 1969; Harborne, 1973), antispasmodic and antibacterial properties of alkaloid (Stray, 1998; Okwu, 2004).The analysis results have shown that the plant *cassia podocarpa* has identified phytochemical compounds which may be the bioactive constituents. If the plant is subjected to very intense research, novel and lead bioactive compounds may be isolated, characterized using various techniques such as NMR, Mass -spectrophotometer, IR and novel compounds may be revealed.

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Synthesis and Characterization of Polyimide Thin Films by Thermal Evaporation and Solid State Reactions

By Ikram Atta AL-Ajaj & Aseel A. Kareem

University of Baghdad, Iraq

Abstract- In this research we describe the preparation of polyimide with pyromellitic dianhydride (PMDA) and *p*-phenylene diamine (PDA) thin films by physical vapor deposition. For this study, FTIR Spectrometer has been used to measure the effect of imidization temperature on the chemical structure of vapor-deposited thin films of the aromatic PI. When temperature increases, a general increase in all the absorption peaks is observed. This suggests that residual PAA monomers continue to be converted into PI. The surface topology of the PI films was further examined by using AFM atomic force microscopy as a function of the imidization temperature at 150,200,250°C for 1 hour each, it can be clearly seen that the surface became rougher with increasing imidization temperature.

The thermal stability of polyimide was also improved by using Thermo gravimetric analysis (TGA).

Keywords: polyimide thin films, thermal imidization temperature, thermal evaporation, polycondensation reactions.

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I. Introduction

Polyimides are one of the most important classes of high temperature polymers available today. They find wide spread application due to the wide range of chemistry and properties accessible [1]. Innovative polyimide design has led to their use in aerospace, microelectronics, automotive and packaging industries [2]. Polyimides have become important materials in the manufacture of a large number of technical products, e.g. varnishes, coatings etc, due to their excellent thermal stability and mechanical strength, high stability to ionizing, good film forming ability, and superior chemical resistance [3]. Since the excellent properties of polyimides are a result of combination of both chemical structure and final morphology of the products, it is important to understand the structural evolution within the material during imidization process, which directly affects the final thermal, mechanical and optical properties [4]. Polyimides are step or condensation polymers derived from both aliphatic or aromatic dianhydrides and diamines[5].

In this research polyimide films prepared by the vapor deposition, which are prepared by the reaction of a dianhydride and diamine mixture, which by solid state reactions is converted to polyimide by thermal treatment usually below 300°C.

Vapor deposition of the precursors and solid state reactions of imidization are of a greater priority than the spin coating and dipping methods.

The physical vapor deposition as a "dry" method provides high purity for producing thin polymer films of controlled thickness, ratio of precursors and composition control of the so prepared layers [6]. The aim of the present work is to study, FTIR Spectrometer has been used to measure the effect of imidization temperature on the chemical structure of vapor-deposited thin films of the aromatic PI PMDA–PDA. AFM has been used to elucidate the effect of heating subsequent to imidization of PI.

Thermal degradation processes were also investigated through dynamic thermogravimetric analysis at different heating rates.

II. Polyimide Synthesization

Polyimide is synthesized by a two-step reaction, as shown in Fig. 2. In this work, pyromellitic dianhydride (PMDA) and p-phenylene diamine (PDA), which are commercially available from Sigma-Aldrich. These two monomers, 2 gm each, were evaporated from two separated boats to form a poly(amic acid) (PAA) thin film on substrate. The substrates used were silicon wafer and glass.The deposition process began at vacuum of 2 X 10^{-5} mbar. Figure 1 shows the scheme of the PVD apparatus. The resultant polyamic acid PAA film was then soft baked to remove nH_2O from the substrate followed by a thermal treatment at (150, 200 and 250°C) for 1 hour each in an air circulating oven.

In the case of PI the purpose of the thermal treatment is the run of polycondensation reactions in solid state till completion of the PI formation. As a consequence of these reactions leading to a release of water and imidization also a certain pack of the layer is achieved. The final thickness of films is 5±0.1 μm.

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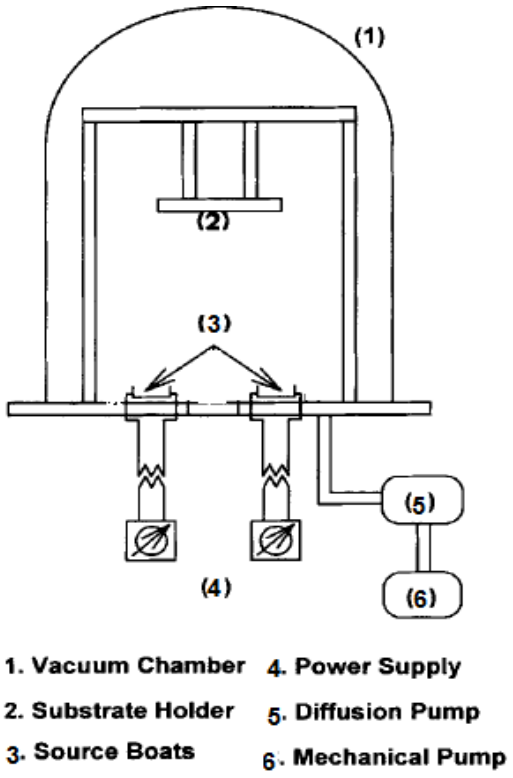

Figure 1 : schematic illustration of the PVD chamber

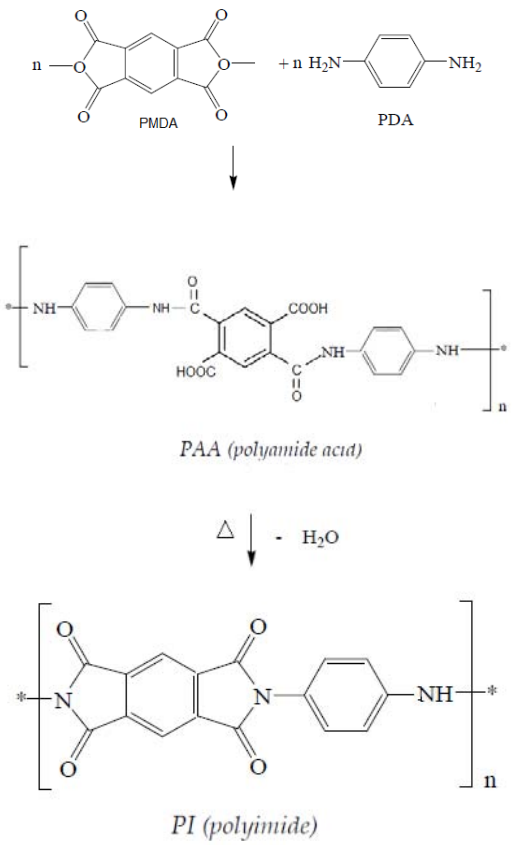

Figure 2 : Synthesis of Polyimide in two steps

III. Results and Discussions

a) FTIR Analysis

FTIR measurements have been performed for different imidization temperatures to determine the completion of the imidization reaction of the polyimide films. This analysis rests on the transmission peak magnitude changes in the functional groups or in the characteristic linkages during the reaction. Figure 3 shows the changes in FTIR spectra of PMDA-PDA for different imidization temperatures(150, 200 and 250°C) for 1 hour each.

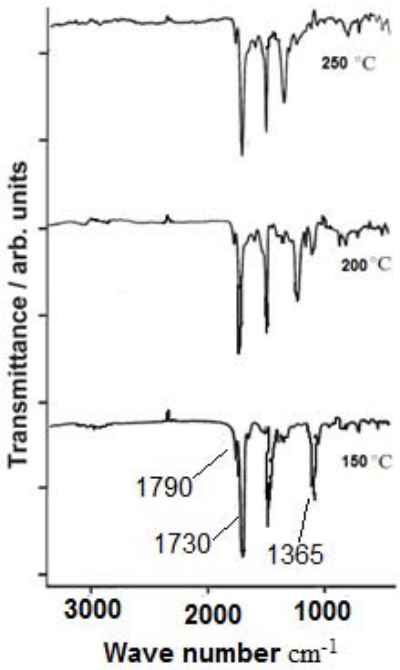

Figure 3 : FTIR spectra of PMDA-PDA for different imidization temperature

When temperature increases, a general increase in all the absorption peaks is observed. This suggests that residual PAA monomers continue to be converted into PI. This evolution is stabilized after exposure to temperature above 250°C[3,7].

Spectra have been normalized to the classical aromatic ring C=C absorption band appearing around 1500 cm^{-1}, and the absorption peak at 1365 cm^{-1} (C-N) stretching vibration of imide ring was monitored during the curing from PAA to PI. The absorption peaks at 1790 cm-1 and 1730 cm^{-1} indicated that there was asymmetry and symmetric stretching vibration of C=O bondings. The absorption peak at 710 cm^{-1} was the flexural vibration of C=O bonds. [8,9].

b) Atomic Force Microscopy (AFM)

The AFM analysis also provides information on the changes in the surface morphology and roughness introduced by the heat treatment. Fig. 4 shows the AFM

topographic images of the polyimide films and those subjected to imidization temperature150, 200 and 250°C for 1 hour each.

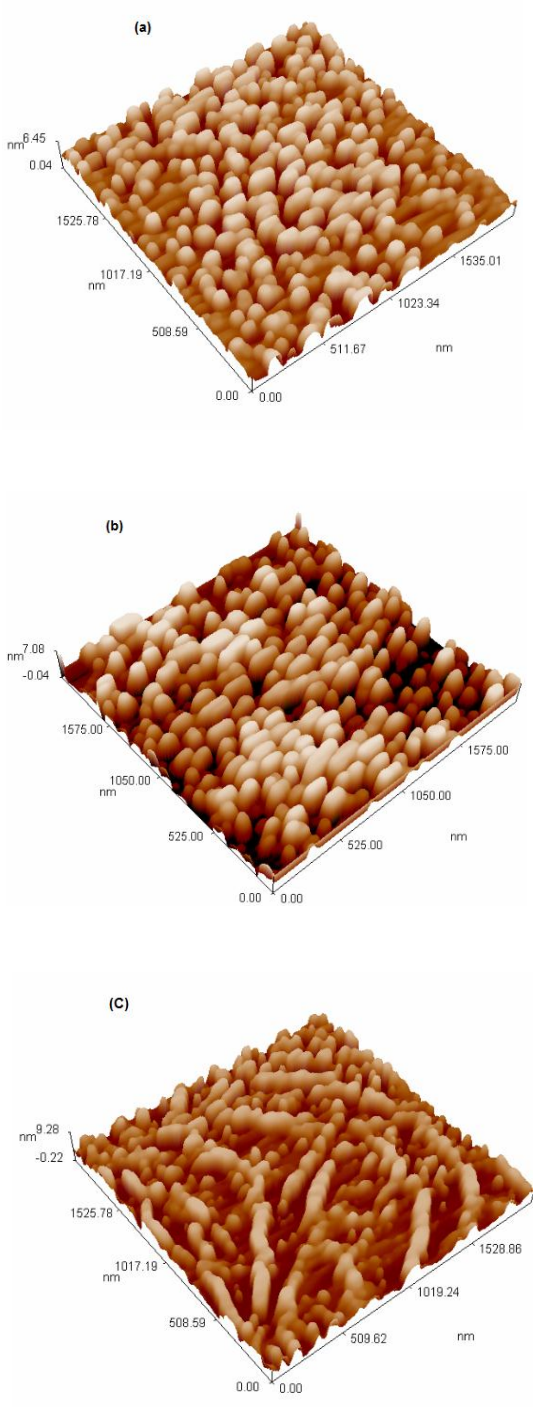

Figure 4 : 3-D AFM images PI thin films The respective imidization temperatures from (a) to (c) are 150, 200 and 250°C

It can be clearly seen that the surface became rougher with increasing imidization temperature, creating a distinctive surface structure[10]. This indicates that films of PAA and fully cured PI have comparable roughness and thickness uniformity; i.e. curing does significantly roughen the surface for the conditions used in this work.

The surface topology of the PI films was further examined by using AFM. nodular aggregates are aligned in several row[11]. Moreover, the area of the dark spots, indicating the troughs on the surface increased when the imidization temperature increase, for instance, some kind of decomposition occurs at the elevated temperatures before the imide chain decomposition [6,12].

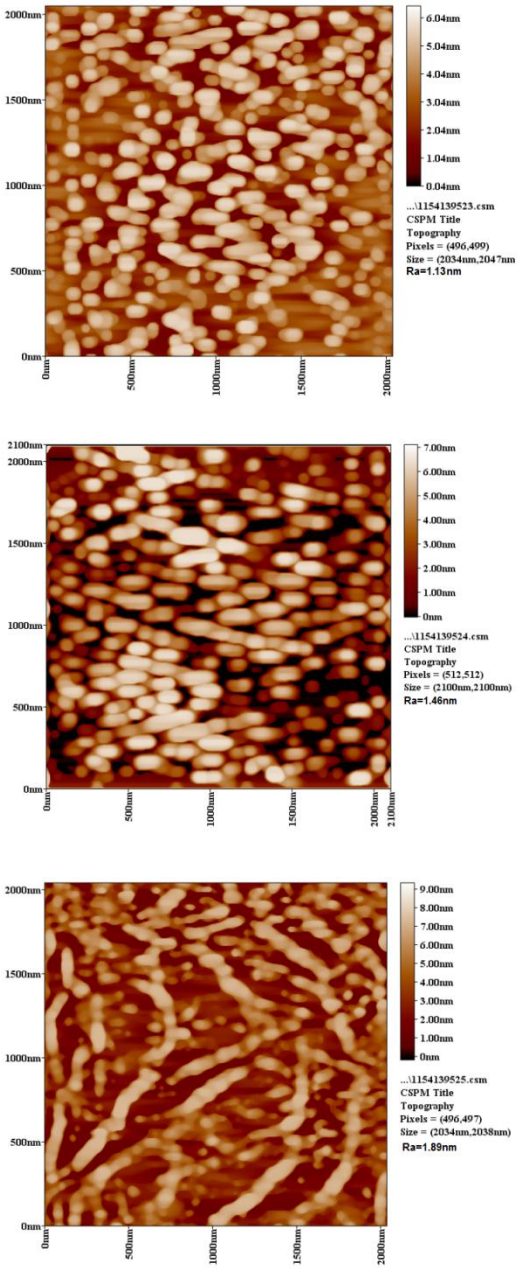

Figure 5 : 2-D AFM images PI thin films The respective imidization temperatures from (a) to (c) are 150,200 and 250°C

c) *Thermal Stability*

Figure 6 showed the weight loss of the PI with temperature at a heating rate of 10℃ /min as measured by TGA in air

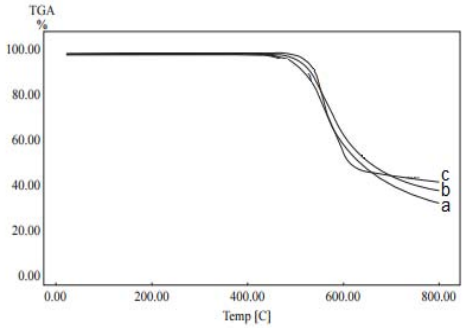

Figure 6 : TGA curves of PI thin films The respective imidization temperatures from (a) to (c) are 150,200 and 250°C

The three curves in the figure indicate the thermal stability of PI which had a thermal imidization temperature at 150℃, 200℃ and 250 ℃ for a,b and c respectively

It can be observed from Figure 6 that the temperature, at which weight loss of occurred, 490℃, 520℃ and 542℃ for PI-a, PI-b and PI-c respectively, a continuous weight loss in the initial stage may be attributed to the evaporation of the preabsorbed water and solvent in the film[9]. It was also found that the temperature of thermal weight loss of was raised with the increasing of thermal imidization temperature of PAA. weight loss becomes more marked, indicating the occurrence of imidization.

The result implied that imidization temperature had a significant influence on thermal weight loss [13,14]. At above 580oC, the sample starts to decompose drastically. For the conventional film, as shown in Figure 6, the rapid weight loss at above 490°C may result from ongoing solvent evaporation and imidization. until decomposition takes place at 585°C[4,15].

IV. Conclusions

In this research polyimide films prepared by the vapor deposition, which are prepared by the reaction of a PMDA-p-PDA mixture, which by solid state reactions is converted to polyimide by different imidization temperature . When temperature increases, a general increase in all the absorption peaks is observed by FTIR. The AFM analysis also provides information on the changes in the surface morphology and roughness introduced by the heat treatment. The thermal stability of polyimide was also improved .The thermal properties of all polyimides were varied, depending on the structure of the monomer and following the stiffness of the polymer backbones makes the polymer thermally stable with increased solubility.

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Studies on the Kinetics and Mechanism of Oxidation of Nitrones by Pyrazolinium Dichromate in Aqueous DMSO Medium

By M. Sekar, A. Santhi, J. Venkatesan & V. Thanikachalam

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Abstract- The kinetics and mechanism of oxidation of N, α- diphenylnitrones by some substituted nitrones by Pyrazolinium dichromateyielding benzaldehyde and nitrosobenzene in aqueous dimethyl sulphoxidemedium have been investigated. First order dependence with respect to both [PyDC] and [NO]. The compound was prepared and purity of the oxidant was estimated by iodometric method. The reaction is fractional order with respect to $[H^+]$. Electron-releasing substituents increase the rate of the reaction and electron withdrawing substituents decrease the rate of the reaction. No polymerisation observed with acrylamide ruling out a free radical mechanism. There was no discernible effect with increasing in ionic strength but the rate of oxidation decreased with decreasing dielectric constant of the medium. Addition of $MnSO_4$ had a significant and acrylonitrile no effect on the reaction rate.

Keywords: N, α- diphenylnitrones, pyrazolinium dichromate, kinetics, isokinetic plot, entropy, enthalpy and rate constants.

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M. Sekar [α], A. Santhi [σ], J. Venkatesan [ρ] & V. Thanikachalam [ω]

Abstract- The kinetics and mechanism of oxidation of N, α- diphenylnitrones by some substituted nitrones by Pyrazolinium dichromateyielding benzaldehyde and nitrosobenzene in aqueous dimethyl sulphoxidemedium have been investigated. First order dependence with respect to both [PyDC] and [NO]. The compound was prepared and purity of the oxidant was estimated by iodometric method. The reaction is fractional order with respect to [H^+]. Electron-releasing substituents increase the rate of the reaction and electron withdrawing substituents decrease the rate of the reaction. No polymerisation observed with acrylamide ruling out a free radical mechanism. There was no discernible effect with increasing in ionic strength but the rate of oxidation decreased with decreasing dielectric constant of the medium. Addition of $MnSO_4$ had a significant and acrylonitrile no effect on the reaction rate. A mechanism involving protonated nitrone and PyDC as the reactive oxidant is proposed. The mechanism proposed and the derived rate laws are conformity with the observed results. The activation parameters were calculated and are presented.

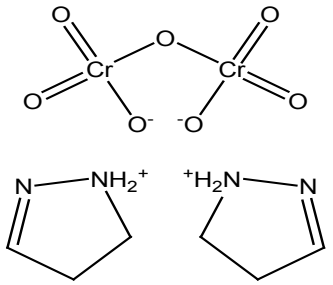
Keywords: N, α- diphenylnitrones, pyrazolinium dichromate, kinetics, isokinetic plot, entropy, enthalpy and rate constants.

I. Introduction

The kinetics and oxidation of mono substituted N,α-diphenylnitronesby Pyrazolinium dichromateto yield the corresponding aldehyde and nitrosobenzene have been studied. The reaction is first order with respect to the nitrone and PyDC. The reaction is negative reaction constants. The reaction is catalysed by the acid and the order with respect to acid is fractional. The effect of temperature, solvent composition and oxalic acid were studied and activation parameters are evaluated. Probable mechanism was discussed.

The kinetics and mechanistic studies of oxidation of great variety of organic compounds by PyDC [1-2]. There is no indication of any unusual effectiveness, utility, or advantage to be gained by the use of pyridinium dichromate as a discrete oxidizing species [3]. The kinetics of oxidation of nitrones as a substrate is reported earlier [4-8]. The present paper describes the kinetics of oxidation of nitrones by Pyrazolinium dichromatein aqueous dimethyl sulphoxidemedium evaluate the reaction constants and the mechanistic aspects are discussed.

The structural formula of PyDC is shown in the following figure.



PYRAZOLINIUM DICHROMATE

$[C_6H_{14}N_4]Cr_2O_7$

II. Materials and Methods

Pyrazolinium dichromate(PyDC) was prepared by reported method [1], nitrones and substituted nitrones were prepared by the literature method[9], purified acrylamide[10] analar sample of sodium perchlorate, perchloric acid, oxalic acid, manganoussulphate and ethylene diamine tetra aceticacid were used. Triply distilled water was used throughout the course of the investigation. Correlation analysis werecarried out using Microcal Origin (Version 6.1) computer software.

a) Preparation of Pyrazolinium dichromate

Chromium trioxide (5g) was dissolved in water (50 ml) and cooled in ice. Then pyrazole (4g) was added, slowly. The solution was diluted with acetone (200 ml) and cooled to 0°C. The orange solid obtained was separated, filtered, washed with acetone, dried and recrystallized from water (dec.160°-161°C).

b) Kinetic measurements

For kinetic runs, a measured amount of PyDC pre-equilibrated at 30°C was rapidly added to the thermally equilibrated mixture containing appropriate amounts of nitrones, acrylamide, perchloric acid, sodium perchlorate and water. The progress of the reaction was followed by iodometric determination of the

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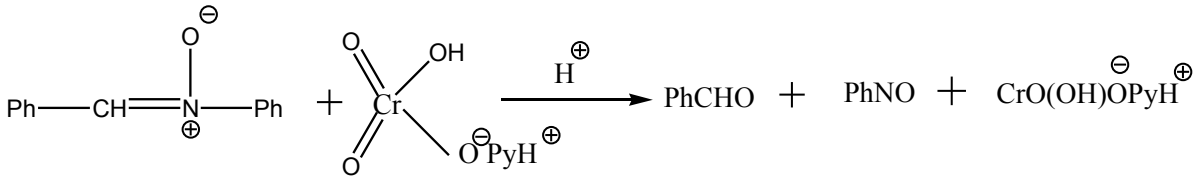
unreacted oxidant[11]. The rate constants were determined by the least squares method. Aliquots (2 ml) of reaction mixture were withdrawn at an appropriate time interval and quenched into ice-cold water containing 10 ml of 4N sulphuric acid. The liberated iodine was titrated against standard sodium thiosulphate to a starch end point. The reaction was carried out at three different temperatures viz., 35^0, 40^0 and 45^0C.



For identifying the product an excess of oxidant was mixed with substrate under kinetic conditions. After the reaction was completed, the reaction mixture was extracted with chloroform. The solvent was removed and obtained solid was analysed by Co-TLC method. The spots of the products were developed in benzene along with the spots of authentic samples of benzaldehyde and nitrosobenzene. After developing the location of the spots was identified using iodine vapour and their positions were compared. Two spots obtained for products were identical with benzaldehyde and nitrosobenzene. IR spectrum was recorded, nitrosobenzene [12] exhibits three bands at 1626, 1500 and 1019cm^{-1} attributed to stretching frequency of C-N, one sharp band at 1452cm^{-1} due to stretching vibration of N-O and band 530cm^{-1} due to ring deformation and CNO bending vibration are similar to that of one of product obtained from the substrate.

c) Stoichiometry and Product analysis

The reaction mixture containing excess of PyDC in the presence of perchloric acid was kept for 24hr under kinetic conditions. The estimation of unreacted PyDC indicates that 1mol of PyDC was used by 1mol of nitrone.

III. Results and Discussion

An inspection of the observed Pseudo-first-order rate constants (k_{obs}) shows that the k_{obs}values constant over a wide range in PyDC(Table-1). The reaction is first order with respect to PyDC as evidenced by a good linearity in the plot of log[PyDC] versus time. The plot of logk_{obs} versus log[NO] was found to be linear(Table-1) with slope unity, indicating a first order dependence on [NO]. The plot of k_{obs}^{-1} versus $[NO]^{-1}$ was linear and passing through the origin, showing that the nitrone-PyDC complex has only transient existence. The effect of acid[$HClO_4$] has been studied by varying the concentration of H^+ at a given concentration(Table-1). The plot of k_{obs} versus log[H^+] was linear with a slope less than unity, indicating fractional order dependence on [H^+]. The rate decreased with increase in ionic strength of the medium by the addition of $NaClO_4$ (Table-1).

Table 1 : Effect of varying [PyDC], [Nitrone], [H^+] and [$NaClO_4$] on oxidation of nitrone in 50 % (v/v) DMSO – H_2O medium at 308 K

[PyDC] x 10^3mol dm^{-3}	[Nitrone] x 10^2mol dm^{-3}	[$HClO_4$] x 10^3mol dm^{-3}	[$NaClO_4$] x 10^1mol dm^{-3}	k_{obs} x 10^4 s^{-1}
0.50	1.00	1.53	1.00	8.44
0.75	1.00	1.53	1.00	8.28
1.00	1.00	1.53	1.00	8.01
1.25	1.00	1.53	1.00	8.17
1.50	1.00	1.53	1.00	8.71
1.75	1.00	1.53	1.00	8.61
1.00	0.50	1.53	1.00	4.01
1.00	0.75	1.53	1.00	6.05
1.00	1.00	1.53	1.00	8.01
1.00	1.25	1.53	1.00	10.19
1.00	1.50	1.53	1.00	11.6
1.00	1.75	1.53	1.00	13.1
1.00	1.00	0.76	1.00	5.77
1.00	1.00	1.53	1.00	8.01[a]
1.00	1.00	2.29	1.00	8.91
1.00	1.00	3.06	1.00	11.4
1.00	1.00	3.82	1.00	12.9
1.00	1.00	4.59	1.00	15.2
1.00	1.00	1.53	0.50	9.08

1.00	1.00	1.53	1.00	8.00
1.00	1.00	1.53	1.50	6.23
1.00	1.00	1.53	2.00	3.67
1.00	1.00	1.53	2.50	2.47
1.00	1.00	1.53	3.00	1.41

[Acrylamide] = 1.00 x 10^{-2}mol dm^{-3}

The reaction is studied on addition of manganous ions reduces [13-15] the rate of oxidation of nitrones. This indicates that Mn(II) has a catalytic effect on the disproportionation of the intermediate valence state of chromium [16] and suggest that Cr(IV) is probably involved in the rate determining step(Table-2). The rate increase with increase in oxalic acid, indicating that oxalic acid enhances the rate of oxidation of aldonitrones by PyDC(Table-2). The increase in [EDTA] [17] inhibits the rate of oxidation of nitrones(Table-2), indicate that complex formation between chromate and PyDC.

