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Chemistry

Highlights

- Approach for Synthesis
- Studies of Dioxouranium
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- Friendly Catalyst Layered

Discovering Thoughts, Inventing Future

Volume 14 Issue 2 Version 1.0

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Chemistry

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Initiation of Hydrogen Flame by a Local Source

By N. M. Rubtsov, B. S. Seplyarsky, K. J. Troshin, V. I. Chernysh & G. I. Tsvetkov

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Abstract- The approximate analytical method is applied for analysis of the problem on local chain-thermal explosion in reaction of hydrogen oxidation in the presence of chemically active additive. It is shown that key parameters defining the critical size of a local source of ignition, are the temperature in the center of local ignition zone; quantity of the active centers of combustion created with the local source; and presence of active chemical additives in combustible gas mixture. Comparison to experimental data has shown applicability of the developed approach for the analysis of critical conditions of local ignition in combustible gas mixtures.

Keywords: initiation, flame, local source, spark dis- charge, hydrogen, air, propagation, combustion.

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Initiation of Hydrogen Flame by a Local Source

N. M. Rubtsov [α] , B. S. Seplyarsky [σ], K. J. Troshin [ρ], V. I. Chernysh [ω] & G. I. Tsvetkov [¥]

Abstract- The approximate analytical method is applied for analysis of the problem on local chain-thermal explosion in reaction of hydrogen oxidation in the presence of chemically active additive. It is shown that key parameters defining the critical size of a local source of ignition, are the temperature in the center of local ignition zone; quantity of the active centers of combustion created with the local source; and presence of active chemical additives in combustible gas mixture. Comparison to experimental data has shown applicability of the developed approach for the analysis of critical conditions of local ignition in combustible gas mixtures.

Keywords: initiation, flame, local source, spark discharge, hydrogen, air, propagation, combustion.

I. INTRODUCTION

The knowledge of regularities of initiation of combustion processes provides the possibility of controlling combustion at its initial stages. It is obvious that conditions of initiation of a combustion wave depend on the size and shape of a reaction initial center created by an external power source in the form of heat or chemically active particles. Action of initiators (spark, heating, introduction of the active centers or additives into combustible mix) is based on the acceleration of chemical transformation both at the expense of increase in gas temperature and of increase in the number of active centers because the vast majority of gas-phase combustion processes has branched chain nature [1, 2]. Thus, controlling of local ignition demands taking into account the changes of temperature of the initial center of combustion and the quantity of active centers in it.

Dynamics of formation of the stationary flame front (FF) at spark ignition of gas mixture remains rather low-studied area of combustion physics [3-5]. One of the reasons is the difficulty of experimental investigation of ignition process, associated, first of all, with small times of stationary FF formation. A primary center of a spherical flame arising in a short period at a place of the spark discharge was experimentally observed in [6] by means of a photo register, however evolution of the center wasn't investigated. In [7] the frames of high-speed shlieren-filming of evolution of the primary combustion center at the place of a spark discharge in stoichiometric propane - air mix are presented. From the given shots it follows that stationary FF occurs within very small delays (tens of microseconds). In [5] it was shown that the use of small chemically active additives in gas mixture allows increasing the values of ignition delays.

The work is aimed at the treatment of the problem on ignition of gas combustible mix by a local source with both analytical and numerical methods. The so-called weak initiation which does not provide any noticeable gas dynamic perturbations of the environment [7] is considered. Establishment of key parameters of initiation process is carried out by the example of the model reaction of hydrogen oxidation at atmospheric pressure. Experimental data on formation of the steady spherical FF obtained with the use of high-speed color cinematography were also used.

II. EXPERIMENTAL

Experiments were performed in the stainless steel reactor 25 cm long and 12 cm in diameter, supplied with removable covers and an optical quartz window 12 cm in diameter at an end face (Fig.1). Electrodes of spark ignition (1 J) were placed in the center of the reactor. The distance between them was 0.5 mm. The previously prepared mixes 40%H_2 + 60% air + (0 - 2%) propene (C_3H_6) were used. For flame visualization 2% of carbon tetrachloride (CCl_4) was added to the mixes. Speed filming of ignition dynamics and FF propagation was carried out from the end face of the reactor with a color high-speed digital camera Casio Exilim F1 Pro (frames frequency –1200 s^{-1}). The filming was turned on at an arbitrary moment before initiation. A video file was stored in computer memory and its time-lapse processing was performed. The pressure change in the course of combustion was recorded by means of a piezoelectric gage, synchronized with the discharge. Before each experiment the reactor was pumped out up to 10^{-2} Torr with a for vacuum pump 2NVR-5D. Gases H_2, C_3H_6 and liquid CCl_4, were chemically pure.