Table 2 : Effect of varying [Mn^{2+}], [EDTA], [$(COOH)_2$] on oxidation of nitrone by PyDC in 50 % (v/v) DMSO – H_2O medium at 308 K

$[MnSO_4]$ x 10^3mol dm^{-3}	k_{obs} x 10^4 s^{-1}	[EDTA] x 10^3mol dm^{-3}	k_{obs} x 10^4 s^{-1}	$[(COOH)_2]$ x 10^3mol dm^{-3}	k_{obs} x 10^4 s^{-1}
0.00	8.01	0.00	8.01	0.00	8.01
2.50	4.82	2.00	6.18	0.75	8.10
5.00	4.58	4.50	6.12	2.00	8.25
7.50	4.24	7.00	5.90	3.25	10.24
10.00	3.65	9.50	5.74	4.50	10.80
12.50	3.51	12.00	5.60	5.75	11.60
15.00	3.24	14.50	5.52	7.00	15.20

[Nitrone] = 1.00 x 10^{-2} mol dm^{-3} ; $[HClO_4]$ = 15.30 x 10^{-4} mol dm^{-3}

[PyDC] = 1.00 x 10^{-3} mol dm^{-3} ; $[NaClO_4]$ = 1.00 x 10^{-1} mol dm^{-3}

An increase in dimethyl sulphoxide content retarded the reaction rate (Table-3). A plot of $logk_{obs}$ versus D^{-1} (where D is the dielectric constant of the medium) was linear with a negative slope indicative of a dipole interaction in the transition. It shows that positive and neutral molecules interact in the rate determining step [18]. No turbidity has been noticed when a clear reaction mixture was allowed to stand with a drop of acrylonitrile ruling out a free radical mechanism.

Table 3 : Effect of varying composition of DMSO on oxidation of nitrone by PyDC at 308 K

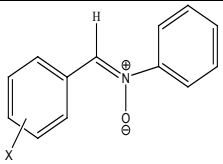
D	k_{obs} x $10^4 s^{-1}$	log k_{obs}	D^{-1}
65.98	6.42	-3.193	0.0151
64.44	6.78	-3.169	0.0155
62.90	8.01	-3.096	0.0158
61.36	8.68	-3.062	0.0162
59.82	10.44	-2.981	0.0167
58.28	11.55	-2.937	0.0171

[Nitrone] =1.00 x 10^{-2} mol dm^{-3}; $[HClO_4]$= 15.30 x 10^{-4} mol dm^{-3}

[PyDC]=1.00 x 10^{-3}mol dm^{-3} ; $[NaClO_4]$ =1.00x 10^{-1} mol dm^{-3}

The rate of oxidation of some para and meta-substituted nitrones was studied at three different temperatures, Viz, 35, 40 and 45^{0}C. The activation parameters are calculated using the Eyring's plot and the values are given in (Table-4).

Table 4 : Second order rate constants and the activation parameters for the oxidation of substituted nitrones by PyDC

S.No		k_2 x 10^2 dm^3mol^{-1} s^{-1}			$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ J K^{-1} mol^{-1}	$^a\Delta G^{\#}$ kJ mol^{-1}	r	sd
	X	308 K	313 K	318K					
1	*p*-OMe	10.71	15.77	22.96	62.126	62.192	81.592	1.000	0.003

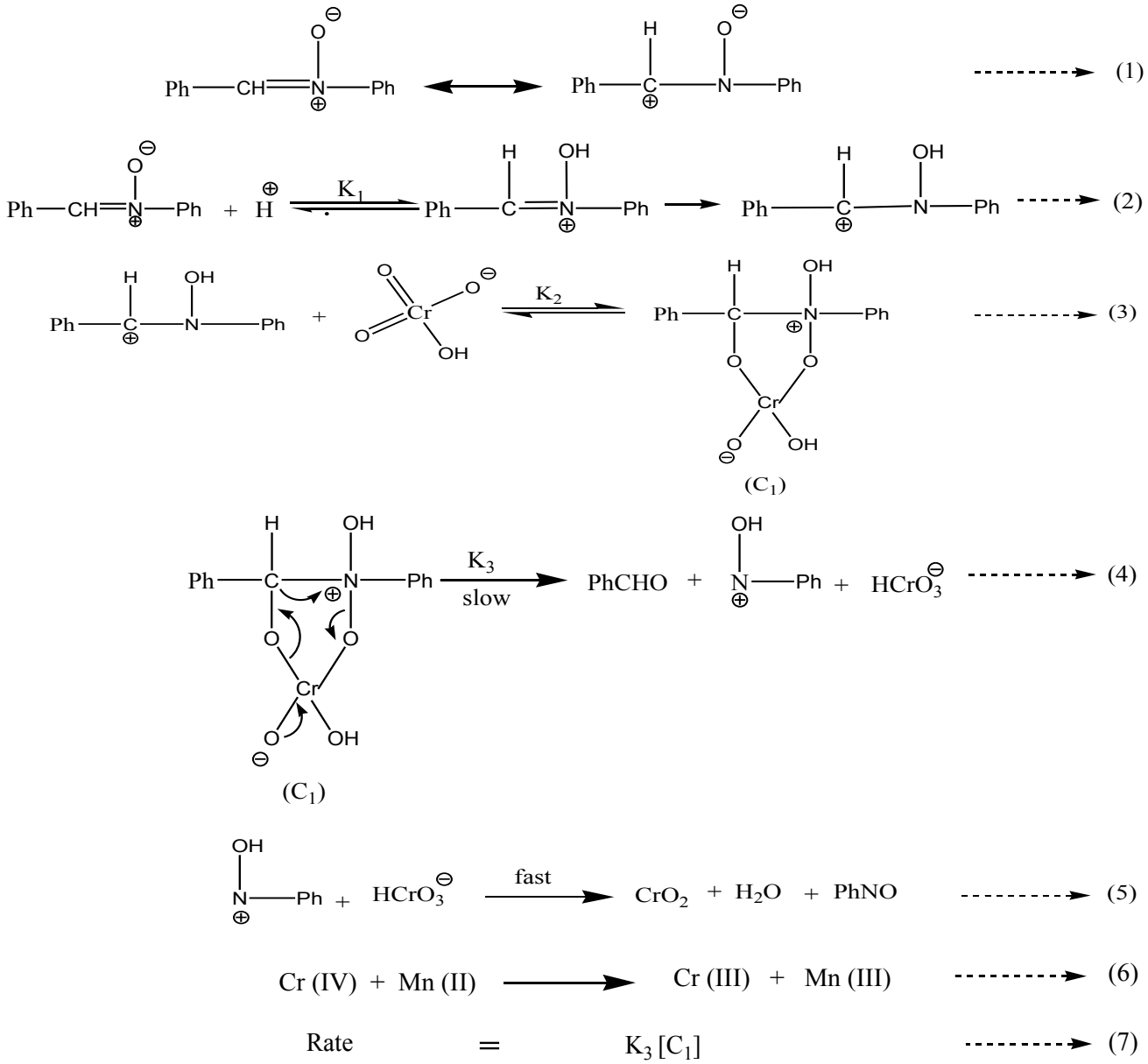
2	*p*-Me	9.67	14.38	20.69	61.976	63.522	81.859	0.999	0.008
3	H	8.01	12.11	18.16	64.080	58.226	82.305	0.999	0.001
4	*p*-F	7.64	10.94	15.77	59.033	75.078	82.533	0.999	0.007
5	*p*-Cl	7.21	10.62	15.02	59.803	73.000	82.653	0.999	0.011
6	*p*-Br	6.70	10.58	13.64	57.999	79.235	82.800	0.988	0.078
7	*p*-NO_2	4.92	06.82	10.62	62.629	67.180	83.657	0.995	0.052

[Nitrone] =1.00 x 10^{-2} mol dm^{-3};[$NaClO_4$] =1.00 x 10^{-1} mol dm^{-3};[$HClO_4$] = 15.30 x 10^{-4}moldm^{-3};
[PyDC]= 1.00 x 10^{-3} mol dm^{-3}; DMSO – H_2O = 50 % (v/v) ; [a]$\Delta G^{\#}$ at 313 K

a) Mechanism and rate law

In aqueous solution PyDC undergo protonation in acidic conditions. This protonated species is more powerful than unprotonated species. The order with respect to PyDC, [NO] is unity and fractional order with respect to [H^+]. The PyDC does not undergo protonation at very low [H^+].The observed salt and solvent effects show that the ionic and neutral species are involved in the slow step. Owing to the above reasons, the nitrone gets protonated before the rate determining step, and it can react with PyDC in the slow step.

Based on the above observation, a probable mechanism and rate law for the oxidation of nitrones by PyDC given in the following Scheme.



Scheme

$$\frac{-d[PyDC]}{dt} = \frac{K_1 K_2 K_3 [nitrone] [PyDC] [H^+]}{1 + K_1 [H^+]} \quad \text{----------} \rightarrow (8)$$

$$K_{obs} = \frac{K_1 K_2 K_3 [nitrone] [H^+]}{1 + K_1 [H^+]} \quad \text{----------} \rightarrow (9)$$

(or)

$$\frac{1}{k_{obs}} = \frac{1}{K_1 K_2 k_3 [nitrone] [H^+]} + \frac{1}{K_2 k_3 [nitrone]}$$

The plot of $1/k_{obs}$ versus $1/ [H^+]$ is linear (r = 0.970; sd = 105.5) and from the plot K_1 and $K_2 K_3$ are calculated (K_1 = 624.54 and $K_2 K_3$ = 0.174). The observed rate constant is consistent with rate law.

b) Effect of substituents

The reaction rate an extension of the present investigation, the kinetics of oxidation of some para-substituted nitrones with PyDC is followed at three different temperatures. The rate data are analysed from the linear free energy relationships [19]. The respective rate constants and the thermodynamic parameters are listed in (Table-4). Isokinetic relationship, the variation in $\Delta S^{\#}$ should be linearly related [20-21] to changes in $\Delta H^{\#}$ by equation (10)

$$\Delta H^{\#} = \Delta H^0 + \beta \Delta S^{\#} \quad \text{----------(10)}$$

A plot of $\Delta H^{\#}$ versus $\Delta S^{\#}$ (Fig-1) gives a straight line with a correlation coefficient r = 0.998. The isokinetic temperature (β)is obtained from the slope is 274K. This temperature is higher than that of experimental temperature, indicating that the reaction is enthalpy controlled. This is further supported by the fact that Ea values are the least for the fast reaction and higher for the slowest reaction. The good correlation implies that the reaction with all the substituted nitrones follow a common mechanism.

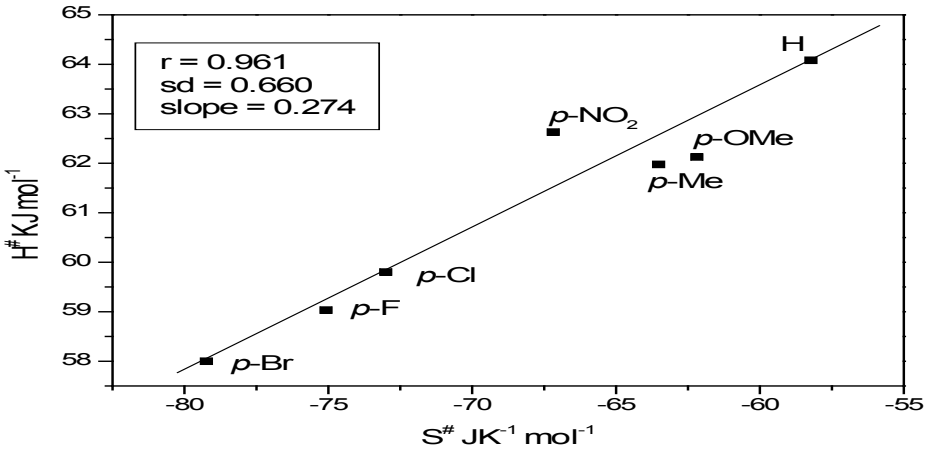


Fig.1. Plot of $H^{\#}$ versus $S^{\#}$ for oxidation of nitrones by PyDc in aqueous dimethyl sulphoxide medium

c) The Exner's Plot

However, Exner [22-23] criticised the validity of such a linear correlation between $\Delta H^{\#}$ and $\Delta S^{\#}$ as these quantities depend on each other when measurements at two temperatures are made, the experiment data can be treated by the following equation [24-25].

$$\log k_{2(T1)} = a + b \log k_{2(T2)} \quad (11)$$

where $T_2 > T_1$

A good correlation (r=0.990) is obtained when $\log k_2$ (25) is plotted against logk (35) shows that the reaction under investigation follows common mechanism.

d) Hammett Plot

The hammet equation applied with the usual substituent constant σ and k_{obs}data of Para substituted nitrones exhibits an straight line (Fig-2).The Hammett plot is also linear (r = 0.981, sd =0.023) with ρ = -0.315 at 318K.

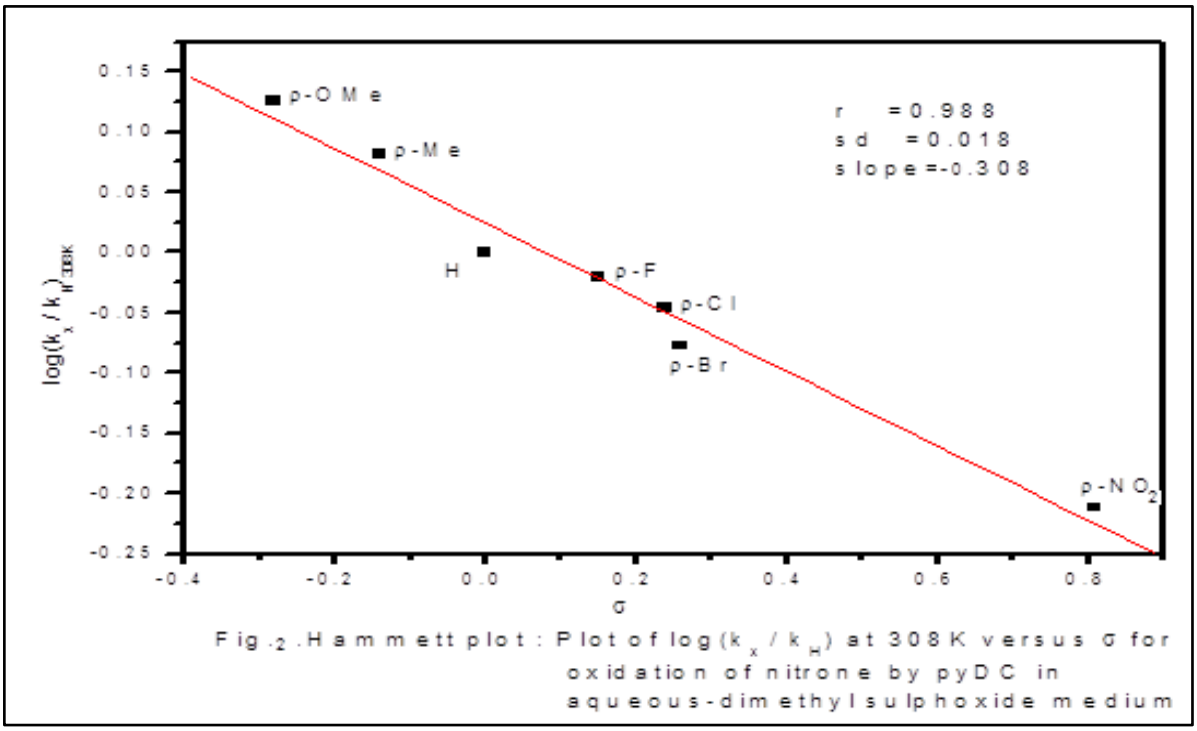


Fig.2. Hammett plot: Plot of log(k_x / k_H) at 308K versus σ for oxidation of nitrone by pyDC in aqueous-dimethylsulphoxide medium

According to Hammett reaction with positive ρ values are accelerated by electron releasing from phenyl ring, whereas those with negative ρ values are retarded by electron withdrawal from phenyl ring[26]. In this oxidation reactions, the electron withdrawing group increases the rate and the electron donating group decreases the rate. These observations supporting the negative ρ value obtained from the Hammett plot. The order of reactivity of different substituents is as follows.

$$p-OMe > p-Me > H > p-F > p-Cl > p-Br > p-NO_2$$

The values of reaction constants (ρ) are calculated at different temperatures and summarised in (Table-5). The reaction constant (ρ) has a small negative value as the oxidation involves loss of electrons. The negative value of the reaction constant is acceptable as transition state is involved in positive-charged species.

Table 5 : Reaction constants for the oxidation of nitrones by PyDC

Temp K	ρ	r	sd
308	- 0.315	0.981	0.023
313	- 0.331	0.995	0.011
318	- 0.308	0.988	0.018

IV. Conclusion

1. Seven N, α- diphenylnitrones were prepared according to the literature methods. The purity of the nitrones were checked by the TLC method and their physical constants.
2. Pyrazolinium dichromate (PyDC) was prepared and purity of the oxidant was estimated by iodometric method.
3. All the kinetic studies were found by iodometric procedure to starch end point.
4. Kinetics and mechanism of oxidation of N,α-diphenylnitrones by Pyrazolinium dichromate (PyDC) in aqueous DMSO medium was followed under different experimental conditions and temperatures. The reaction followed first order dependence with respect to [PyDC], [Nitrones] and fractional order with respect to [H^+].The effect of change in ionic strength and dielectric constant were also studied. The rate of oxidation decreased with increasing [Mn^{+2}], which implies the disproportionate of the Cr(IV) by Mn(II). All the above results indicate that a protonated nitrone reacted with chromate ion to form intermediate complex in the slow step. Linear Hammett plot obtained clearly showed that the common mechanism operated under the experimental condition.
5. Isokinetic plots (Exner's and$\Delta H^{\#}$versus $\Delta S^{\#}$) gave satisfactory straight lines with good correlation

coefficient. This proves that all these substituents follow a common mechanism.

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Thermodynamics Studies of a Novel Calix[4]arene Derivative Designed to Bind Herbicides

By Ahmed Yahya Issa Rubaye

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Abstract- Calix[4]arenes can be modified to produce materials which can capture and remove contaminants effectively such as herbicides. Chlorophenoxy acids have been selected out of groups of herbicides to carry out this investigation. A new calix[4]arene derivative containing mixed pendant arms in its lower rim, 5, 11, 17, 23- *tetra- butyl-* 25,27- bis (diethylamino) ethoxy- 26, 28- (bis-methoxyethoxy) calix [4] arene (L2), has been synthesized. ^{1}H NMR investigations seems to indicate that the receptor L2 interacts with acid herbicides. Conductometric measurements were performed in acetonitrile at 298 K. In all cases, 1:2 (ligand: acid herbicide) complexes are formed. Standard thermodynamics parameters of complexation (log K_s, ΔH°_c, ΔS°_c, ΔG°_c) of L2 with herbicides in acetonitrile were determined using the Nano ITC (isothermal titration calorimetry). For all the systems investigated, the complexation process between these acid herbicides and the receptor L2 was enthalpically controlled.

Keywords: Calix[4]arene receptor, Detection of herbicides, 1H NMR investigations, Conductance measurements, Thermodynamics parameters of complexation.

GJSFR-B Classification : FOR Code: 030602

Strictly as per the compliance and regulations of :

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I. Introduction

The use of pesticides can cause problems to the environment because 98% of insecticides and 95% of herbicides can spread through the air to contaminate other areas. Herbicides can cause water pollution and soil contamination [1]; some are persistent organic pollutants and as such they contribute to soil contamination. Of all the classes of herbicides, chlorophenoxy acids have been selected for this investigation (Table 1) [2, 3]. Chlorophenoxy acids are known to be hazardous substances and their use as herbicides has been banned in many countries. These substances can pose a serious threat to human health and the environment, mainly contaminating groundwater and drinking water [4, 5]. The development of novel technological approaches for their removal from water and soil by the use of efficient extracting agents is a challenging task.

Investigations on the capacity of macrocycles to respond to the presence of herbicides in different media are very limited .The prevalent research studies concentrate on the binding between calixarenes and toxic metals and pay little attention to the interaction between the calixarene derivatives and organic compounds such as herbicides. It is important to explore the potential offered by calixarene based receptors for the removal of these pollutants from contaminated sources. Thus efforts have been made to produce calixarene derivatives which are able to interact selectively with these pollutants.

Although the procedures used to synthesize these macrocycles are established, the design of calixarene-based receptors able to interact selectively with a given guest is a challenging area of research.

A great deal of effort has been focused on the design of selective macrocyclic extracting agents for the removal of these species from water and soil. Particular attention is paid to herbicides due to the toxicological impact of these species on human health.

Calix[4]arenes are strong size-selective receptors for a variety of substrates, in particular, for inorganic and organic cations [6]. Calixarenes can be used as ion selective electrodes or sensors [7], optical sensors [8], chiral recognition devices for solid phase extraction, as a stationary phase and modifiers [9]. In the ' cone ' conformation of *p-tert*-butylcalix[4]arene is characterised by a hydrophobic cavity which can complex neutral guest molecules, such as toluene [10]. Upon functionalization, calixarenes have become versatile hosts for cations, anions, and neutral molecules. They are used widely in chemical separations, ion-selective electrodes, chromatography, phase transfer catalysis, and as catalytic platforms [11].

Calix[4] arene derivatives bind weakly with herbicides. In order to modulate the anion binding behavior, the core size of calix [4]arene was extended through the induction of suitable spacer units as a rigid wall . Thus, this study concerns the design of receptor which is able to interact with these pollutants. Fully substituted calixarene with different lower rim functionalities have been prepared for the detection of herbicides (Fig. 1). A good response to herbicides was obtained by full functionalisation of the lower rim with ether-amine groups.

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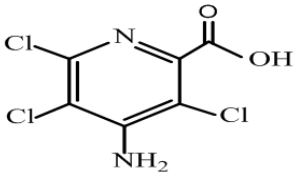
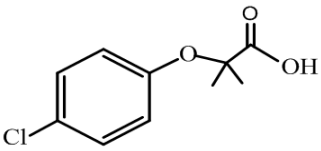
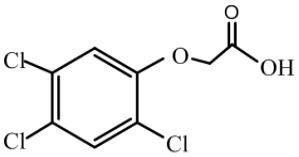
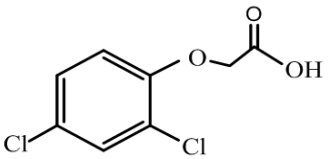
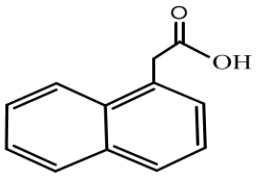
Table 1 : Group of pesticides selected to perform this investigation

Pesticides	pKa values at 20 °C in water
 **Picloram (P1)**	**2.3**
 **Clofibric acid (P2)**	**2.84**
 **2,4,5-Trichlorophenoxyacetic acid(P3)**	**2.88**
 **2,4-dichlorophenoxyacetic acid (P4)**	**2.73**
 **1-Naphthaleneacetic acid (P5)**	**4.23**

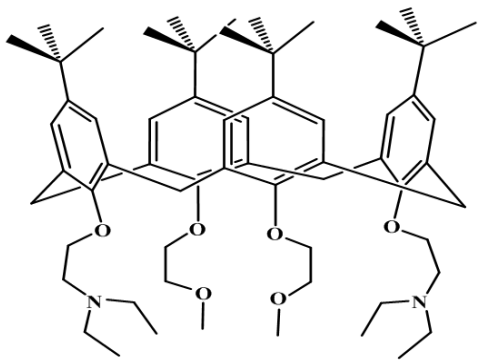


Figure 1 : Structure 5,11,17,23-*tetra-butyl* 25,27bis(diethylamino)ethoxy-26,28-(bis methoxyethoxy)calix[4]arene(L2)

Calix(4)arenes containing ether and amine functional groups at the lower rim have shown pronounced selectivity for herbicides in different media, particularly acetonitrile. It can be observed that the presence of the amino groups (basic) in the lower rim for calix[4]arene makes these ligands attractive to explore their complexation with herbicides. This receptor is capable of binding phenoxy acid molecules through hydrogen- bonding interaction. The interaction of the calix[4]arene amine derivative and a pesticide is shown in Fig. 2.

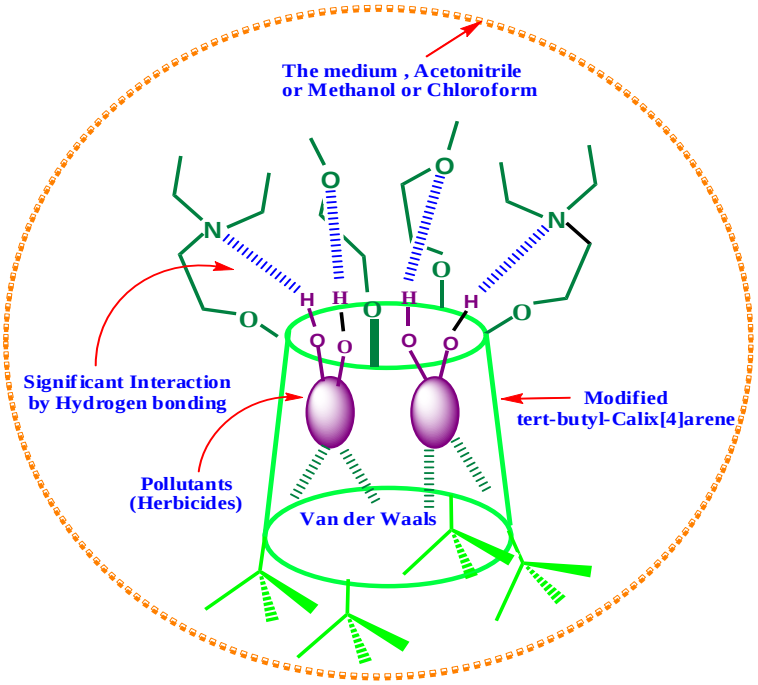


Figure 2 : The interaction model of the calix[4]arene based receptor for herbicides

The conformational changes that the calix[4]arene ligand undergoes upon complexation with ionic or neutral species can be assessed from ^{1}H NMR investigations [12]. Gutsche and co-workers [13] established that the conformations of calixarenes and their derivatives can be established by observing the resonance of the methylene protons (axial and equatorial) in the ^{1}H NMR spectrum. In the ' cone ' conformation $\Delta\delta_{ax\text{-}eq}$ is about 0.90 ppm while values of 0.50 ppm and higher than 0.90 ppm are found for calixarenes in their flattened and distorted conformation respectively.

A detailed investigation on the complexation of L2 with herbicides in a wide variety of solvents (methanol, acetonitrile and chloroform) using a variety of techniques such as ^{1}H NMR (to establish the binding sites and the conformational changes that these ligands undergo upon complexation with herbicides), conductance measurements (to establish the composition and the type and strength of the host-guest complexes) , nano ITC to derive the thermodynamics of complexation (stability constant, log *K*s, hence standard Gibbs energy, $\Delta_c G°$; enthalpy, $\Delta_c H°$; and entropy, $\Delta_c S°$ of complexation). Stability constants are used to assess quantitatively the selective behavior of this ligand for one herbicide relative to another.

II. Experimental Section

a) Chemicals

All chemicals were obtained from Sigma-Aldrich, Fluka and Fisher UK Scientific and were either analytical or reagent grade. Solid chemicals were used as received without further purification. All solvents were dried and purified as described in the literature [14].

b) ^{1}H NMR measurements

^{1}H NMR measurements were recorded at 298 K on A Bruker DRX-500 pulse Fourier Transform NMR Spectrometer. The operating conditions involved pulse or flip angle of 30°, spectra width (SW) of 15 ppm, spectral frequency (SF) of 500.150 MHz, delay time of 0.3 s, acquisition time (AQ) of 3.17s, and line broadening of 0.3 Hz. Solutions of the samples of interest (1×10^{-3} mol.dm^{-3}) were prepared in the appropriate deuterated solvent. These were placed in 5 mm NMR tubes using TMS (tetramethylsilane) as the internal reference.

c) Conductometric measurements

A Wayne-Kerr Autobalance Universal Bridge type B642 was used for conductometric measurements. The Wayne-Kerr is connected to a platinum glass bodied electrode housed in a cylindrical glass vessel where the reaction takes place. A thermostated bath circulating water in the vessel jacket was used to maintain the temperature of the vessel at 298.15 K. A magnetic stirrer was used to keep homogeneous the solutions throughout the time of the experiment.

d) Determination of the constant of the conductivity cell

The cell constant was determined by titrating a solution of KCl (0.1 mol dm^{-3}) in deionised water (25 cm^3) **[15]**. The cell was immersed in a thermostated bath at 298.15 K. The conductance of the solution was recorded after addition of KCl once the stability of the system was ensured.

e) Nano ITC (Isothermal Titration Calorimetry)

ITC measurements were performed in a Nano Isothermal Titration Calorimeter, models 5300 (TA Instruments). All measurements were carried out in acetonitrile solvent at a fixed temperature of 298.15 K. The basic principle of ITC is simply to measure the heat released or absorbed in a liquid sample after the addition of another liquid sample. This heat is proportional to the total amount of binding that occurs within the calorimeter cell. The instrument has a pair of identical cells (1.4 ml), denoted as the reference and sample cells. These cells, along with access stems, are enclosed in a temperature-controlled thermal jacket. The reference cell was filled with acetonitrile. The ligand solution (1 m M) placed in the sample or reaction cell. The herbicides (20 m M) loaded in the syringe. The interval time between two readings was set at 240 s. The experiments were designed for a total of 25 consecutive injections. The power (or heat) difference between the sample and reference cells is used to determine reaction stoichiometry or number of binding sites (n), stability constant (K_a), and the enthalpy (ΔH^o) **[16, 17]**. The first data point was removed from the data set prior to curve fitting. The data was analyzed to determine the heat of interaction by using Origin 7.0 and Nano Analyzer data analysis softwares supplied by Microcal and TA Instruments, respectively with the 'independent sites' model.

i *Calibration of the Equipment*

To determine the accuracy of measurements carried out in the Nano ITC, a chemical calibration should be performed. The following equilibrium is established upon the addition of barium chloride to 18-crown-6 ether in water at 298.15 K **[18]**. The sample cell was filled with an aqueous solution of 18-Crown-6 (1×10^{-3} mol dm^{-3}) and titrated incrementally from the burette stirring system with $BaCl_2$ (0.015 mol dm^{-3}).

f) Synthesis

i *Synthesis 5, 11, 17, 23 -p- ter t- butyl -25 ,27 dihydroxy 26, 28- bis (2-ethoxymethoxy) Calix(4) arene, L1*

The preparation of this derivative was achieved by procedure reported in the literature **[19]**.

ii *Synthesis of 5, 11, 17, 23- tetra- butyl 25, 27- bis (diethyl amino) ethoxy- 26, 28- (bis- methoxy ethoxy) calix[4] arene, L2*

5, 11, 17, 23- *p- tetra*- butyl- 25,27- dihydroxy- 26, 28- bis- (2-ethoxy) calix[4] arene, **L1** (1.6 g, 1.75 mmol), sodium hydride (1.7 g, 60 mmol) were suspended in 150 ml mixture of freshly refluxed THF and 30 ml of DMF dried on molecular sieves. Then 2-chlorotriethylamine hydrochlorid (1.5 g, 11.05 mmol) in 10 ml of DMF was syringed to the reaction mixture. Then the reaction was stirred and refluxed for 6 h. The reaction was monitored by TLC using DCM/Methanol (9:1) as the developing solvent mixture. After cooling down the reaction, the solvent was filtered through filter paper and removed under vacuum, to give an oily product which was broken by acetonitrile. **L2** was obtained in 80 % yield. The compound was characterized by ^{1}H-NMR in $CDCl_3$ at 298 K and microanalysis. ^{1}H-NMR ($CDCl_3$, 500 MHz) ; δ(ppm) = 6.61 (s, 1H, Ar-**H**); 6.95 (s, 1H, Ar-**H**); 4.41 (d, 2H, Ar-**CH_2(ax)**-Ar); 4.19 (t, 2H, Ar-O-**CH_2**$CH_2N(CH_2CH_3)_2$); 3.95 (t, 2H, Ar-O-**CH_2**CH_2-O-CH_3); 3.44 (s, 3H, Ar-O-CH_2CH_2-O-**CH_3**); 3.15 (d, 2H, Ar-**CH_2(eq)**-Ar); 3.0798 (t, 2H,Ar-CH_2-**CH_2**-O-CH_3);2.65 (Ar-O CH_2CH_2N(**CH_2**$CH_3)_2$));1.08 (s, 9H, -C-**$(CH_3)_3$**); 0.9482 (s, 9H, -C-**$(CH_3)_3$**). ^{13}C NMR ($CDCl_3$, 500 MHz) ; δ(ppm) = 30.95 (C1), 32.15 (C2), 33.17 (C3), 33.90 (C4), 134.01 (C5), 122.15 (C6),127.80 (C7),155.48 (C8),30.87 (C9), 128.55 (C10),122.25 (C11),135.90 (C12),157.17 (C13), 72.88 (C14),72.62 (C15),15.12 (C16),58.72(C17), 52.56 (C18),47.61 (C19), 11.96 (C20). Elemental analysis ;($C_{62}H_{94}O_6N_2$), Mw. (963.56). % calculated, C, 77.28, H, 9.85 and N, 2.91. % found for C, 77.36, H, 9.09 and N, 2.83.

III. Results and Discussion

a) ^{1}H NMR characterization of L1 and L2

The NMR spectra of these receptors in non-aquous deuterated solvents were recorded **(Appendix A)**.

b) ^{13}C NMR of L2 in $CDCl_3$ at 298.15 K

^{13}C NMR spectrum of L2 in $CDCl_3$ at 298.15 K is shown in **(Appendix A).**

c) ^{1}H NMR complexation studies of calix[4]arene derivative at 298 K

^{1}H NMR spectra of the herbicides - receptor complexes at 298 K in CD_3CN, CD_3OD and $CDCl_3$ were recorded **(Appendix A)**. The relevant ^{1}H NMR chemical shift changes of the protons observed by the addition of

acid pesticides (P1, P2, P3, P4, P5) to the receptor L2, in deuterated solvent at 298 K are listed in Tables 2 - 4.

Tables 2- 4 shows the chemical shift changes of the ligand protons after addition of the appropriate excess of herbicides in different solvents at 298 K. These chemical shift changes ($\Delta\delta$) were calculated by subtracting the chemical shift of the free ligand (δ_{FL}) from that of the ligand- pesticides (δ_{LP}).

The receptor L2 with herbicides was investigated in acetonitrile, methanol and chloroform at 298 K with the aim of assessing the medium effect in the interaction of this receptor with herbicides. It is well established that calix [4]arene derivative are able to form inclusion complexes with some solvents due to the hydrophobic nature of the upper cavity of the receptor, which hosts small organic molecules [20]. Therefore, the effect of the solvent on the free ligand, L2 was investigated through ^{1}H NMR measurements in acetonitrile, methanol and chloroform at 298 K.

Table 2 : Chemical shift changes ($\Delta\delta$) for L2 after addition of an excess amount of appropriate herbicides in CD_3CN at 298 K (0.09 mol of L2 + 0.9 mol of herbicides)

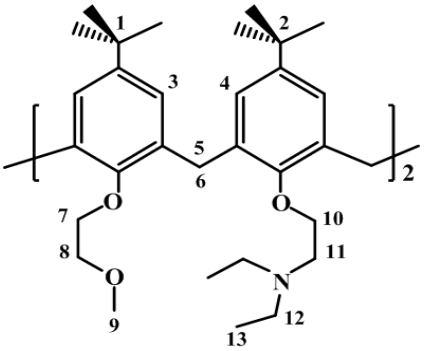
Receptor L2	$\Delta\delta$ in CD_3CN	L2	L2 + P1	L2 + P2	L2 + P3	L2 + P4	L2 + P5
	H-1	1.17	-0.10	-0.34	-0.1	-0.09	-0.09
	H-2	1.10	0.11	0.07	0.12	0.1	0.07
	H-3	6.99	0.14	0.08	0.15	0.13	0.11
	H-4	7.09	-0.17	-0.16	-0.16	-0.16	-0.14
	H-5(eq)	3.22	-0.07	-0.07	-0.06	-0.07	-0.01
	H-6(ax)	4.46	0.07	0.09	0.11	0.12	0.16
	$\Delta\delta_{(ax-eq)}$	1.24	1.39	1.41	1.42	1.43	1.41
	H-7	3.94	0.15	-0.07	-0.05	-0.05	0.02
	H-8	3.03	-0.44	-0.41	-0.44	-0.44	-0.37
	H-9	3.41	0.11	-0.30	0.08	0.07	0.13
	H-10	4.14	0.11	-0.19	-0.24	-0.23	-0.09
	H-11	3.90	0.11	0.17	0.17	0.17	0.33
	H-12	2.62	-0.63	-0.51	-0.60	-0.60	-0.27
	H-13	1.04	-0.29	-0.24	-0.26	-0.25	-0.05

Table 3 : Chemical shift changes (Δδ) for L2 after addition of an excess amount of appropriate herbicides in CD_3OD at 298 K (0.09 mol of L2 + 0.9 mol of herbicides)

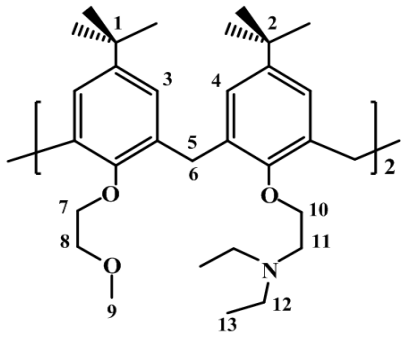
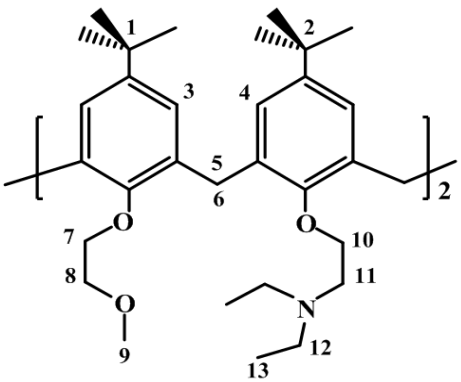
Receptor L2	Δδ in CD_3OD	L2	L2 + P1	L2 + P2	L2 + P3	L2 + P4	L2 + P5
	H-1	1.14	0.15	0.13	0.15	0.16	0.16
	H-2	1.09	-0.25	-0.17	-0.20	-0.20	-0.21
	H-3	6.83	-0.29	-0.18	-0.23	-0.23	-0.25
	H-4	6.90	0.28	0.25	0.27	0.28	0.28
	H-5(eq)	3.19	0.04	0.06	0.10	0.04	0.02
	H-6(ax)	4.48	-0.09	0.08	-0.09	-0.09	-0.14
	$\Delta\delta_{(ax\text{-}eq)}$	1.28	1.15	1.30	1.08	1.14	1.11
	H-7	4.08	0.42	0.31	0.37	-0.08	0.23
	H-8	3.15	-0.17	-0.31	-0.20	-0.21	-0.36
	H-9	3.47	0.10	-0.06	-0.05	-0.07	-0.09
	H-10	4.14	-0.15	-0.11	-0.13	0.31	-0.20
	H-11	3.92	0.43	0.55	0.48	0.46	0.36
	H-12	2.72	0.6	0.49	0.56	0.55	0.18
	H-13	1.15	0.18	0.16	0.18	-0.02	-0.04

Table 4 : Chemical shift changes (Δδ) for L2 after addition of an excess amount of appropriate herbicides in $CDCl_3$ at 298 K (0.09 mol of L2 + 0.9 mol of herbicides)

Receptor L2	Δδ in $CDCl_3$	L2	L2 + P1	L2 + P2	L2 + P3	L2 + P4	L2 + P5
	H-1	1.21	-0.07	0.08	-0.07	-0.07	-0.06
	H-2	0.94	0.07	-0.08	0.08	0.08	0.00
	H-3	6.61	0.08	-0.12	0.09	0.10	0.04
	H-4	6.95	-0.12	0.08	-0.12	-0.10	0.00
	H-5(eq)	3.15	-0.02	0.03	-0.01	-0.02	0.12
	H-6(ax)	4.41	0.14	0.14	0.14	0.02	0.25
	$\Delta\delta_{(ax\text{-}eq)}$	1.25	1.41	1.36	1.41	1.31	1.38
	H-7	3.95	0.00	-0.06	0.01	-0.09	0.22
	H-8	3.08	-0.45	-0.47	-0.46	-0.55	-0.23
	H-9	3.44	0.11	0.12	0.10	0.07	0.31
	H-10	4.19	-0.18	-0.03	-0.19	-0.33	0.05
	H-11	3.92	0.29	0.28	0.28	0.26	0.58
	H-12	2.65	-0.49	-0.48	-0.53	-0.61	-0.12
	H-13	1.08	-0.15	-0.10	-0.17	-0.28	0.17

The results in Tables 2- 4, show that L2 interact with the acid herbicides in protic and dipolar aprotic media. Gutsche [13] suggested that the difference between the chemical shift of axial and equatorial protons ($\Delta\delta_{ax\text{-}eq}$) of the methylene bridge of calix[4]arene derivatives provides information regarding the conformation adopted by these ligands in solution. Based on this suggestion, $\Delta\delta_{ax\text{-}eq}$ values were calculated and these data are also included in Tables 2- 4. It can be observed that $\Delta\delta_{ax\text{-}eq}$ values for L2 are 1.24, 1.28 and 1.25 ppm in CD_3CN, CD_3OD and $CDCl_3$ respectively. These results indicate that in these solvents, L2 adopt a distorted 'cone' conformation. This might be due to the steric and electrostatic effects between the pendent arms at the lower rim. Thus, these groups try to move away as possible from each other to reduce the steric and electrostatic effects.

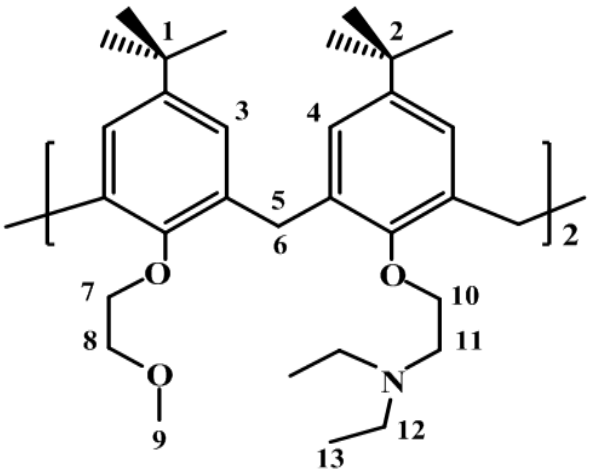
The results show that the conformation of L2 is not altered in moving from one solvent to another, indicating that no specific ligand-solvent interaction are taking place in these solvents at 298 K.

As can be seen from Tables 2- 4, the chemical shift changes of the ligand (L2) after addition of an excess amount of the herbicides are very significant in CD_3CN, CD_3OH and CD_3Cl , suggesting that interaction between this receptor and the herbicides are taking place. It can be seen that L2 has a slight change in the conformation in these solvents.

Approximately, all protons for ligand L2 have been affected upon the addition of the herbicides in CD_3CN, CD_3OD and $CDCl_3$ at 298 K. Some protons have shielding effects and others have deshielding effects. Deshielding effects were observed for protons (H-4, H-5(equatorial), H-7, H-11 and H-12). Shielding effects were observed for protons (H-3, H-6(axial), H-8 and H-10). It can be noted that the protons closest to the nitrogen and the oxygen atoms such as H-7, H-8, H-11 and H-12 have considerable chemical shift changes relative to others. This is an indication that the lower rim groups of the receptors interact with the pesticides. Protons such as H-1, H-2, H-3 and H-4 have been also affected as a result of this interaction.

^{1}H NMR titrations provide useful information regarding of active sites of the receptor interacting with the pesticides. ^{1}H NMR spectra for L2 with herbicides are shown in Fig. 3.

Fig. 4 shows ^{1}H NMR titration curves (plots of $\Delta\delta$(in ppm) for the titration of L2 with acid herbicides in CD_3CN at 298 K vs. [P]/ [L2] concentration ratio). These Figs shows the plot of the chemical shift changes observed upon an increase in the concentration of herbicides in CD_3CN at 298 K. The plot may illustrate that one ligand unit interacts with two units of herbicides but this will be confirmed more accurately by conductance measurements.



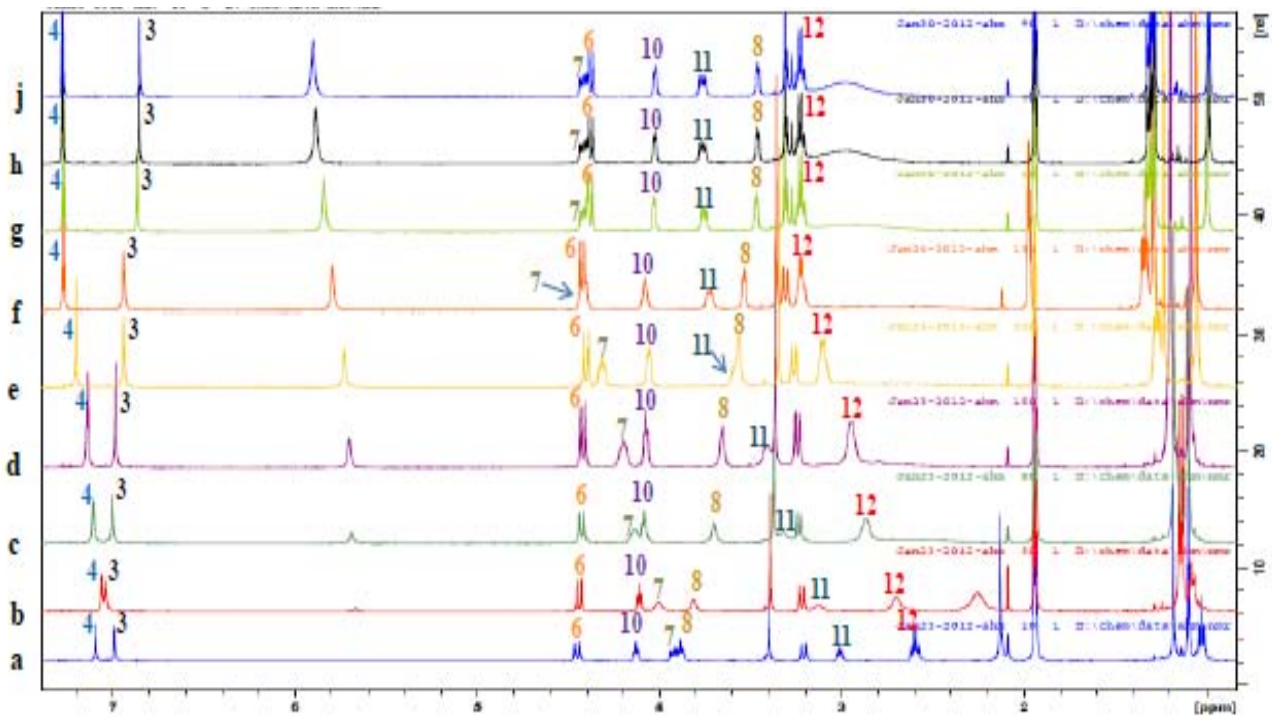


Figure 3 : Partial ^{1}H NMR (CD_3CN, 500 MHz) spectra showing the shift of the protons in L2 upon the addition of P1(4.14E-02 M), (a) L2 receptor(1.56E-02 M), (b) [P1]/[L2]=0.16, (c) [P1]/[L2]= 0.96, (d) [P1]/[L2] = 1.92, (e) [P1]/[L2] = 2.72, (f) [P1]/[L2] = 3.52, (g) [P1]/[L2] = 4.31, (h) [P1]/[L2]=5.11, (j) [P1]/[L2] = 5.43

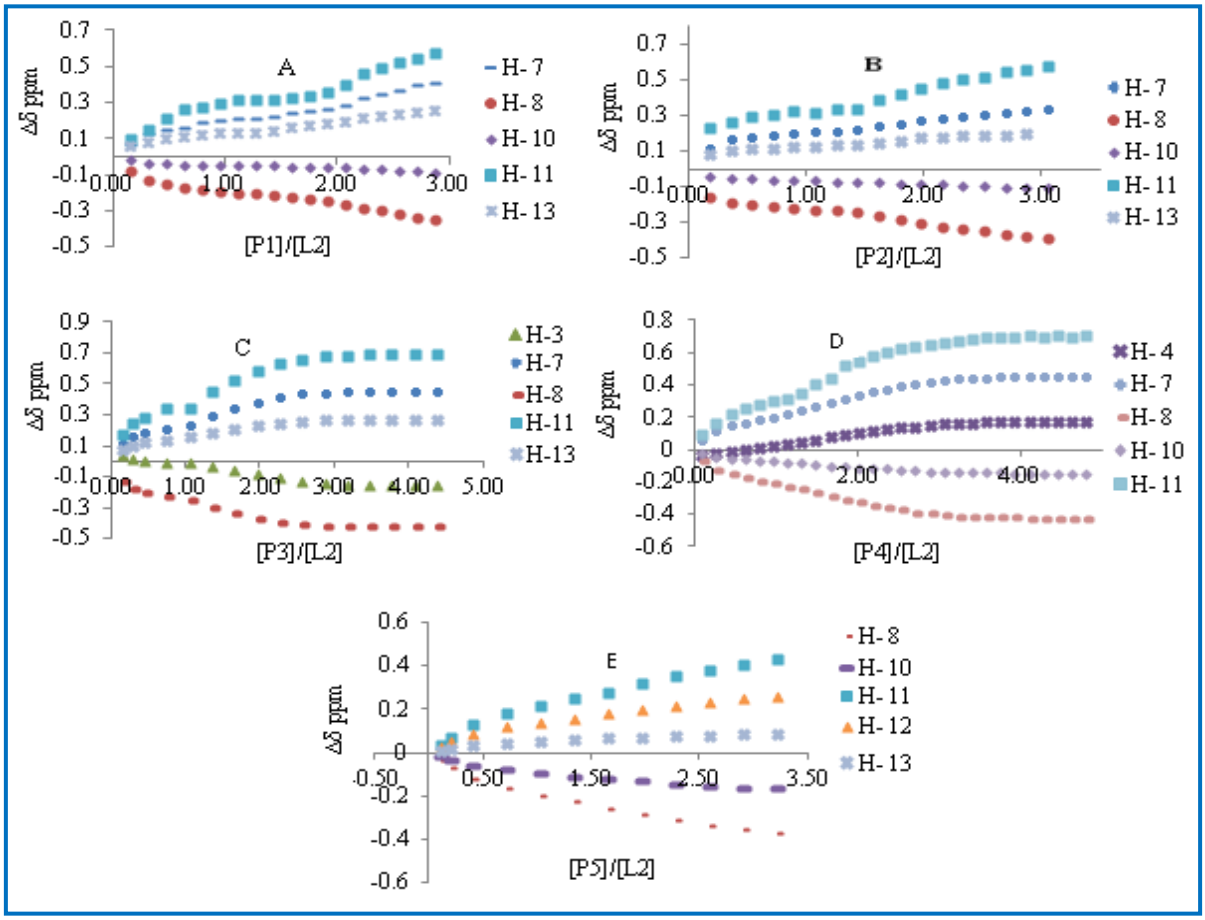


Figure 4 : ^{1}H NMR titration curves for the titration of Pesticides with the receptor L2 in acetonitrile at 298.15 K, (a) P1+ L2, (B) P2 + L2, (C) P3 + L2, (D) P4 + L2, (E) P5 + 5

d) Conductometric measurements

Fig. 5 shows the conductomeric curves (plots of Λ_m vs [L]/ [P]) for the titration of herbicides in acetonitrile at 298 K. From these Figs, It can be seen that all herbicides are likely to be strongly associated in acetonitrile as observed from the very low molar conductance value before starting the titration. Then the molar conductance increases. This is because there is a proton transfer reaction from acid pesticide to the amine group of the receptor. The conductomeric titration curves of P1 with L2 given in Fig.5, A shows an increase in molar conductance of the complexes throughout the titration, until the ligand/ P1 concentration ratio reaches 1: 2. Then the molar conductance remains almost constant until the end of the experiment. This increase in conductance reflects that the addition of the macrocycle (non electrode) to these herbicides substantially increases ion formation in solution. This may be attributed to a proton transfer reaction from the acid to the calixarene amine derivative. The conductomeric curve of L2 with P2 (Fig. 5, B) does not show significant changes in the curvature suggesting that the interaction of these ligand with P2 are weak in this solvent. This may be attributed to the steric hindrance effects because these acid herbicides contain two methyl groups which prevents or reduce formation hydrogen bonding. While significant shift changes were found for this herbicides in the ^{1}H NMR (Table 2). Conductometric curves for the titration of P3 and P4 with L2 in acetonitrile at 298.15 K are shown in Fig.5, C and D. Inspection of these titration curves shows that there is a marked increase in Λm values as the titration proceeds with a clear break at the molar conductance ratio of (0. 5) indicating that each ligand unit takes up four protons.