III. RESULTS AND DISCUSSION

Influence of small chemical additive (propene, C_3H_6) on an ignition delay was investigated by the example of combustion of hydrogen in air at atmospheric pressure. In Fig. 2 (a-d) the results of high-speed filming of formation of a steady flame front in 40% H_2 + 60% air mix illuminated with 2% of CCl_4 at 1 atm in the presence of 1, 1.5 and 2% of propene are shown. We observed that without C_3H_6 additive FF reaches the edges of an optical window already at the 3rd shot after

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spark ignition. It means that the small propene additive (1-2%) leads to considerable reduction of FF velocity. It should be noted that the additive of 2% of CCl_4 under these conditions is inert and doesn't show noticeable action on hydrogen combustion in accordance with the results [3,8]. FF occurrence in the presence of 2% of propene was observed not at once, but after six initiations by the spark discharge in this mix (Fig. 2d). Fig. 2c corresponds to 3 initiations by the spark discharge. As is seen the primary center of combustion was formed, but it didn't lead to flame propagation. From Fig. 2c,d it is seen also that under conditions of three spark initiations the limit of flame initiation is observed at the size of the primary combustion center much smaller than the reactor radius. Under these conditions heat losses into reactor walls are missing. Therefore, the observed limit of flame initiation is caused by an active chemical additive in the mix. From Fig. 2e in which experimental dependencies (see Fig. 2a-c) of the diameter of the flame zone on time are shown, it is possible to estimate the smallest diameter of the primary combustion center which makes up ~ 0.3 cm.

Strong influence of small chemically active additive on the time and conditions of FF formation means that evolution of the primary center is determined by not only the thermal effect of the reaction, but also by the chemical mechanism of interaction of the active centers of combustion (atoms and radicals) with the additive.

Before performing analysis of the process of local ignition of hydrogen-air mix it is important to illustrate the features of development of the primary center by the example of a problem on local thermal explosion of a flat Π-shaped warming-up center in which a zero order chemical reaction occurs. According to [9, 10] the problem is described by the equation:

$$\partial\theta/\partial\tau = \partial^2\theta/\partial\xi^2 + \exp\{\theta/(1+\beta\theta)\}, \qquad (1)$$

$$\tau = 0, \quad \theta = 0 \quad at \quad \xi \le R_0, \quad \theta = -\theta_{\text{н}} \quad at \quad \xi > R_0,$$
$$\xi = 0, \quad \xi = \infty, \quad \partial\theta/\partial\xi = 0.$$

where, $\theta = (T - T_0)E/RT_0^2$,

$$\xi = r\{\lambda RT_0^2/(Q\rho k_a E)\exp(E/RT_0)\}^{-0.5}$$

$$\tau = tQk_a E/(cRT_0^2)\exp(-E/RT_0),$$

$$R_0^2 = Fk = Q\rho k_a E/(\lambda RT_0^2)\exp(-E/RT_0)r_0^2 = r_0{}^2/at_{del}$$
$$\theta_n = (T_{\text{н}} - T_0)E/RT_0^2$$

Here T_0 is the initial temperature of the center, T_n- environment temperature, r_0- the initial size of the center, t - time, E, k_a, Q - energy of activation, a pre exponent and the thermal effect of a zero order reaction respectively, λ - heat conductivity, C - thermal capacity, ρ - density, *a* – heat diffusivity, t_{del} – the delay period of ignition.

The analysis of results of numerical investigation of the problem leads to the following conclusions:

a) The dimensionless delay period of thermal explosion has an order of unit, i.e. an order of the adiabatic delay period of thermal explosion. The time of thermal relaxation of the primary center is equal to Fk value in chosen scales. Critical Fk value is about 10 — 20 (depending on the shape of the center). Therefore, for local ignition it is characteristic that t_{del} is much less than the time of a thermal relaxation of the primary center τ_T:

$$\tau_{del} << \tau_T$$

It means that during development of thermal explosion in the primary center only the layer at the surface of the center (in which the whole temperature gradient is concentrated) is considerably cooled down, and the substance in the central part of the center isn't practically cooled.

b) For local ignition initial temperatures in the center and in its environment are markedly different ($\theta_n > 4$). Therefore at high activation energy a chemical heat source is localized in a narrow temperature interval in the vicinity of the maximum temperature. Therefore it is possible to allocate two zones in the center: 1) a reaction zone, where $\theta > -1$, in the central part of the primary center; 2) a zone of inert cooling, where $\theta < -1$, settling down at a border of a surface of the primary center ($\theta = (T - T_0)E/RT_0^2$), T_0 is the temperature of the center.

As is stated above, the whole temperature gradient is practically concentrated in the zone of inert cooling inside the center. Eventually substance cools down at the primary center surface and the border of the reaction zone moves to the middle of the center. Therefore critical condition is the equality of heat losses and thermal emission in the reaction zone by the time of the termination of the delay period. From here we will estimate the critical size of reaction zone $\Delta\xi_p^{cr}$:

$$\partial^2\theta/\partial\xi^2 = \exp\{\theta/(1+\beta\theta)\}; \quad 1/(\Delta\xi_p^{cr})^2 \approx 1, \quad \Delta\xi_p^{cr} \approx 1.$$

Thus, for ignition of the center it is necessary that the size of the reaction zone exceeds the critical one during the delay period.