No changes in the molar conductance were observed by the addition receptor 5 to P5 (Fig. 5, E). This suggests the absence of interaction of this ligand and this pesticide in this solvent while significant chemical shift changes were found in ^{1}H NMR. This may be P5 are unable to transfer the proton that it strongly associated but may able to interact through hydrogen bond formation and this may be observed in the ^{1}H NMR spectra. These findings are in agreement with ^{1}H NMR measurements where significant chemical shift changes were observed by the addition of P1, P2, P3, P4 and P5 to the ligand in CD_3CN.

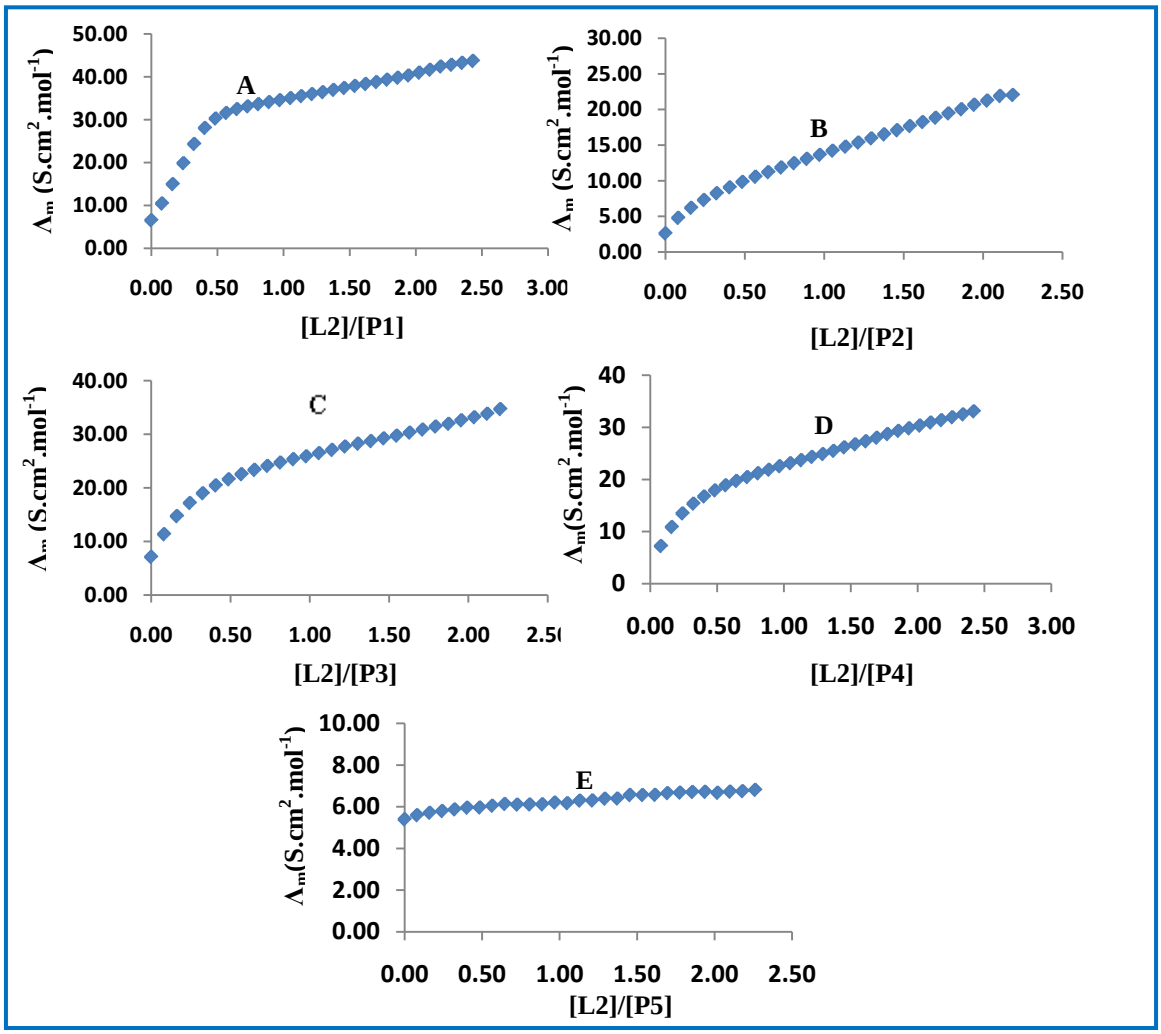


Figure 5 : Conductomeric curves for the titration of herbicides with the receptor 5 in acetonitrile at 298.15 K. (a) P1+ L2, (B) P2 + L2, (C) P3 + L2, (D) P4 + L2, (E) P5 + L2

e) Thermodynamics of complexation

Standard thermodynamics parameters of complexation (log K_s, ΔH°_c, ΔS°_c, ΔG°_c) of L2 with different herbicides in acetonitrile were determined using the Nano ITC. For this purpose the instruments were electrically and chemically calibrated prior to measurements. Calorimetric titration curves for the titration of herbicides with the receptor L2 in acetonitrile at 298 K were recorded (Appendix B).

i *Calibration of the Nano ITC instrument*

The reaction of complexation of 18-C-6 and Ba^{2+} in aqueous medium was used as a standard reaction to check the accuracy and reliability of the Nano ITC instrument following the procedure described in the Experimental Part [18]. Calorimetric titration curves for the titration of Ba^{2+} with 18-C-6 in water at 298 K were recorded (Appendix B).

The stability constant (expressed as log K_s), standard Gibbs energy, $\Delta_c G^\circ$, enthalpy, $\Delta_c H^\circ$ and entropy $\Delta_c S^\circ$ of complexation of 18-C-6 with Ba^{2+} in aqueous medium obtained at 298.15 K from nanocalorimetric titrations are summarized in Table 5. For comparison purposes, values reported in the literature are also included .The thermodynamic parameters for the complexation of Ba^{2+} with 18-C-6 in aqueous medium show a good agreement with the values reported in the literature by Briggner and Wadso [18].

Table 5: Thermodynamic parameters of $BaCl_2$ binding to 18-crown-6 by Nano-ITC in aqueous medium (deionized water) at 298.15 K

Log K_s	$\Delta_c H^\circ$(k J. mol^{-2})	$\Delta_c G^\circ$(KJ. mol^{-2})	$\Delta_c S^\circ$(J. mol^{-1}.K^{-1})	Ref.
3.63	-30.82	-20.73	-33.8	This work
3.77	-31.39	-21.49	-33	[18]

ii *Thermodynamic parameters of complexation of L2 with herbicides in acetonitrile at 298.15 K*

Titration calorimetry was used to obtain the log Ks and the enthalpy of complexation of L2 with herbicides in acetonitrile. Combination of Gibbs energies and enthalpies led to the calculation of the entropies associated to the complexation process. Calorimetric titration curves for the titration of the herbicides with the receptor L2 in acetonitrile at 298 K were recorded **(Appendix B)**. Thermodynamic data for the complexation of L2 with the herbicides in acetonitrile are summarized in **Table 6**.

Table 6: Thermodynamics of complexation of L2 and herbicides in acetonitrile at 298.15 K

Complexes	Log K_s	$\Delta_c H^\circ$(kJ. mol^{-2})	$\Delta_c G^\circ$(kJ. mol^{-2})	$\Delta_c S^\circ$(J. mol^{-1}.K^{-1})	n
L2 + P1	4.49	-41.04	-25.65	-51.6	2. 18
L2 + P2	3.81	-21.37	-20.47	-16.4	2.12
L2 + P3	4.18	-38.90	-23.86	-50.45	2.17
L2 + P4	4.14	-32.42	-23.64	-29.43	2.21
L2 + P5	3.42	- 17.51	-19.53	6.77	2.07

Inspection of stability constant data (expressed as log K_s) shows that this ligand interacts selectively with herbicides in acetonitrile following the sequence

P1> P3 > P4 > P2

This decrease may be attributed to the presence of the phenol groups which may either (i) lead to steric effects by which the phenol units may form rigid walls restricting the easy access of the herbicides to interact with the the amino groups and ethoxy protons in the lower rim for calix[4]arene or (ii) to electronic effects, since the aromatic phenol rings may form an induced magnetic field which may act as a repulsive force for these anionic guests. It can be observed that the selective behaviour of L2 for P1 relative to other acid pesticides in this solvent. This is corroborated by the ^{1}H NMR data where significant chemical shift changes were found in H-2, H-3, H-4, H-5, H-7, H-8, H-10 and H- 11 upon complexation of L2 with these acid pesticides.

A general analysis of the thermodynamic parameters shows that the complexation process is favored in terms of enthalpy $\Delta H^\circ < 0$) but not in terms of entropy ($\Delta S^\circ < 0$) in all the above systems. Therefore, the complexation process is enthalpically controlled. The only exception is P5 which shows the opposite behaviour (entropy controlled). This may be attributed to the higher desolvation that the pesticide undergoes upon complexation. The data in **Table 6** show the ΔG° values are obtained for the L2 and the different herbicides studied in acetonitrile are close to each other.

IV. Conclusions

From the above discussion on the calix[4]arene derivative, the following conclusion can be drawn. The ligand under investigation (L2) were successfully synthesised in good yields and characterized by ^{1}H NMR. From ^{1}H NMR studies, it is concluded that L2 interact with herbicides. Therefore, in this study, it is essential to investigate the factors why other receptors did not interact with these herbicides. The presence of the amino groups (basic) in the lower rim for calix[4]arenes makes these ligands attractive for exploring their complexation with herbicides. The ^{1}H NMR technique was successfully used for establishing the binding sites and the conformational changes that these ligands undergo upon complexation with the herbicides.

The interaction of 5, 11, 17, 23- tetra- butyl- 25, 27-bis(diethylamino)ethoxy-26, 28- (bis- methoxyethoxy) calix[4] arene (L2) with several acid herbicides were carried out in different solvents at 298 K.

From **Tables 2 - 4**, the results obtained seem to indicate that the sites of interaction of this ligand with the acid herbicides are amine group and ethoxy group. Indeed significant chemical shift changes in the proton close to the amine group and ethoxy group were observed. Stoichiometries of 2:1 (acid herbicides:ligand) were found in CD_3CN , CD_3OD and CD_3Cl.

Conductomeric measurements were carried out with the aim of determining the composition of the receptor-acid herbicides interaction and gaining information regarding the type and strength of interaction of these receptors with acid herbicides in acetonitrile at 298 K. From the conductance measurements of the acid herbicide at different concentration, it was concluded that these acids are highly associated in non-aqueous solvents.

Nano isothermal titration calorimetry is the most powerful tool to determine the enthalpies of binding of various reactions, including herbicides-ligand binding. Isothermal titration calorimetry (ITC) provides the most accurate and direct measurement of the enthalpy of any reaction under isothermal and isobaric conditions. It is also the only method capable of determining the enthalpy, entropy, and the Gibbs free energy of a reaction in a single titration experiment. Future work will

involve the attachment of the receptor to a solid support to generate recyclable materials for herbicides removal.

V. Acknowledgments

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Author Contributions

Author contributions designed and performed experiments, prepared figures, analysed data and wrote the paper.

Conflicts of Interest

The author declares no conflict of interest.

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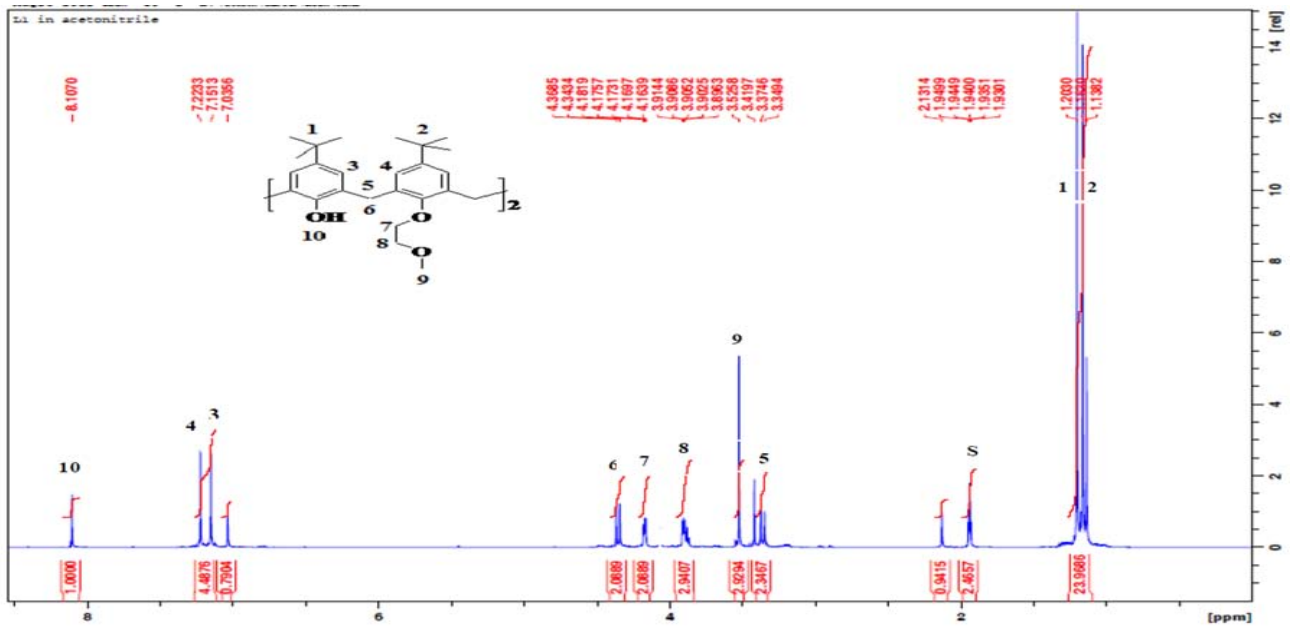
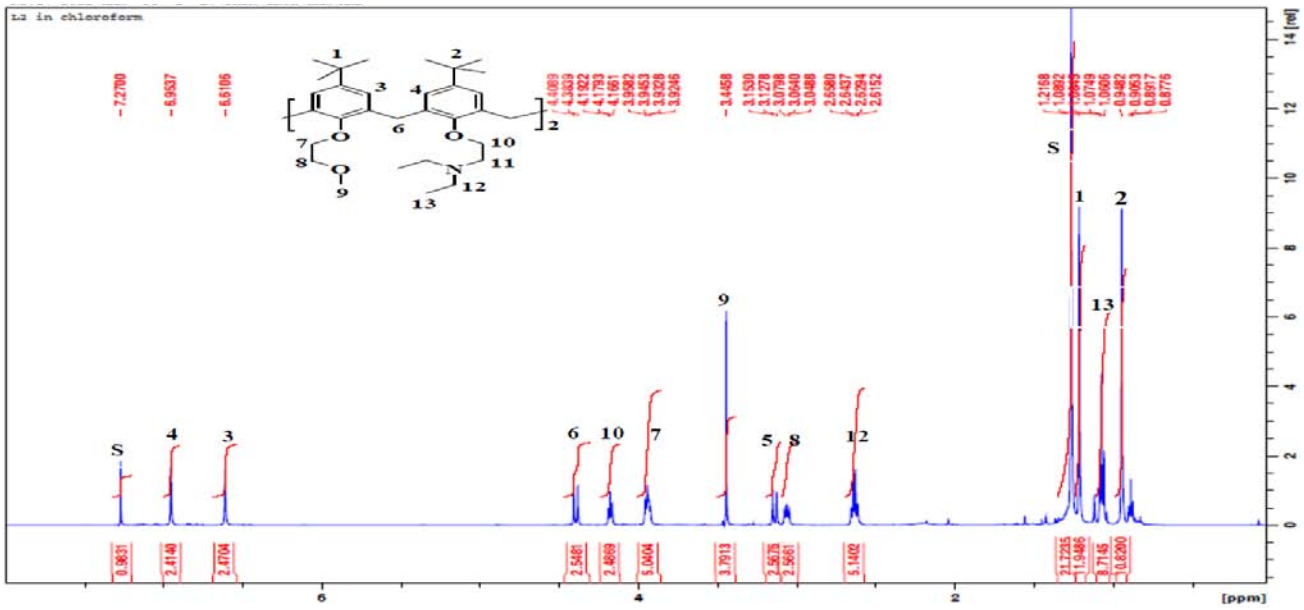
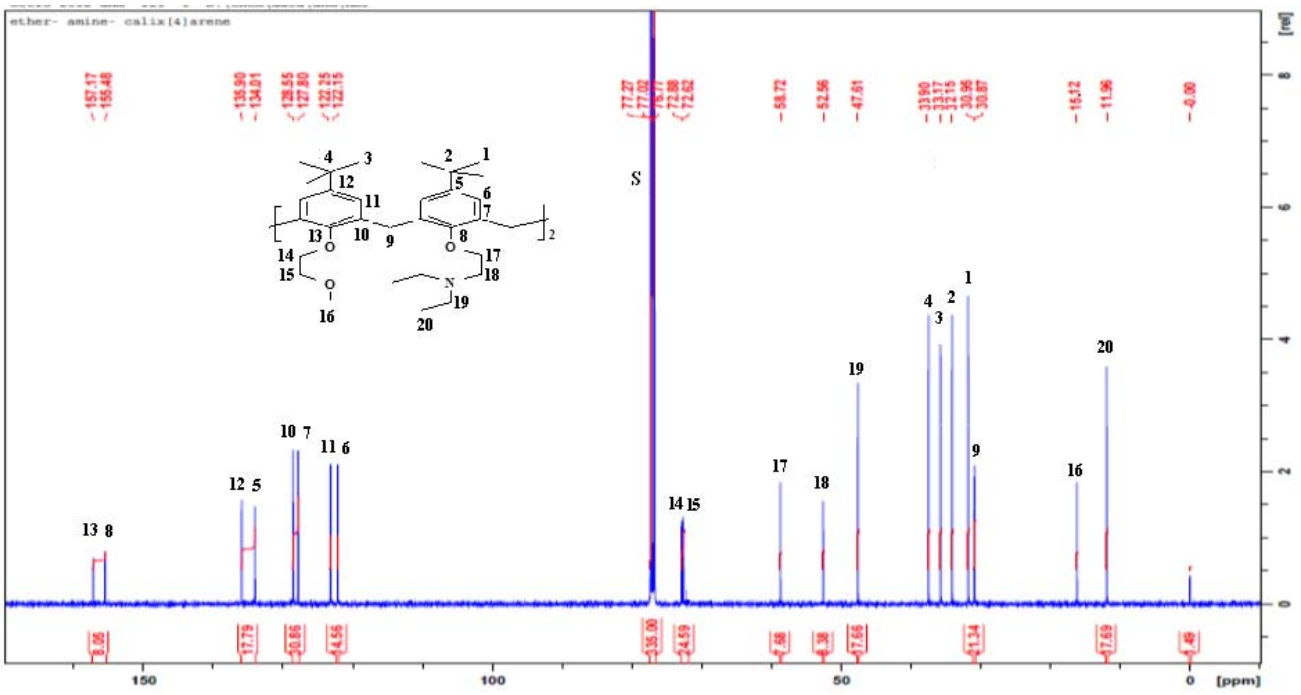
(Appendix A)



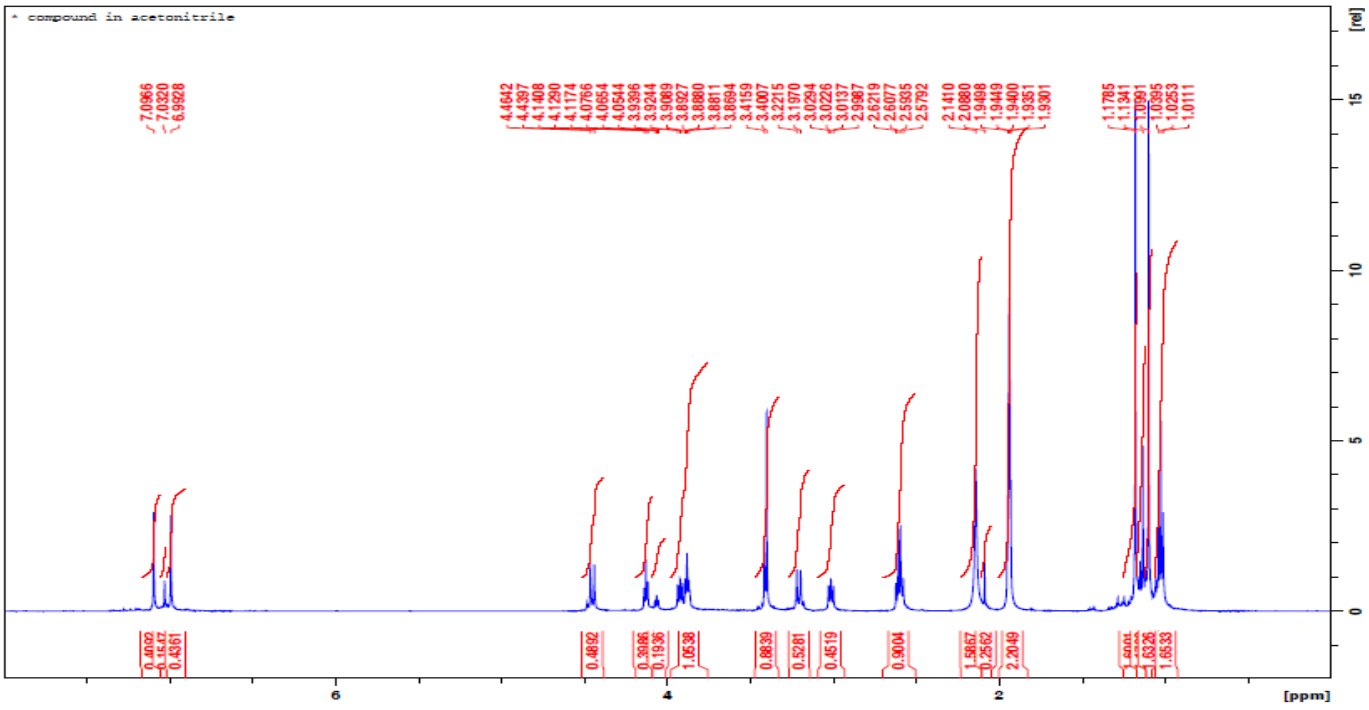
^{1}H NMR spectrum of L1 in CD_3CN at 298 K



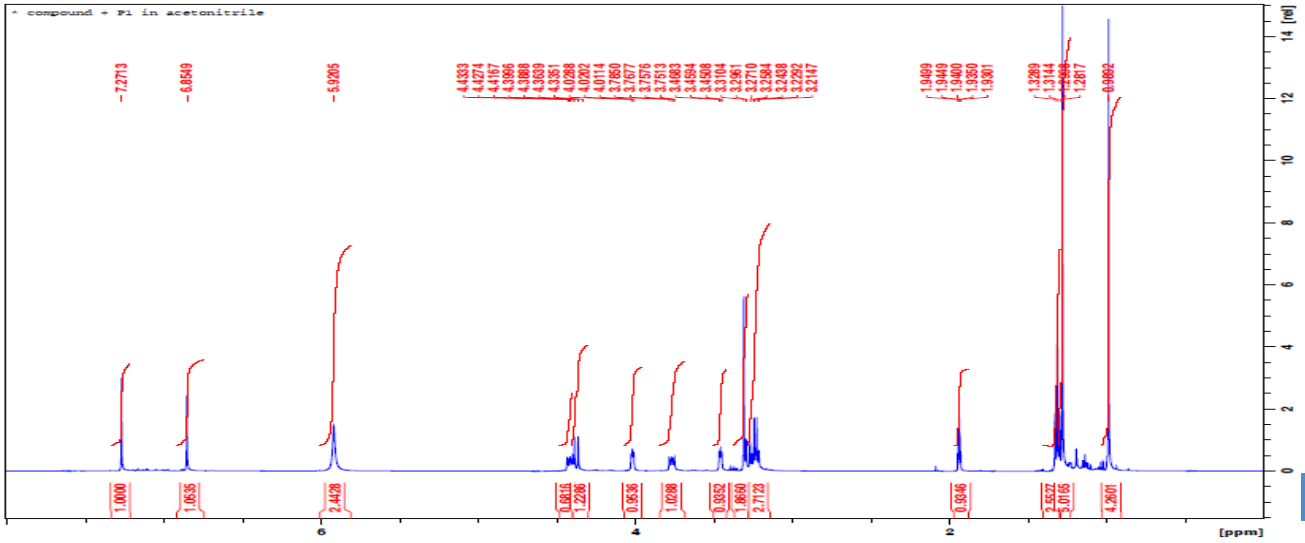
^{1}H NMR spectrum of L2 in $CDCl_3$ at 298 K



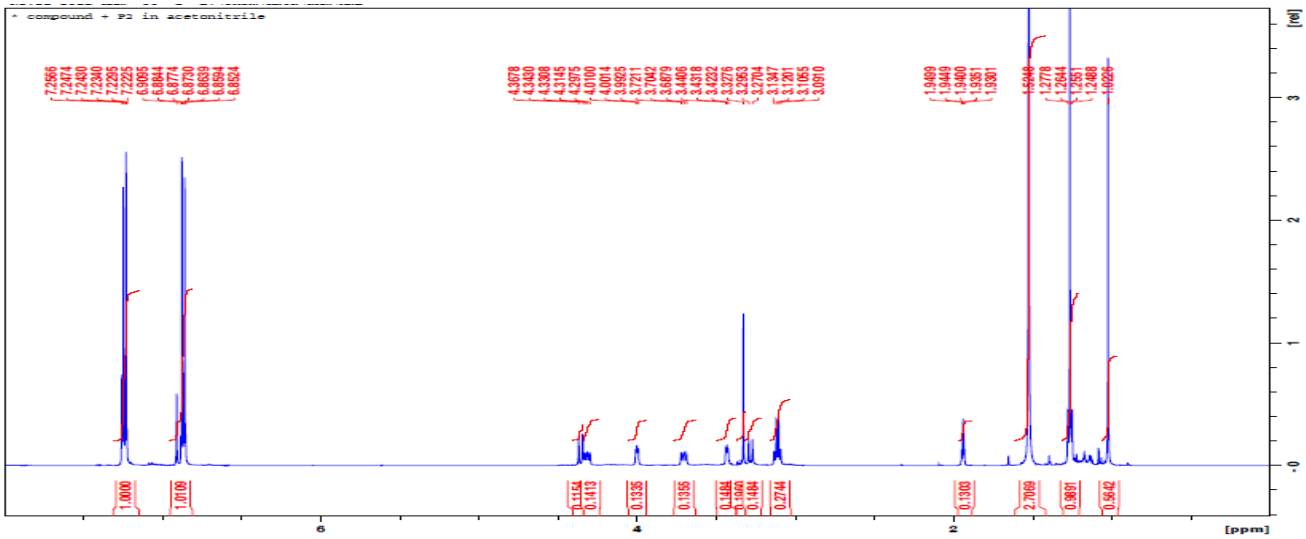
^{13}C NMR spectrum 5,11,17,23-tetra-butyl 25,27-bis(diethylamino)ethoxy-26,28-(bis-methoxyethoxy)calix[4]arene, L_2 in $CDCl_3$ at 298 K



^{1}H NMR spectrum of L2 in CD_3CN at 298 K



^1H NMR spectrum of L2 + P1 in CD_3CN at 298 K



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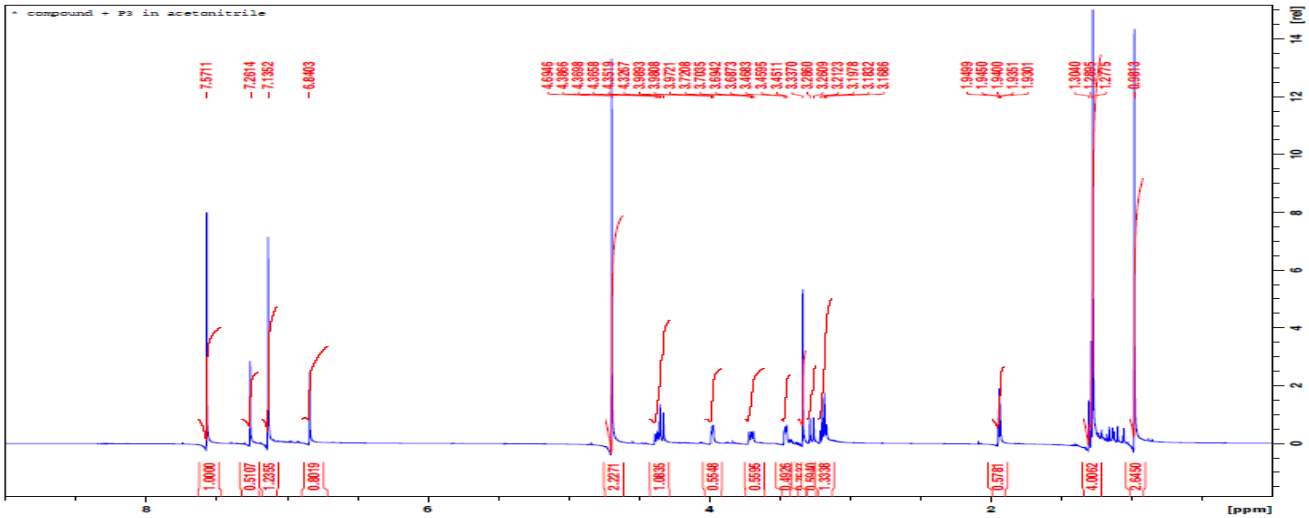
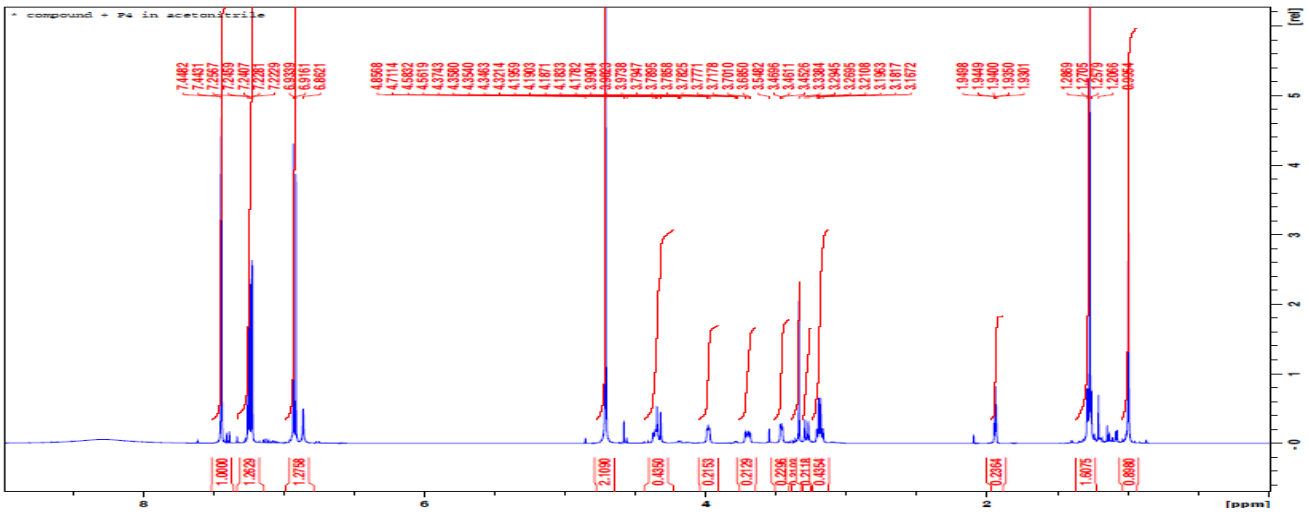
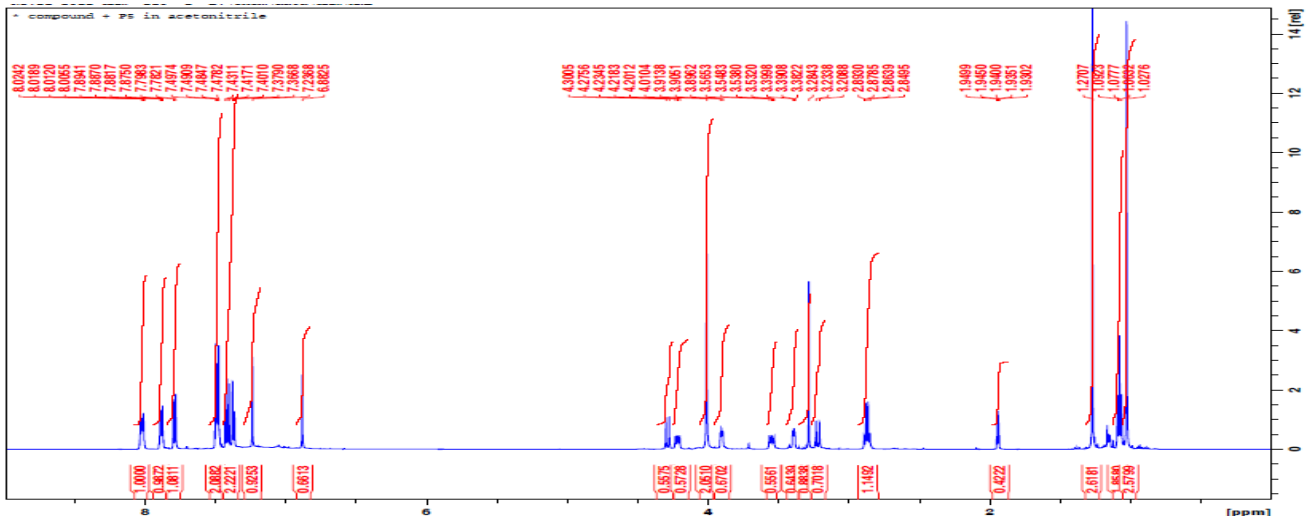


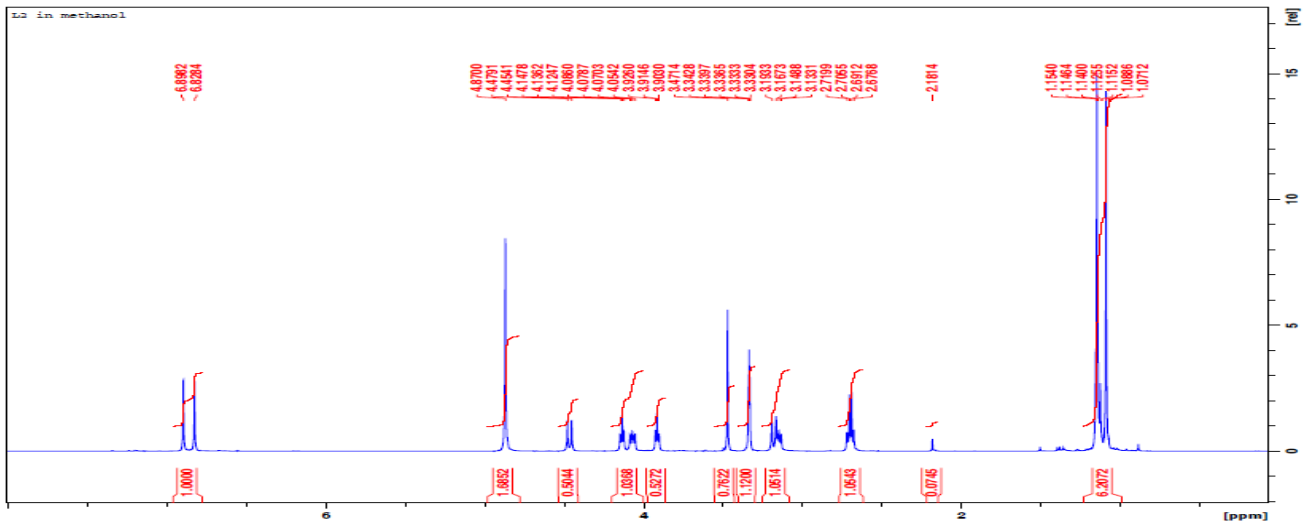
^1H NMR spectrum of L2 + P3 in CD_3CN at 298 K



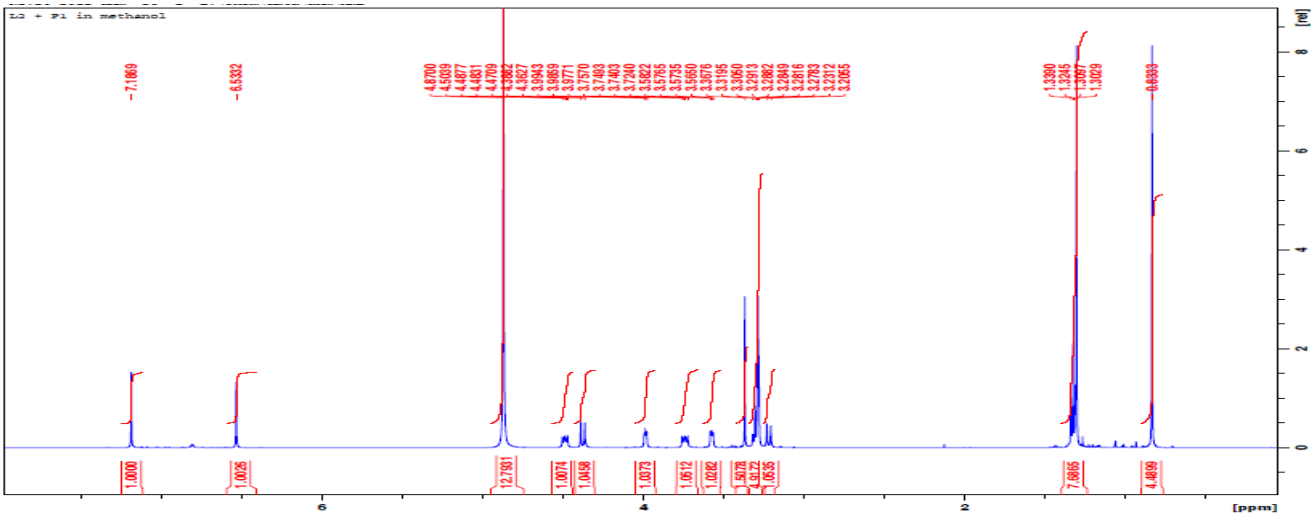
^{1}H NMR spectrum of L2 + P4 in CD_3CN at 298 K



^{1}H NMR spectrum of L2 + P5 in CD_3CN at 298 K



^{1}H NMR spectrum of L2 in CD_3OD at 298 K



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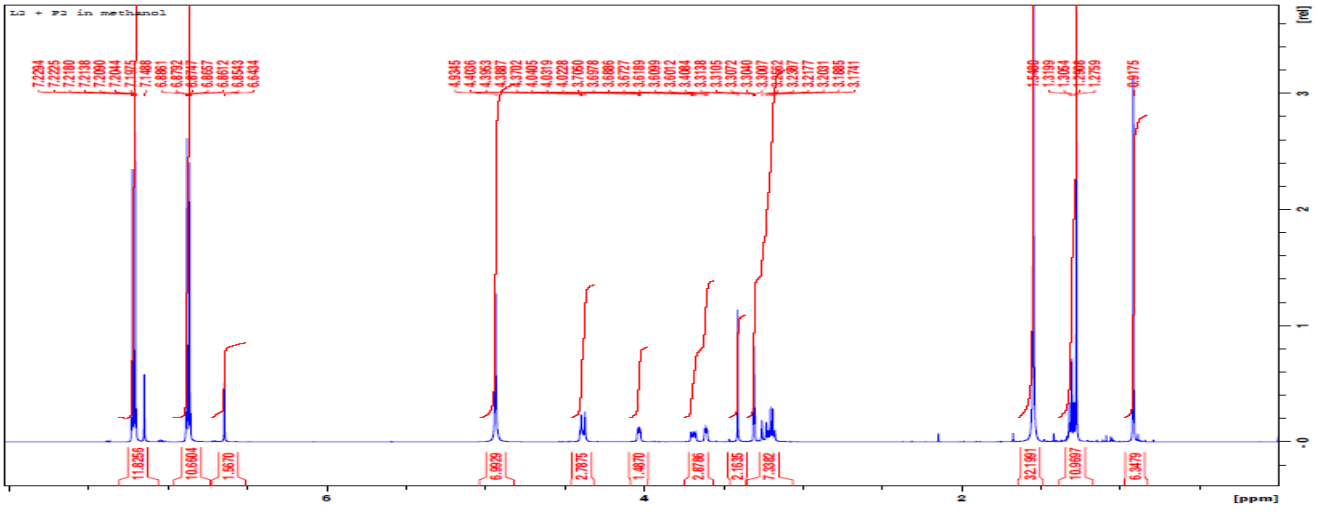

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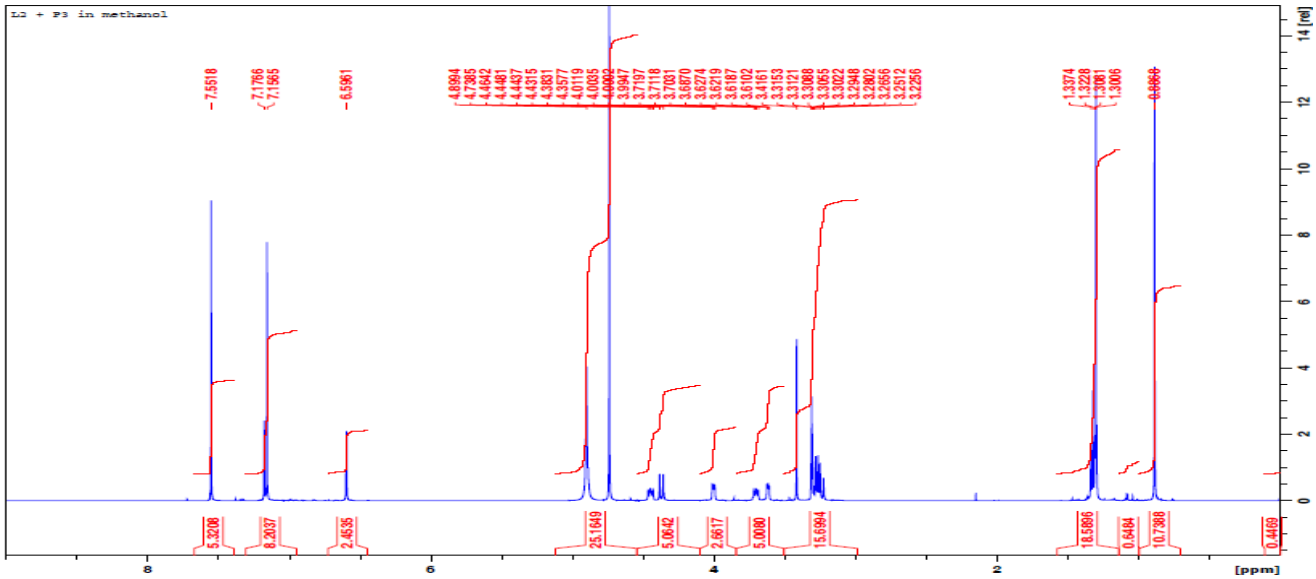

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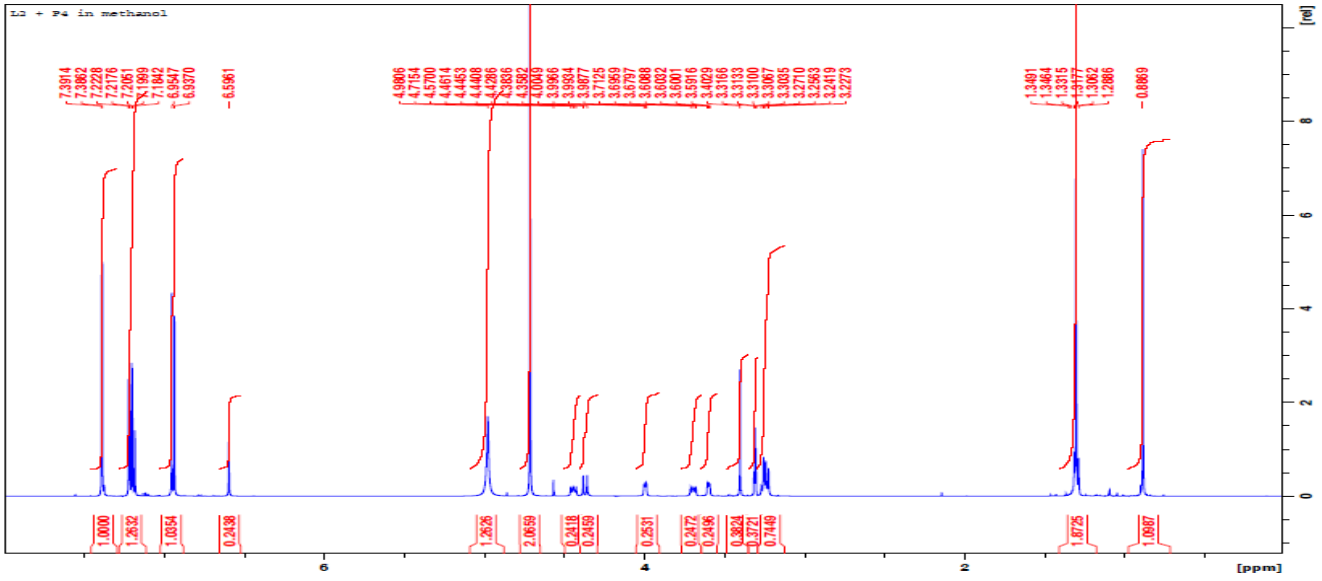
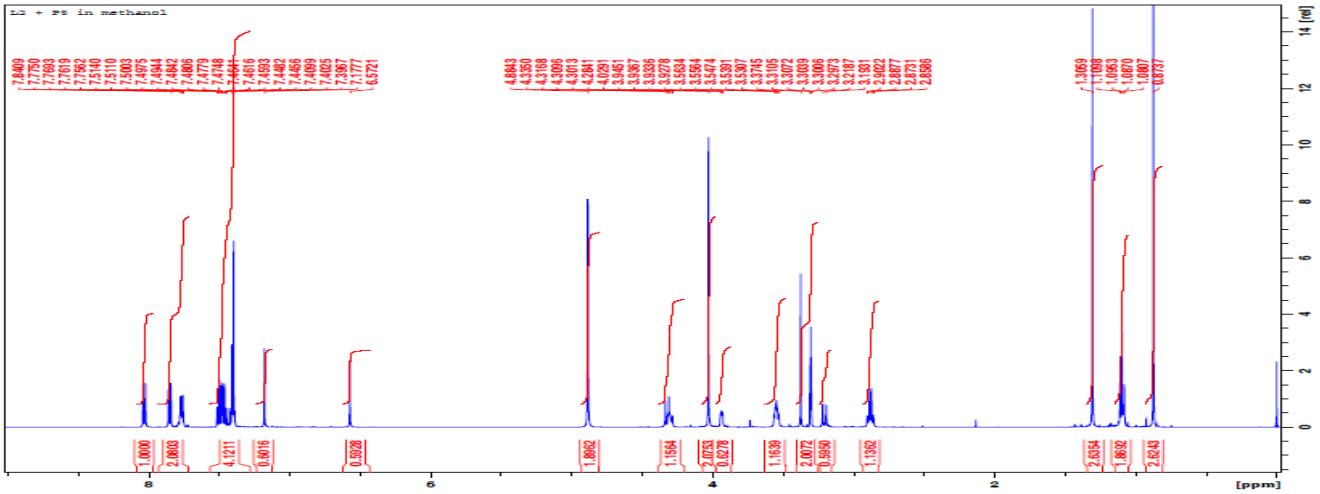
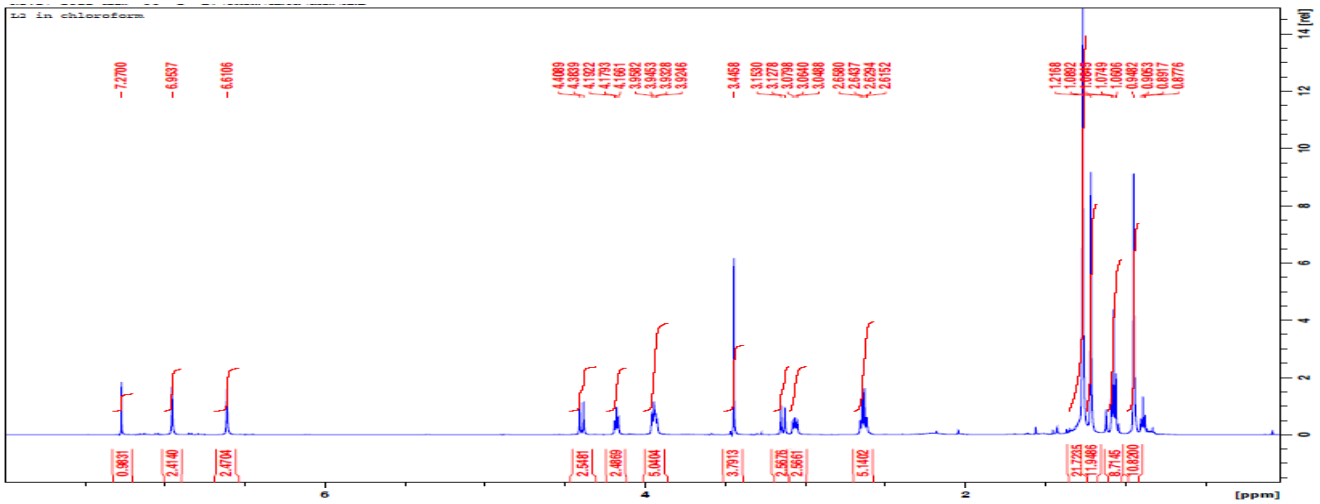


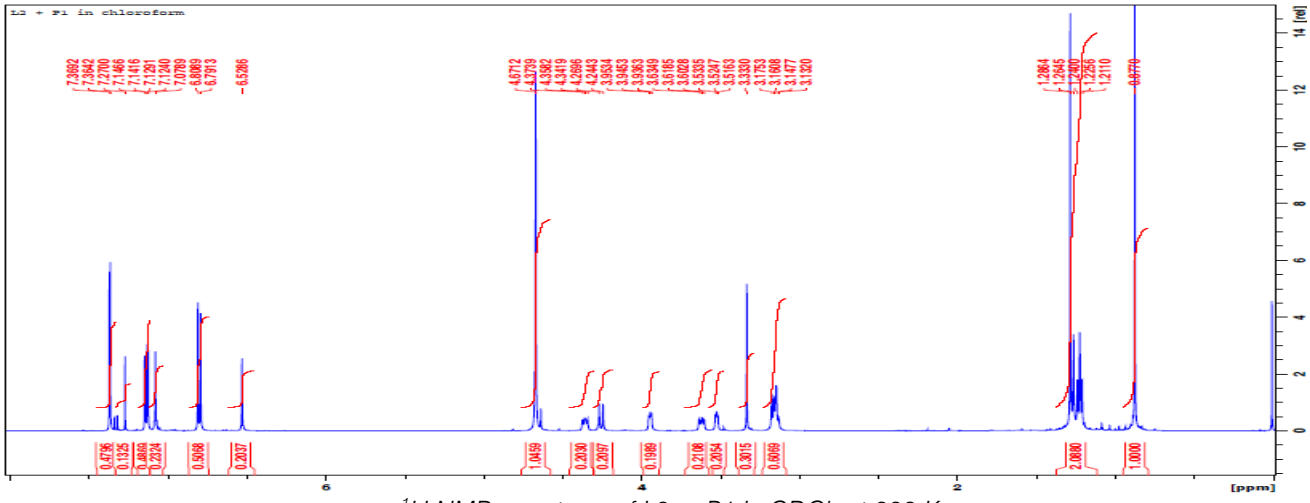
^{1}H NMR spectrum of L2 + P4 in CD_3OD at 298 K



^{1}H NMR spectrum of L2 + P5 in CD_3OD at 298 K



^{1}H NMR spectrum of L2 in $CDCl_3$ at 298 K



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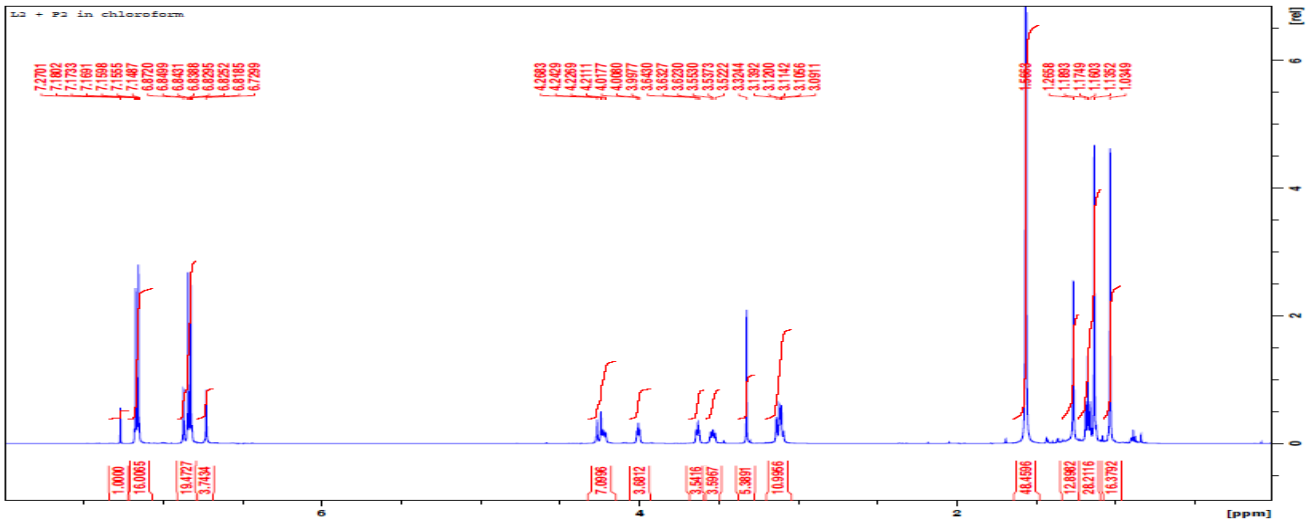
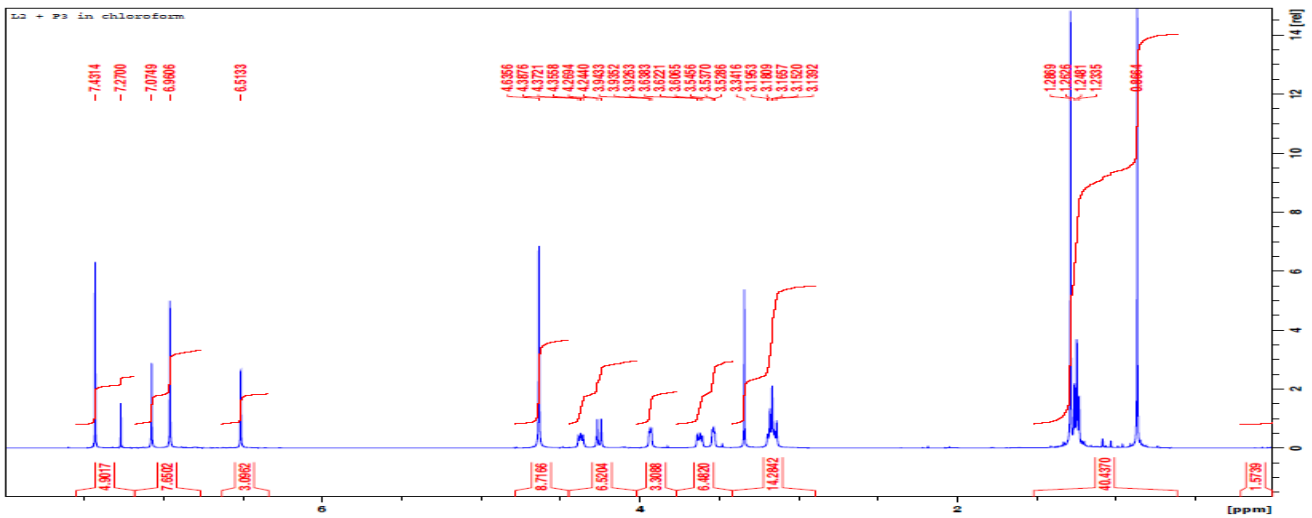
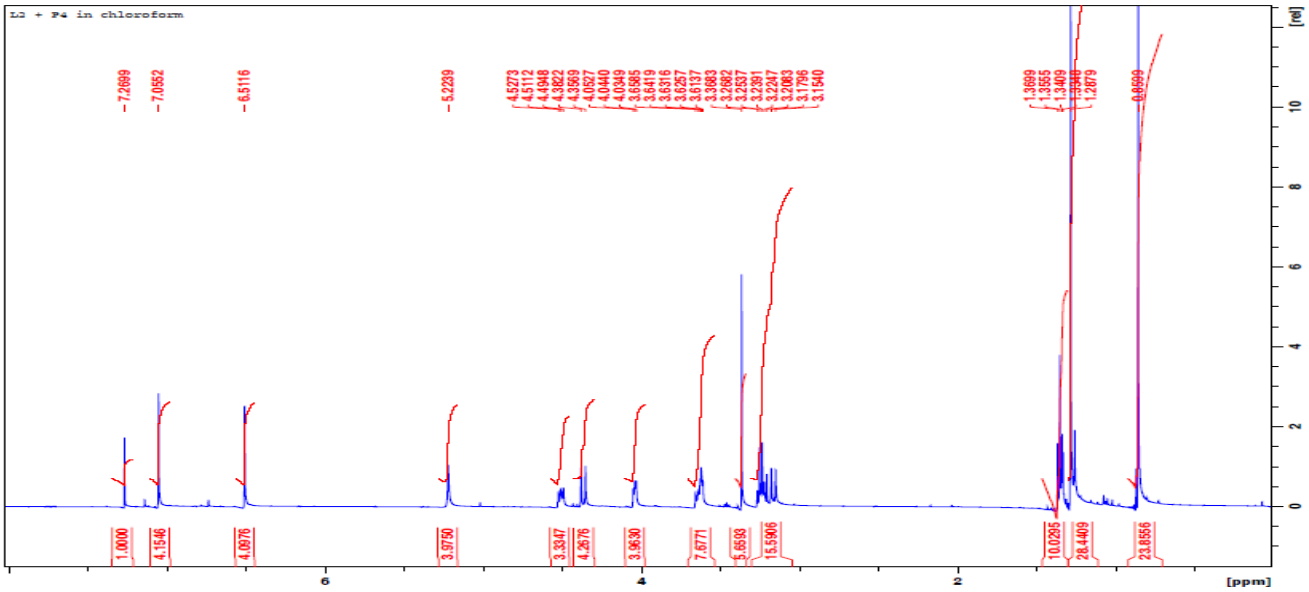


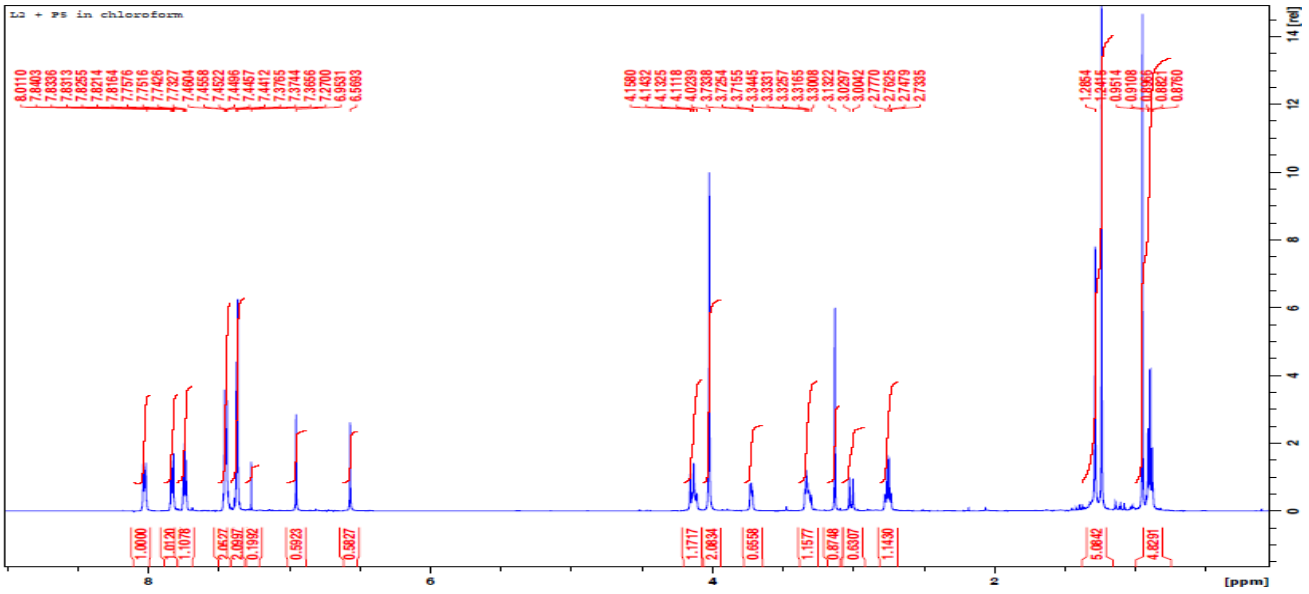
^{1}H NMR spectrum of L2 + P2 in $CDCl_3$ at 298 K



^{1}H NMR spectrum of L2 + P3 in $CDCl_3$ at 298 K

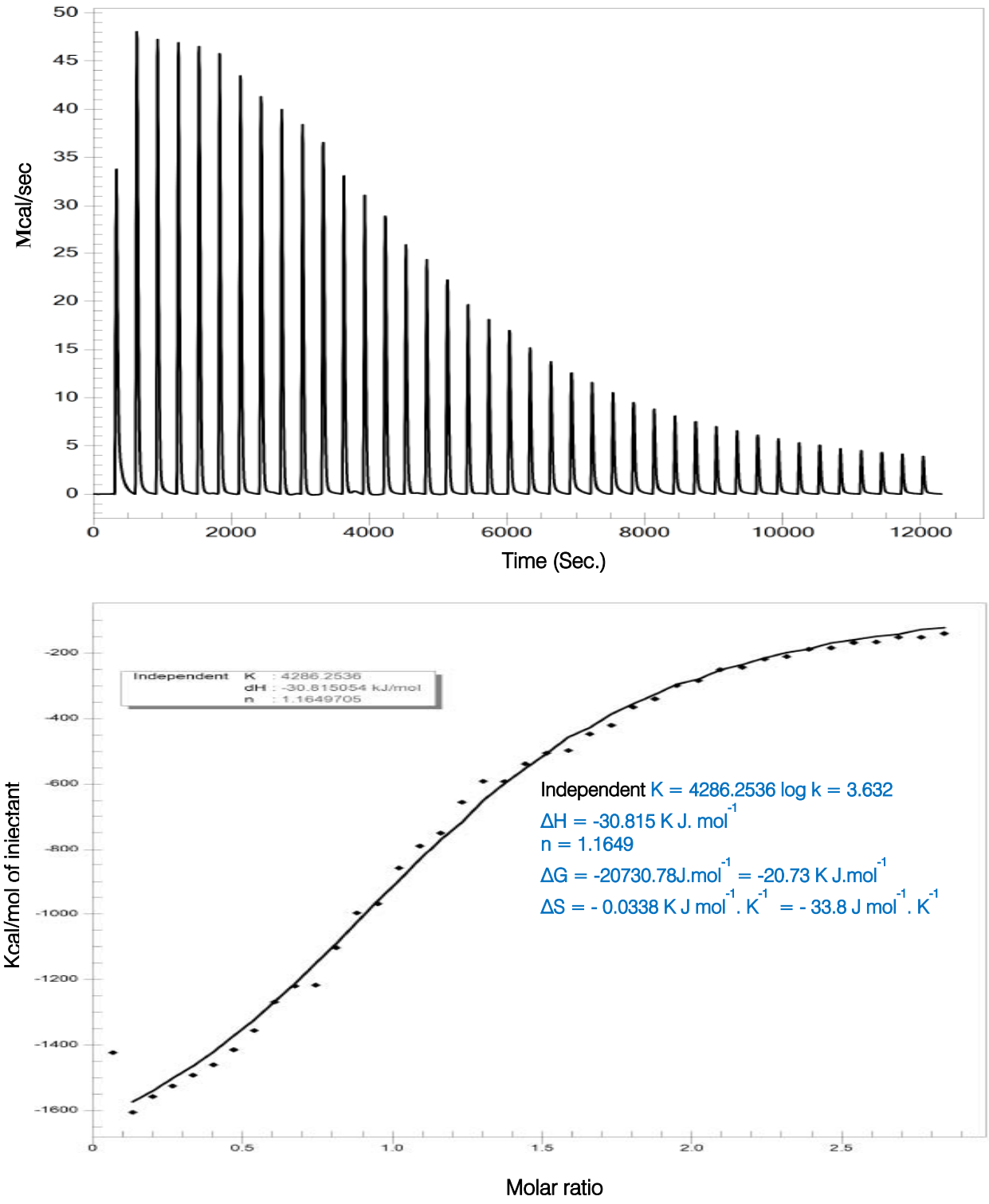


^1H NMR spectrum of L2 + P4 in $CDCl_3$ at 298 K

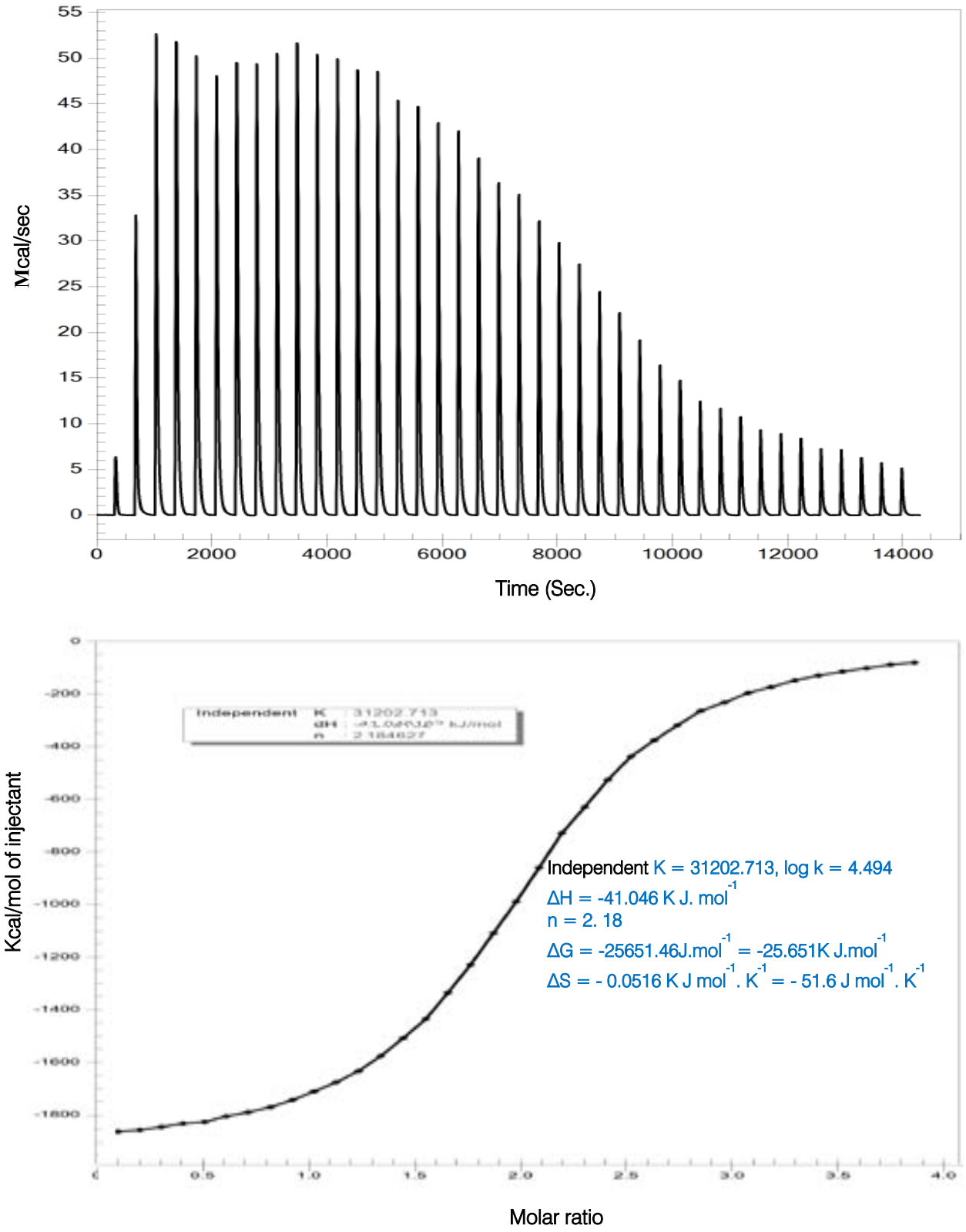


^1H NMR spectrum of L2 + P5 in $CDCl_3$ at 298 K

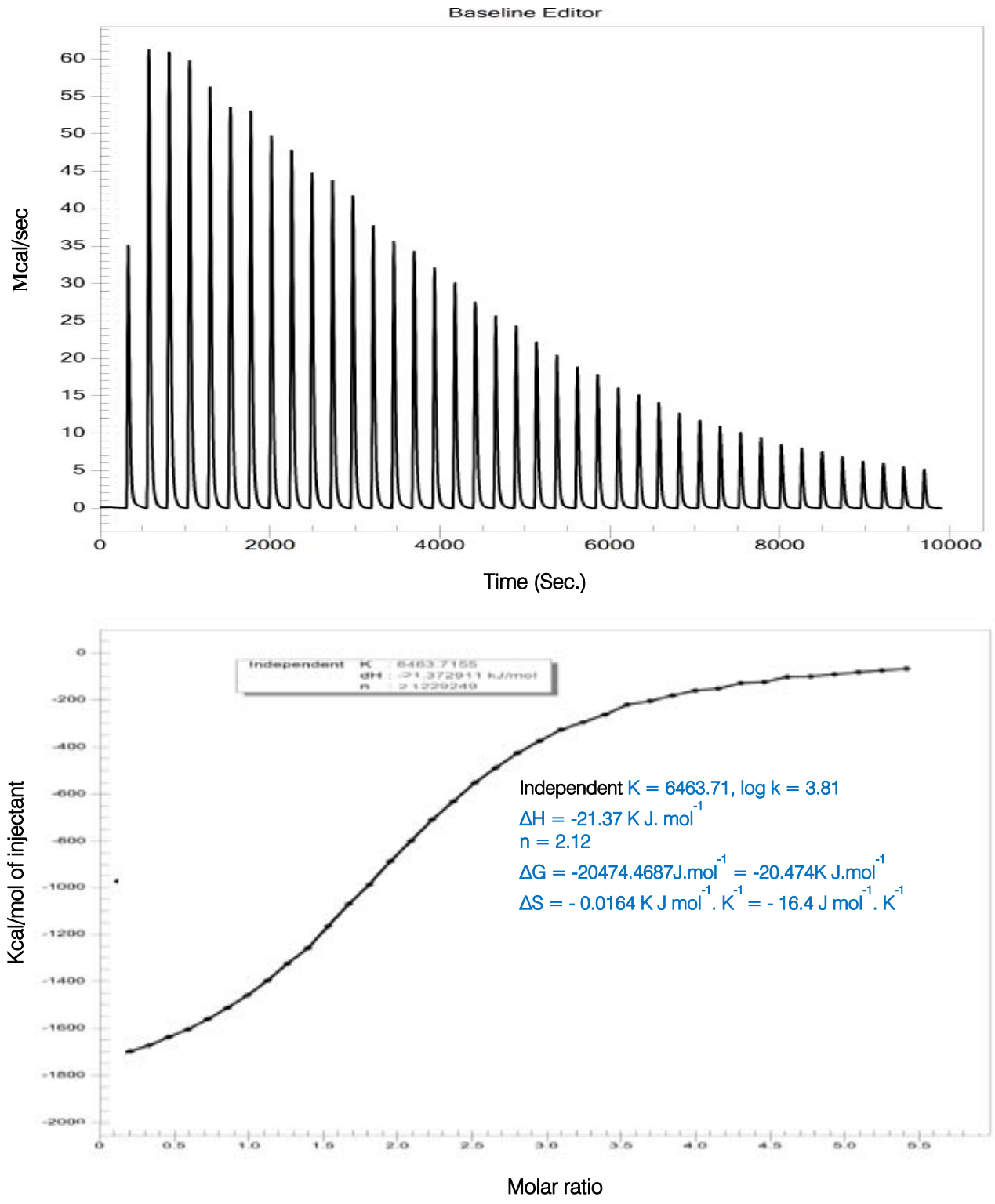
(Appendix B)



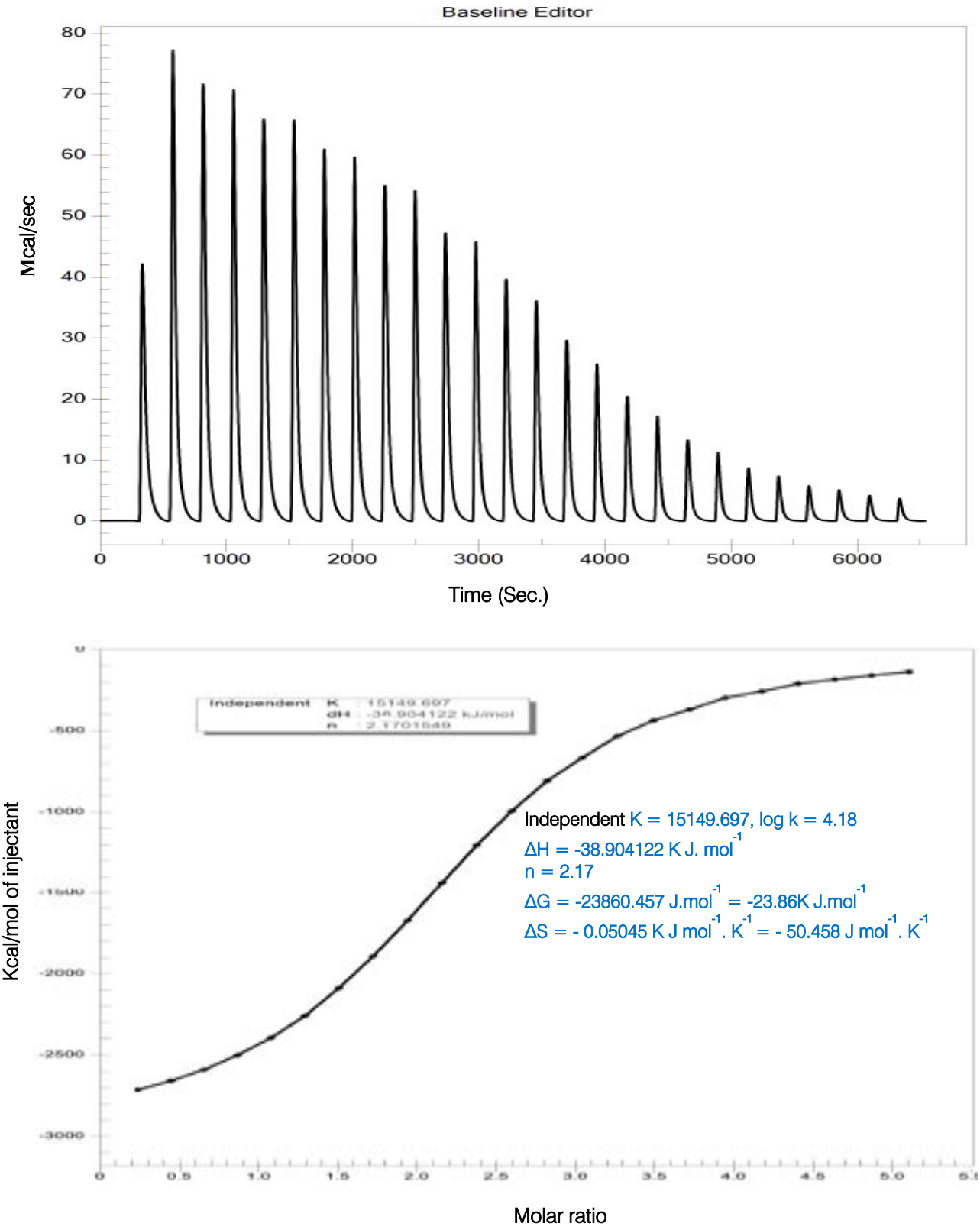
Representative calorimetric titration curves. The upper curve was obtained by titrating 18-crown-6 with Ba^{+2} in deionized water.



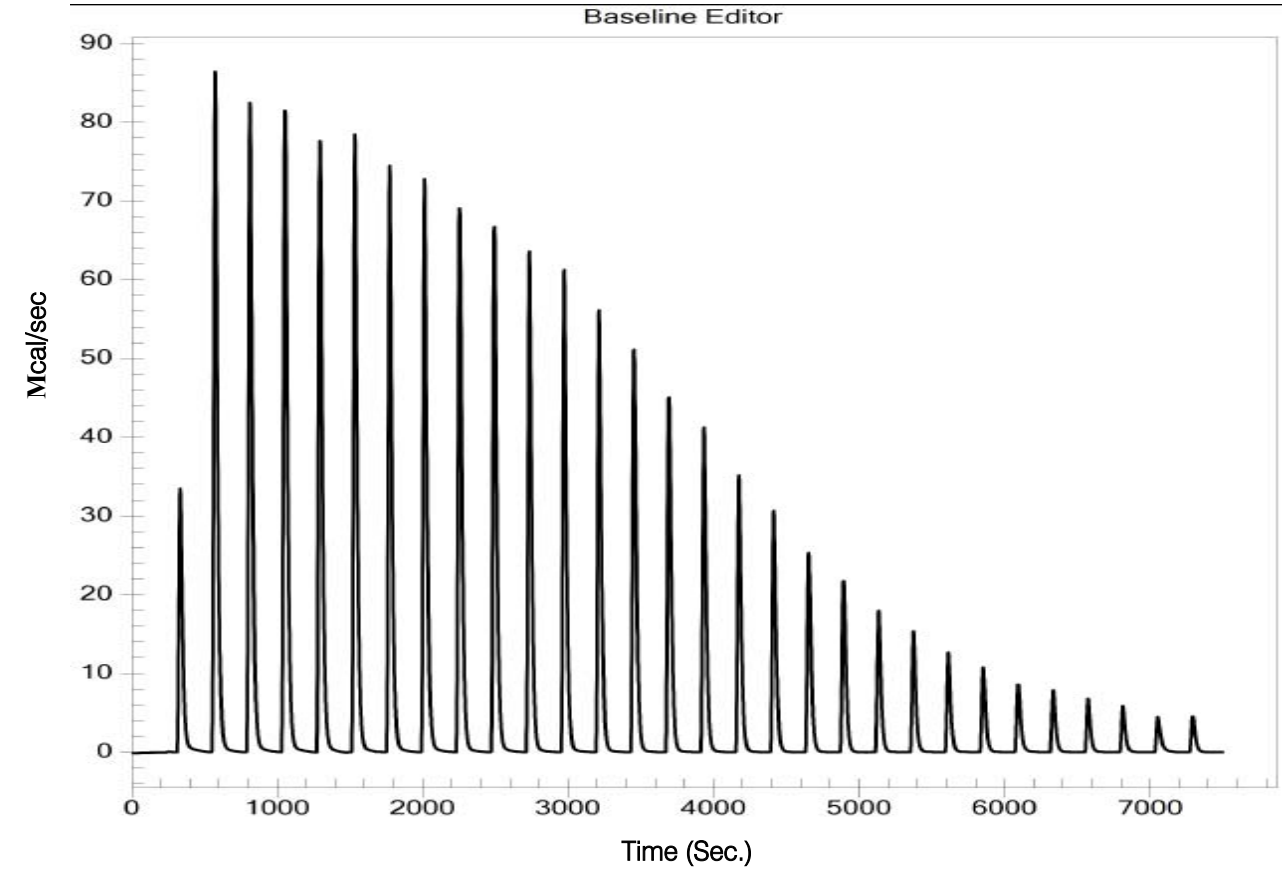
Representative calorimetric titration curves. The upper curve was obtained by titrating receptor 5 withP1 [Picloram].

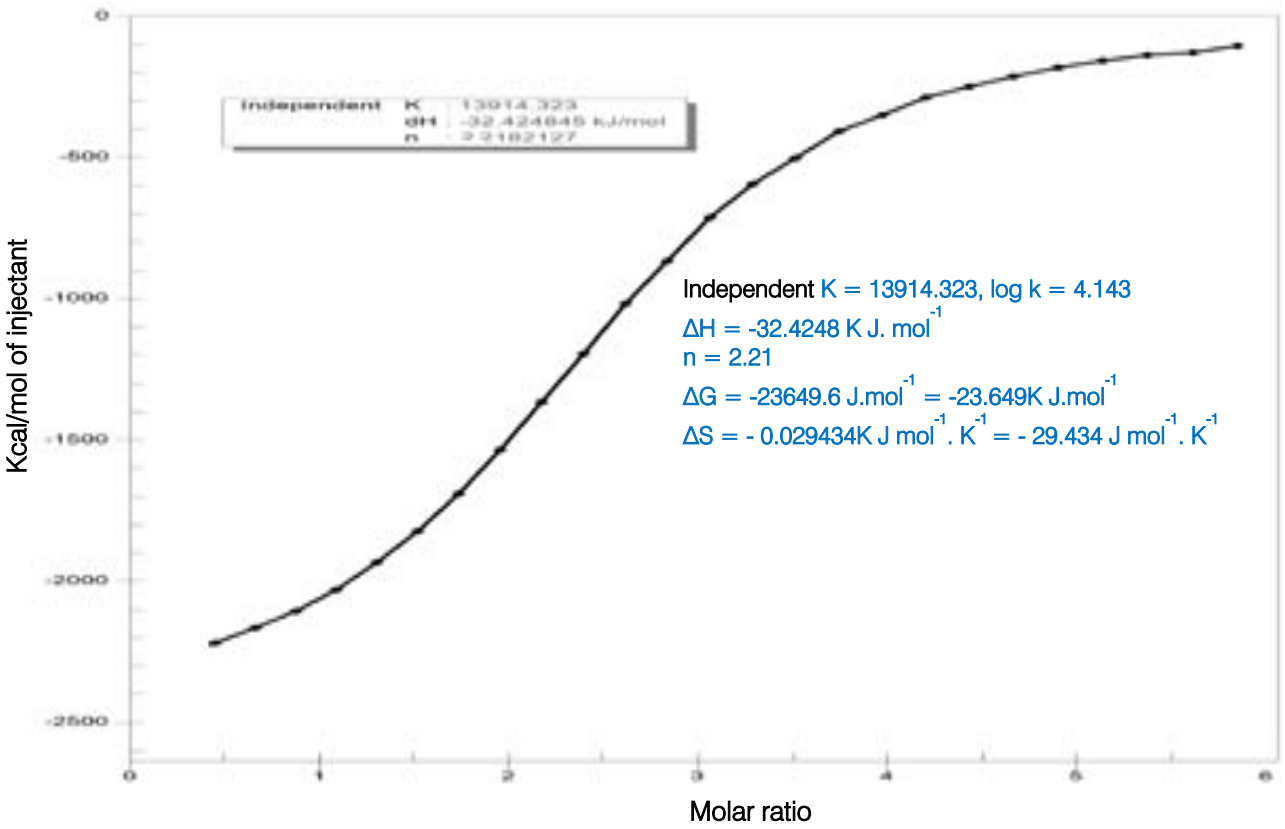


Representative calorimetric titration curves. The upper curve was obtained by titrating receptor 5 with P2 [Clofibric acid].

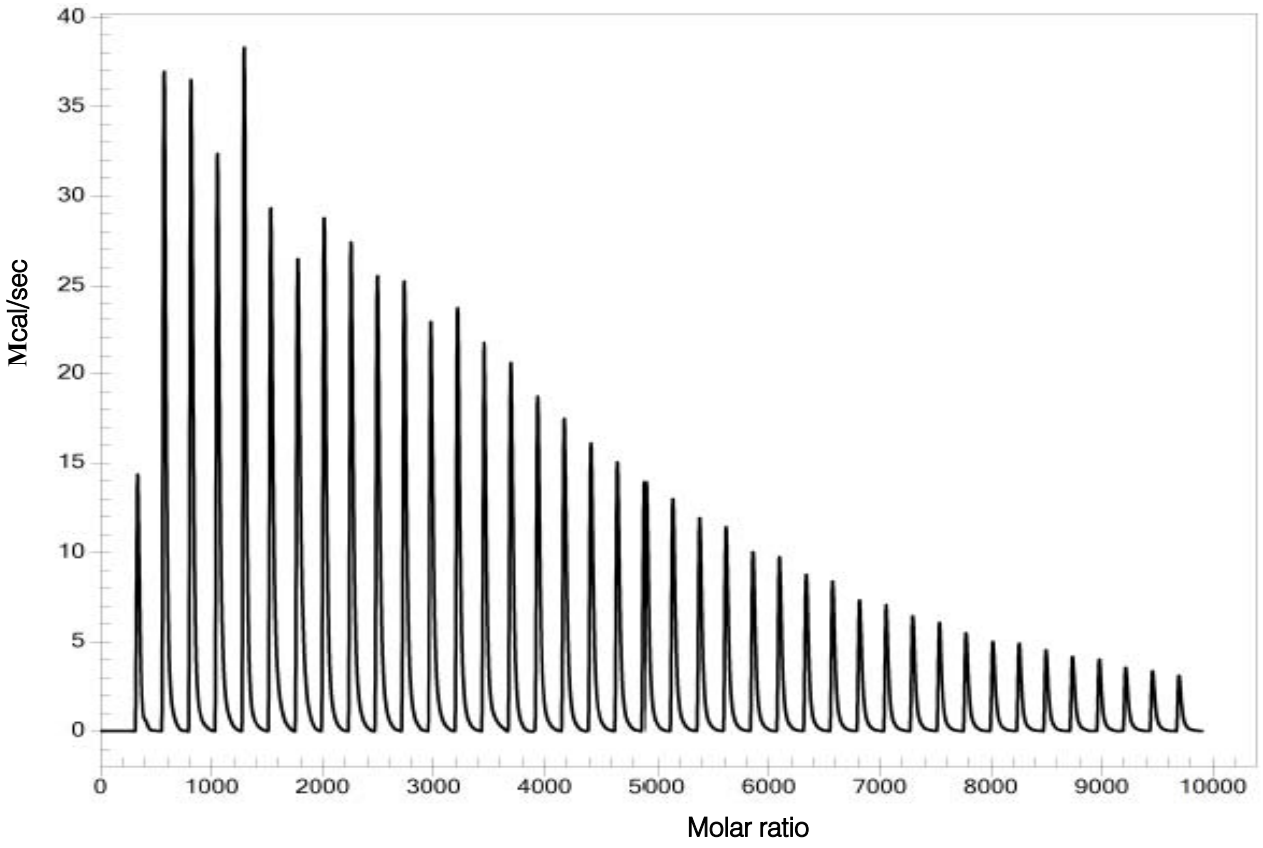


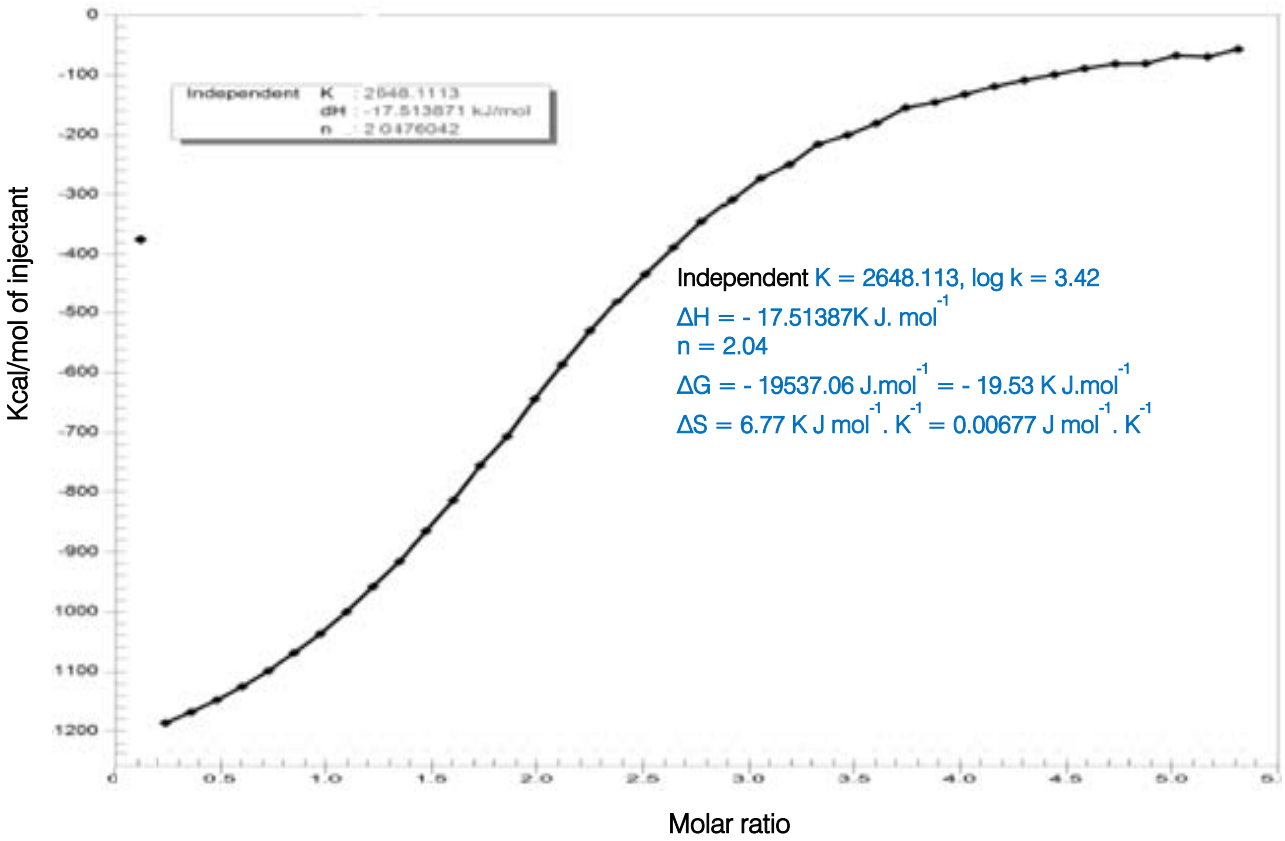
Representative calorimetric titration curves. The upper curve was obtained by titrating receptor 5 with P3 [2, 4, 5 - T].





Representative calorimetric titration curves. The upper curve was obtained by titrating receptor 5 with P4 [2,4, - T].





Representative calorimetric titration curves. The upper curve was obtained by titrating receptor 5 with P5.

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Electro-Oxidation of Methanol at Copper and Nickel Modified Clay Electrodes

By N. Kouider, J. Bengourram, M. Mabrouki & A. Chtaini

University Sultan Moulay Slimane, Morocco

Abstract- Cu/Clay/316L and Ni/Clay/316L anodes were prepared by the electroplating of a Cu and Ni catalyst layer onto Clay/Stainless Steel plates for a direct methanol fuel cell (DMFC). The morphology and structure of the catalyst layers were analyzed by AFM and Optical microscopy. The catalyst coating layer shows an alloy character. The results show that oxides formation at the electrode surface is necessary for the methanol oxidation.

Keywords: modified electrodes; catalyst; DMFC, square wave voltammetry.

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Electro-Oxidation of Methanol at Copper and Nickel Modified Clay Electrodes

N. Kouider [α], J. Bengourram [σ], M. Mabrouki [ρ] & A. Chtaini [ω]

Abstract- **Cu/Clay/316L and Ni/Clay/316L anodes were prepared by the electroplating of a Cu and Ni catalyst layer onto Clay/Stainless Steel plates for a direct methanol fuel cell (DMFC). The morphology and structure of the catalyst layers were analyzed by AFM and Optical microscopy. The catalyst coating layer shows an alloy character. The results show that oxides formation at the electrode surface is necessary for the methanol oxidation.**

Keywords: modified electrodes; catalyst; DMFC, square wave voltammetry.

I. Introduction

Fuel cells are efficient and environmentally acceptable conversion devices. Electric current is generated in the fuel cell by the direct electrochemical oxidation of either hydrogen (proton exchange membrane fuel cell, PEM) or methanol (Direct Methanol Fuel Cell, DMFC). The electrochemical processes that yield energy are essentially pollution free. Water formed during operation of the device is beneficial in space travel and submarines. Various applications of fuel cells range from stationary (individual homes or district schemes) or mobile (transportation as cars, buses, etc.) to mobile phones and lap top computers [1, 2]. Hydrogen is currently the only practical fuel for use in the present generation of fuel cells. The main reason for this lies in its high electrochemical reactivity compared with that of the more common fuels from which it is derived, such as hydrocarbons, alcohols, or coal. Also, its reaction mechanisms are now rather well understood [3, 4] and are characterized by the relative simplicity of its reaction steps, which lead to no side products. Pure hydrogen is attractive as a fuel, because of its high theoretical energy density, its innocuous combustion product (water), and its unlimited availability as a suitable source of energy available to decompose water. One of the disadvantages of pure hydrogen is its low density gas under normal conditions, so that storage is difficult and requires considerable excess weight with regard to that of liquid fuels. Methanol has been considered for fuel cell power generation for a number of years because it can be processed into a hydrogen-rich fuel gas fairly, easily and efficiently, by steam or auto thermal reforming. Methanol, as a liquid fuel is easily transported and stored in comparison to hydrogen gas. The methanol fuel has a superior specific energy density (6000 Wh/kg) with regard to the best rechargeable battery, lithium polymer and lithium ion polymer (600 Wh/kg) systems. This means longer conservation times using mobile phones, longer times for laptop computers' usage and more power available on these devices to support consumer demand. Another significant advantage of the direct methanol fuel cells over the rechargeable battery is their potential for instantaneous refuelling [5-7]. The performance of direct ethanol fuel cells (DEFCs) is still limited by the electrocatalysts available for ethanol oxidation, which are mostly based on expensive noble metals such as platinum or its alloys[8-11]. Past research on the development of DEFCs has focused mainly on the so-called PEMDEFCs that use PEM as the electrolyte, a Pt-based catalyst on the anode, and a pure Pt catalyst on the cathode [12-13].

The purpose of the present work is to establish the electro oxidation of methanol on stainless steel electrodes modified with respectively, by clay and copper and/or nickel in acidic solution.

II. Experimental Section

a) Apparatus

Electrochemical experiments were performed using a Voltalab Potentiostat (model PGSTAT100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (Voltalab master 4 software).

All the electrochemical experiments were performed in a standard one-compartment three-electrode cell. The reference electrode was SCE and the counter electrode was platinum. All electrode potentials were referred to this reference electrode. The working electrodes were copper modified kaolin/stainless steel and nickel modified /kaolin/ stainless steel.

b) Reagents and Solutions

All chemicals were of the highest quality. $CuSO_4$ and NiO were obtained from Merck chemicals. Deionized water was used to prepare all solution. Electrolytic solution is 0.1M H_2SO_4.

c) Preparation of the modified electrodes

Stainless steel (type 316L) plates were cut into rectangular strips with typical dimensions of 1 cm^2. The chemical composition of stainless steel investigated in

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this work is: (wt.%) C ≤ 0.02, Mo : 3.5-4.5, Cr: 24-26, Ni: 6-8, N ≥ 0.25, Fe remainder. Strips were abraded with SiC paper in successive grades from 400, 600 up to 1200 grit and then cleaned in distilled water and dried. The current was maintained by a galvanostat with a function generator. The anode electrode was a platinum wire, and a stainless steel electrode was used as cathode. Then, the electrodes were immersed in a glass chamber containing electrolyte of clay gel, and subjected to anodic oxidation by applying 100 mA for 6 hours. In the same way the Cu and Ni catalysts are deposited onto clay / stainless steel plate. Before each experiment, the electrode surface was activated via the cyclic voltammetry at scan rate of 500 mV/s for 20 cycles. The working electrodes (Ni-clay/stainless steel (Ni-arg-316L) and Cu-clay/stainless steel (Cu-arg-36L)) were sealed in Teflon jacket. The apparent surface area was calculated from geometrical area and the current density was referred to it.

III. Results and Discussion

a) Modified electrodes characterization

The prepared electrodes were imaged by AFM (Fig. 1) and optical microscopy (Fig. 2). The clay particles (Fig. 1-b) appear coagulated on stainless steel and their density is very important. It was observed that the powder layers exhibited a porous microstructure with micro pores, which were relatively well separated and homogeneously distributed over the surface. The films formed are continuous and not disintegrated from substrate surface.

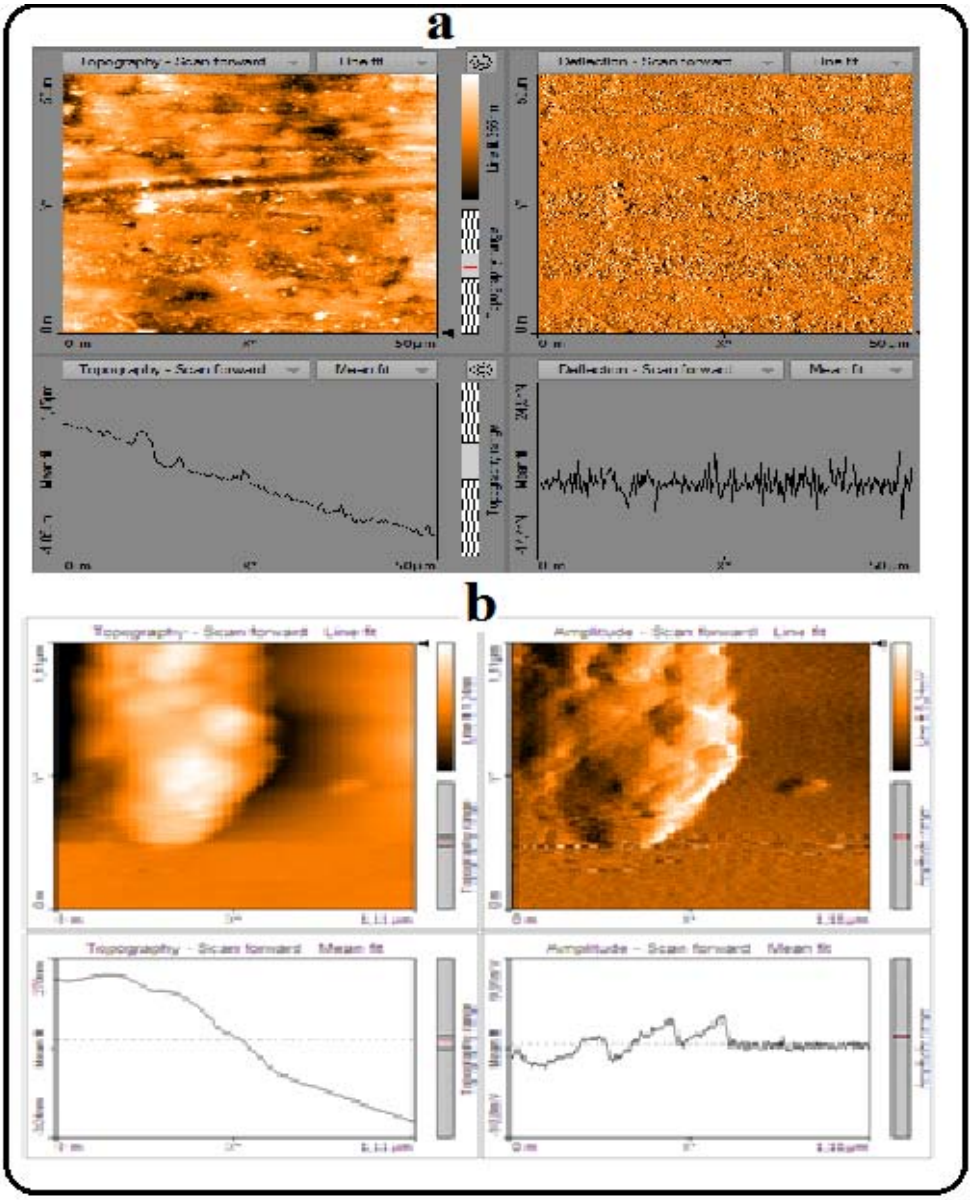

Figure 1 : Topography images of, a- stainless steel and b- clay/stainless steel

Copper is deposited electrochemically onto clay/316L surface; it forms a film continuous and porous. Copper deposit has very rough topography and it is deposited on the entire clay surface. Nickel clusters are deposited on the surface of clay/316L, they occupy sites clay conductors. Wecan observe discovered clusters of clay.

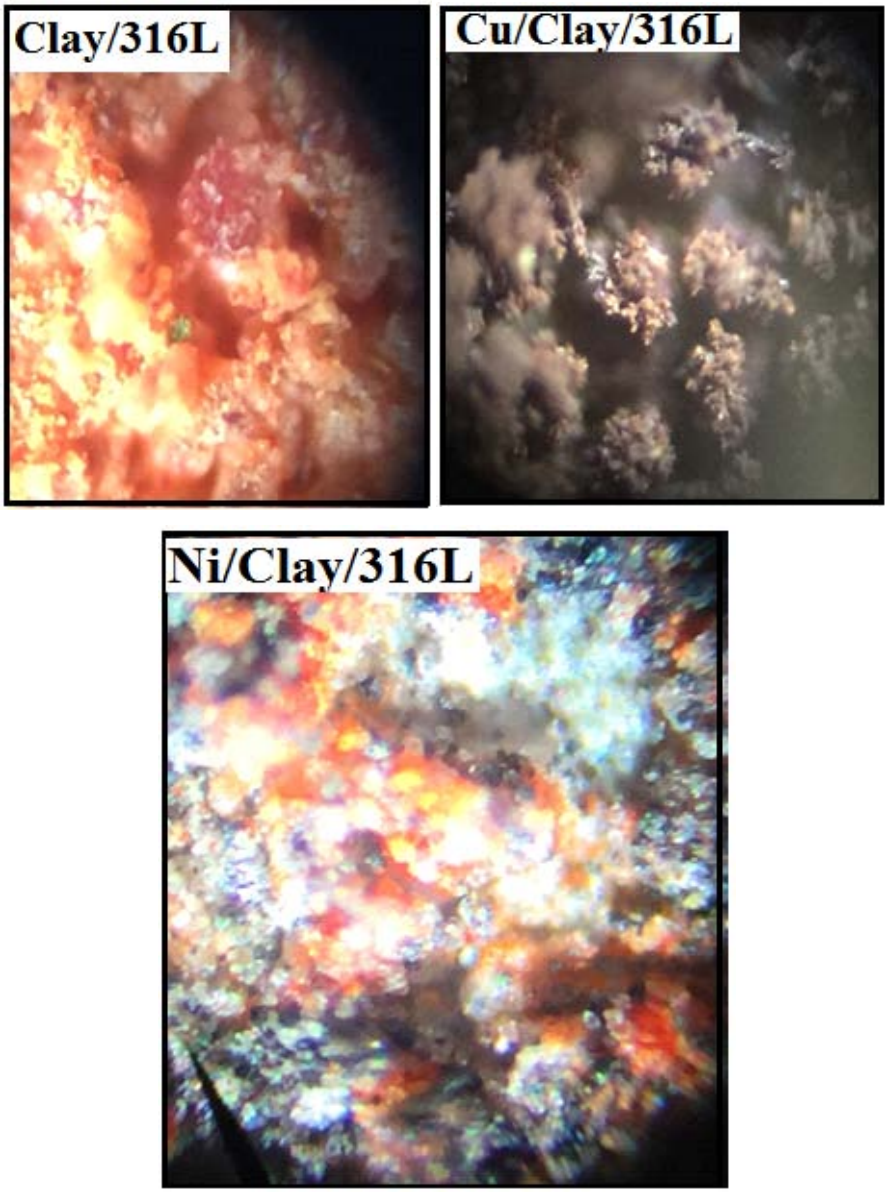

Figure 2 : Optical microscopy images

b) Methanol oxidation

The cyclic voltamma grams recorded respectively, for the Cu/clay/316L and Ni/clay/316L, in electrolytical solution, containing or not methanol, are shown in Figures 3 and 4. The CV was carried out to analyze the activity of the synthesized catalyst towards methanol electro oxidation in acidic media. As we can see, the presence of copper to the clay/316L surface generates elevated current densities in the presence of a small amount of methanol in the solution (Fig. 3-b). This phenomenon is confirmed by the square wave voltammetry SWV (Fig. 4). The SQW voltammetry has the advantage of increasing the sensitivity of an electrode by the cancellation of the capacitive term of the overall value of the current density. The SQW shows three peaks respectively, at -0.4 V, 0.3 V and about 1.4 V. The presence of methanol in the electrolytic solution (Fig. 4-b) increases the current density of the two peaks, 0.3V and 1.3V. These findings allow us to draw the following conclusions:

- In the absence of methanol, in the electrolytic solution, the first peak which appears on the SQW to -0.3V, corresponding to the reduction of the copper surface, while the peaks which appear successively at 0.1 and 1.4 V may correspond to the copper oxidation.

- The oxidation of methanol is encouraged by the formation of oxides on the copper surface.

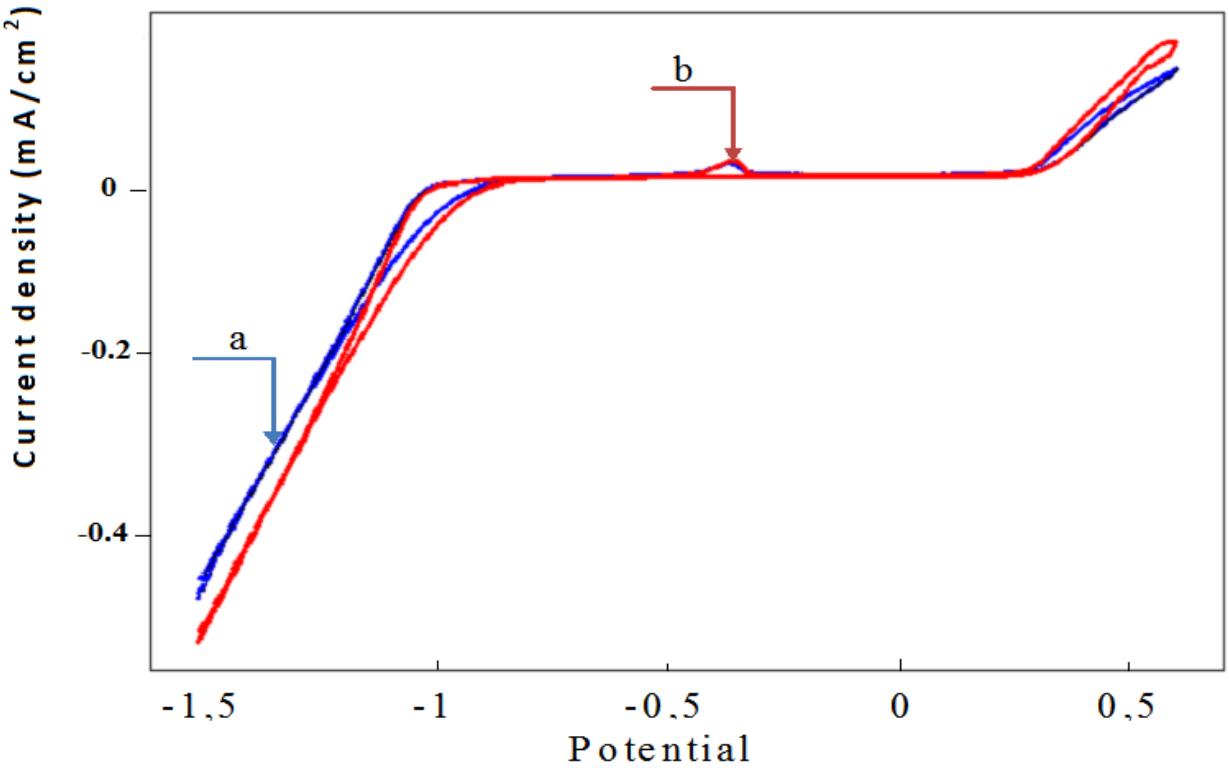

Figure 3 : Steady state cyclic voltammograms recorded for Cu/clay/316L, in 0.1M H_2SO_4 + 0.1 mmol methanol, scan rate 100mV.s^{-1}, at room temperature

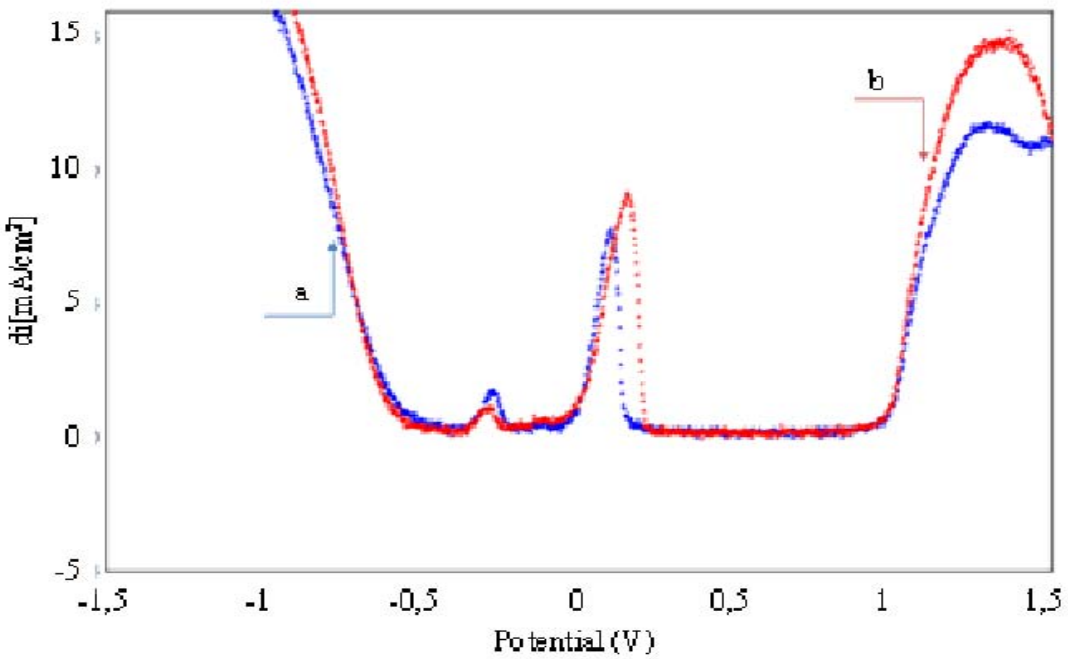

Figure 4 : SQW voltammograms recorded for Cu/clay/316L, in 0.1M H_2SO_4 + 0.1 mmol methanol

The Taffel lines recorded for the electrode Cu/Clay/316L, are represented in Figure 5. We find that the value of the equilibrium potential is shifted towards lower values in the presence of methanol in the solution, meaning that the reaction requires less energy, so (that) the reaction rate is increased.

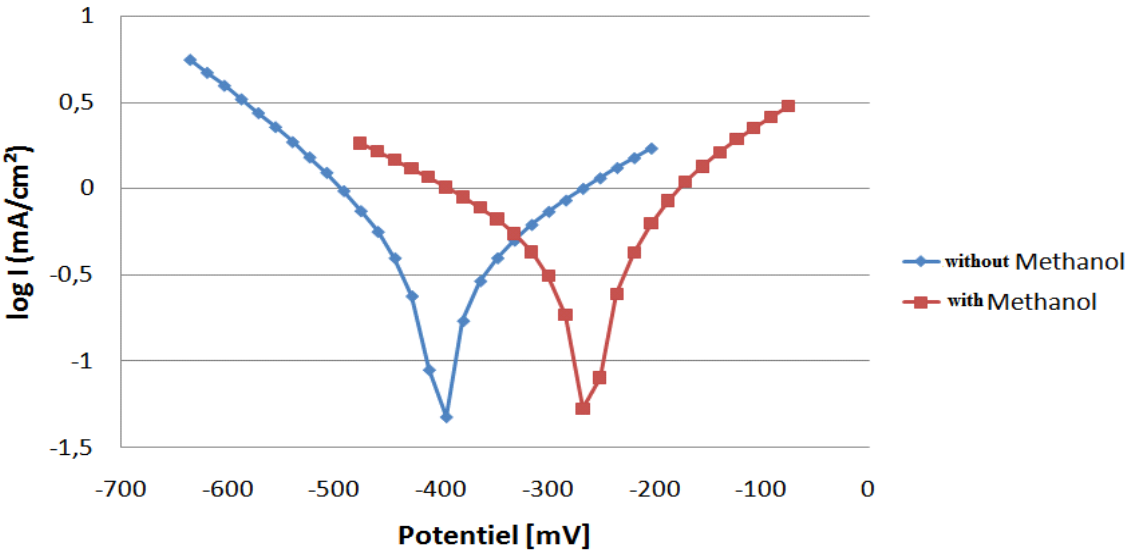

Figure 5 : Taffel lines recorded for the electrode Ni/Clay/316L, in H_2SO_4 medium containing or not methanol

Figure 6 shows the cyclic voltammograms recorded for the electrode Ni/Clay/316L, in electrolytic medium containing or not methanol. No peak is observed in the VC indicating that nickel exhibits no activity for the oxidation of methanol. On the contrary the SQW voltammetry (Fig 7) identifies a well defined peak of oxidation at 1.5V, in the presence and absence of methanol in the solution. The current density of the peak decreases in the presence of methanol, which allows concluding that nickel, has difficulty to oxidize in acidic medium, and as methanol oxidation is accelerated by the formation of oxides on the surface, hence the low activity observed in the VC.

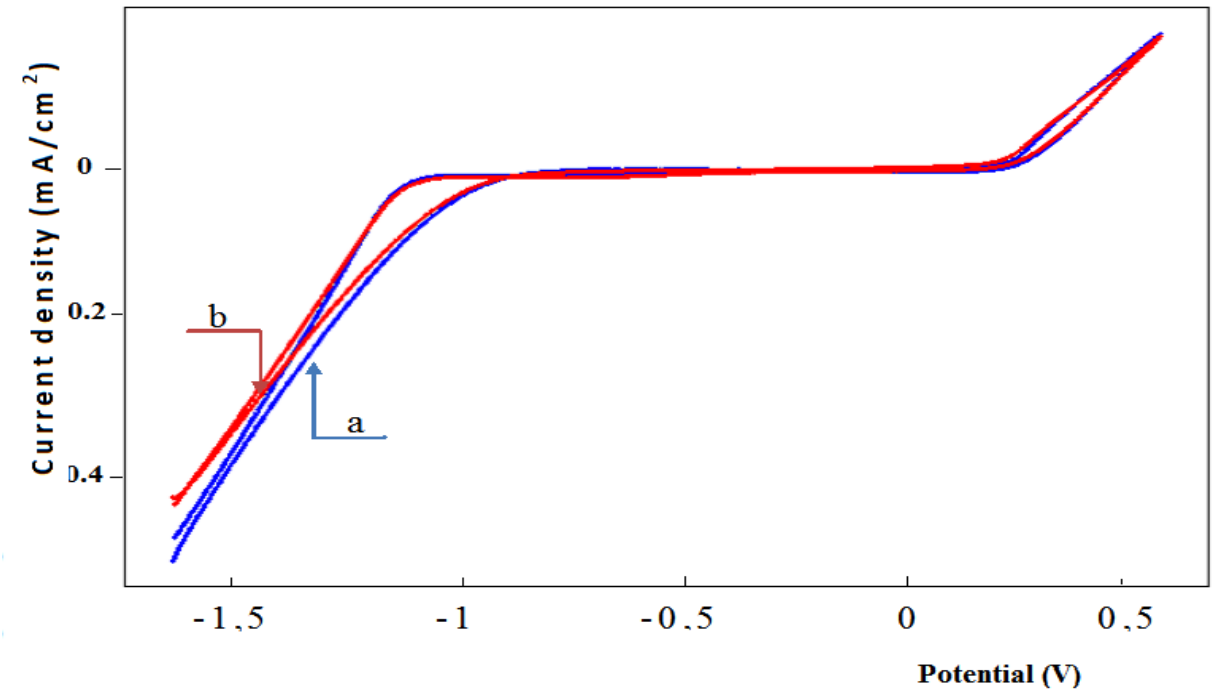

Figure 6 : cyclic voltammograms recorded for Ni/clay/316L, in 0.1M H_2SO_4 + 0.1 mmol methanol, scan rate 100mV.s^{-1}, at room temperature

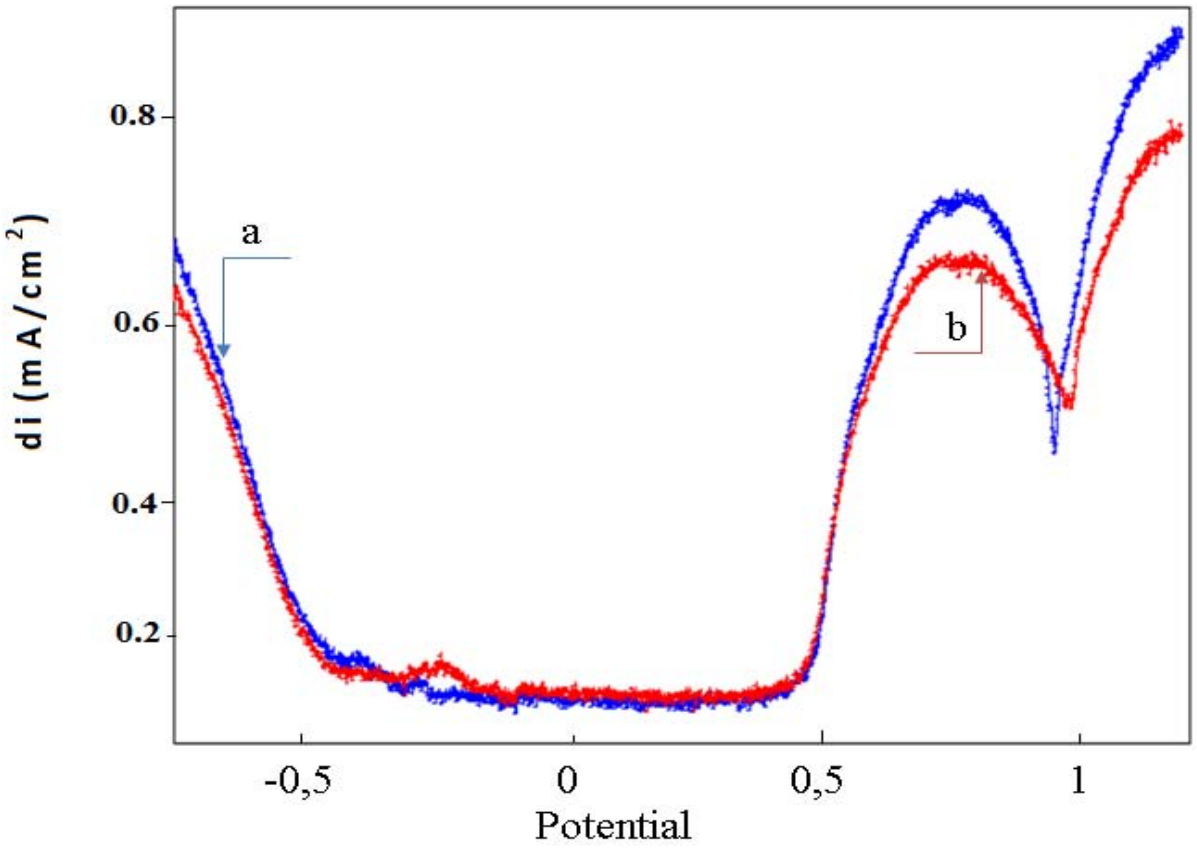

Figure 7 : SQW voltammograms recorded for Ni/clay/316L, in, a- 0.1M H_2SO_4 and b-0.1M H_2SO_4 + 0.1 mmol methanol

The EIS registered for the electrode Ni/Clay/316L, in electrolytic medium containing or not methanol (Fig. 8), we find that the diameter of the half loop decreases in the presence of methanol. In an acid medium, methanol inhibits the oxidation of the nickel surface. These results are confirmed by the drawing of straight Taffel (Fig. 9). The presence of methanol in the electrolytic medium moves the value of the potential corrosion, of the electrode Ni/Clay/316L to the highest values, and causes the decrease in the corrosion rate.

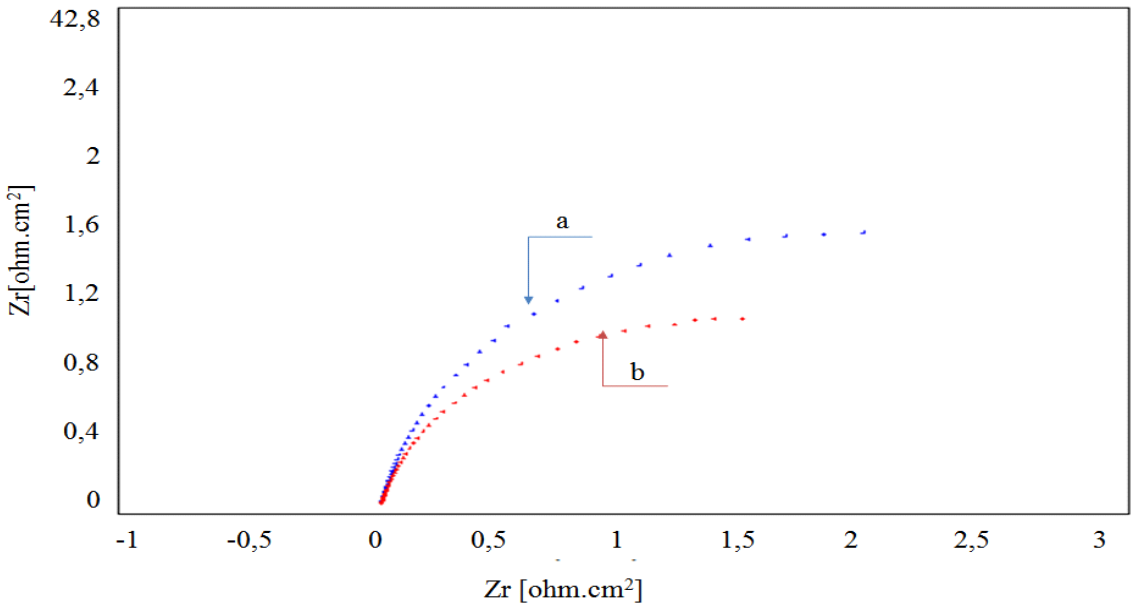

Figure 8 : EIS recorded for Ni/clay/316L, in, a- 0.1M H_2SO_4 and b-0.1M H_2SO_4 + 0.1 mmolmethanol

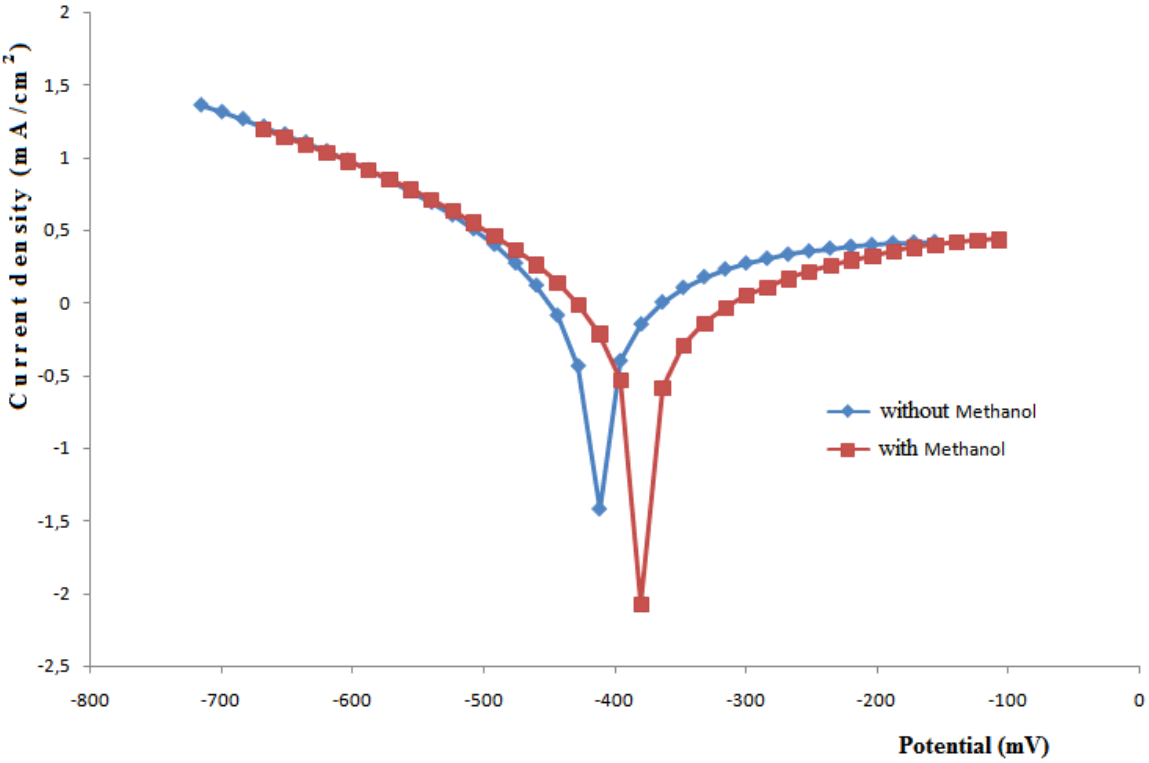

Figure 9 : Taffel lines recorded for the electrode Ni/Clay/316L, in H_2SO_4 medium containing or not methanol

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

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

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

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

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

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

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

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

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

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

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

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

It is mandatory to read all terms and conditions carefully.

AUXILIARY MEMBERSHIPS

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

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

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

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

The Institute will be entitled to following benefits:

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

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

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

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

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

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

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

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

The following entitlements are applicable to individual Fellows:

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

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

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

Other:

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

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

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

Note :

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

"

Process of submission of Research Paper

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

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

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

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

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

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You can use your own standard format also.
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1. General,

2. Ethical Guidelines,

3. Submission of Manuscripts,

4. Manuscript's Category,

5. Structure and Format of Manuscript,

6. After Acceptance.

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Scope

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

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

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

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

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

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

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

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

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

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

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

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

Research articles: These are handled with small investigation and applications

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

5.STRUCTURE AND FORMAT OF MANUSCRIPT

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

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

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

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

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

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

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

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

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

(h) Brief Acknowledgements.

(i) References in the proper form.

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

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

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

Format

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

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

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

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

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

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Optimizing Abstract for Search Engines

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

Key Words

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

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

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

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

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

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

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

Acknowledgements: Please make these as concise as possible.

References

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

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

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

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

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

TECHNIQUES FOR WRITING A GOOD QUALITY RESEARCH PAPER:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Informal Guidelines of Research Paper Writing

Key points to remember:

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

Final Points:

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

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

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To make a paper clear

· Adhere to recommended page limits

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

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· Use standard writing style including articles ("a", "the," etc.)

· Keep on paying attention on the research topic of the paper

· Use paragraphs to split each significant point (excluding for the abstract)

· Align the primary line of each section

· Present your points in sound order

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· Use past tense to describe specific results

· Shun familiar wording, don't address the reviewer directly, and don't use slang, slang language, or superlatives

· Shun use of extra pictures - include only those figures essential to presenting results

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

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

Approach:

- Single section, and succinct
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- A conceptual should situate on its own, and not submit to any other part of the paper such as a form or table
- Center on shortening results - bound background information to a verdict or two, if completely necessary
- What you account in an conceptual must be regular with what you reported in the manuscript
- Exact spelling, clearness of sentences and phrases, and appropriate reporting of quantities (proper units, important statistics) are just as significant in an abstract as they are anywhere else

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

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

Approach:

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- Present surroundings information only as desirable in order hold up a situation. The reviewer does not desire to read the whole thing you know about a topic.
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Materials:

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

Methods:

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

Approach:

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

What to keep away from

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

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

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

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

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

Approach

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

Figures and tables

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- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

- When you refer to information, differentiate data generated by your own studies from available information
- Submit to work done by specific persons (including you) in past tense.
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	A-B	**C-D**	**E-F**
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Introduction	Containing all background details with clear goal and appropriate details, flow specification, no grammar and spelling mistake, well organized sentence and paragraph, reference cited	Unclear and confusing data, appropriate format, grammar and spelling errors with unorganized matter	Out of place depth and content, hazy format
Methods and Procedures	Clear and to the point with well arranged paragraph, precision and accuracy of facts and figures, well organized subheads	Difficult to comprehend with embarrassed text, too much explanation but completed	Incorrect and unorganized structure with hazy meaning
Result	Well organized, Clear and specific, Correct units with precision, correct data, well structuring of paragraph, no grammar and spelling mistake	Complete and embarrassed text, difficult to comprehend	Irregular format with wrong facts and figures
Discussion	Well organized, meaningful specification, sound conclusion, logical and concise explanation, highly structured paragraph reference cited	Wordy, unclear conclusion, spurious	Conclusion is not cited, unorganized, difficult to comprehend
References	Complete and correct format, well organized	Beside the point, Incomplete	Wrong format and structuring

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