The heat flux which is aimed away from the reaction zone is more than the thermal flux which chemical reaction can provide during a delay period. They become equal only under critical conditions at the moment of the termination of the delay period. Therefore the law of movement of the border of a reaction zone can be found from the solution of a problem on plate cooling in infinite environment [9, 10]:

$$\theta = -(\theta_n/2)\left\{erfc\left[\frac{R_0-\xi}{2\tau^{0.5}}\right]+erfc\left[\frac{R_0+\xi}{2\tau^{0.5}}\right]\right\} \tag{2}$$

Temperature profile in a zone of inert cooling is approximately described by the first term of expression (2) [11]:

$$\theta = -(\theta_n/2)\left\{erfc\left[\frac{R_0-\xi}{2\tau^{0.5}}\right]\right\}.$$

As the border of the reaction zone is the point in which $\theta = -1$, we get the law of its movement:

$$2/\theta_n = \left\{erfc\left[\frac{R_0-\Delta\xi_p}{2\tau^{0.5}}\right]\right\}.$$

Thus, if the independent calculation or definition of the adiabatic delay period of the reaction in the primary center for exothermic self-accelerated reaction (for example, branched chain reaction) is possible, the use of the equation (3) will allow calculating the center radius R_0^{cr}; as according to [9,10] adiabatic delay period is related to the critical size of a reaction zone by a ratio $\Delta\xi_p^{cr} = \sqrt{\tau_{del}}$ because under critical conditions at the time of $\tau=1$ $\Delta\xi_p = \Delta\xi_p^{cr} \approx 1$ [9]. Then the expression for the critical size of the primary center takes the form:

$$2/\theta_n = \left\{erfc\left[\frac{R_0^{cr}-\tau_{del}{}^{0.5}}{2\tau_{del}{}^{0.5}}\right]\right\}$$

in which $\theta = (T_0-T_n)E/RT_0^2$, then we get:

$$2/\theta_n = erfc\frac{R_0^{cr}-1}{2} = erfc\left[\frac{(Fk)^{1/2}-1}{2}\right] = erfc\left[\frac{r_0^{cr}/a\sqrt{t_{del}}-1}{2}\right] \tag{4}$$

Thus, the value of the adiabatic delay period t_{del} is one of the key parameters of the process of local ignition. Observed marked influence of small chemically active additive on the time of FF formation (see Fig. 2) according to eq.(4) means that the additive has strong impact on the value of t_{del}.

We will illustrate influence of the chemical mechanism of combustion reaction on critical conditions of local ignition by the example of the branched chain process of hydrogen oxidation which is considered to be well-known [1, 3, 4].

To describe hydrogen oxidation we will take into account only main stages of the process of chemical transformation: chain origination $H_2 + O_2 \rightarrow 2OH$ (k_0), chain propagation (k_1, k_3) and chain branching (k_2), tri molecular chain termination (k_6, k_{11}), termination of hydrogen atom on the additive in the reaction H + In → products (k_5) [4]. Nonlinear reactions of chain propagation and chain branching during the delay period are ignored [3, 4].

In a chain unit of hydrogen oxidation

$$OH + H_2 \rightarrow H_2O + H\ (k_1),$$
$$H + O_2 \rightarrow OH + O\ (k_2),$$
$$O + H_2 \rightarrow OH + H\ (k_3)$$

heat isn't practically released [1]. Here k_i are velocity constants of the corresponding reactions. The heat of reaction of hydrogen oxidation is released in recombination of the active centers. In rich mixes these are hydrogen atoms which concentration markedly exceeds concentrations of atoms O and radicals OH [1]. Atoms of hydrogen recombine with each other and with oxidizer molecules with participation of the third particle M with thermal effects Q_2 and Q_1 respectively in the following reactions:

$$H + H + M \rightarrow H_2 + M\ (k_{11}) + Q_2,$$
$$H + O_2 + M \rightarrow HO_2 + M\ (k_6) + Q_1 .$$

We will qualitatively analyse influence of various factors (initial gas temperature, initial concentration of atoms of hydrogen and concentration of additive) on the delay period of thermal ignition of a stoichometric hydrogen – oxygen mix. The system of the equations describing adiabatic process of thermal ignition was analyzed in dimensionless variables. The characteristic time scale was chosen as $t_0 = 1/(k_2^0 [O_2]_0)$, where k_2^0 is the reaction pre exponent of (2). In the chosen scale of dimensionless time 1 second corresponds approximately ~ 10^5 dimensionless units along the τ axis in Fig. 3. Dimensionless variables and parameters were defined as follows: $\tau = t/t_0$, Y_0, Y_1, Y_3 = [concentration of atoms of hydrogen, molecular oxygen and an additive respectively] / [initial concentration of molecular oxygen], T – temperature (K)

$$dY_0/d\tau = 3k_0/k_2^0 + 2\exp(-8380/T)\, Y_0Y_1 - k_5/k_2^0 Y_0Y_3 - k_6/k_2^0 MY_0Y_1 - k_{11}/k_2^0 (Y_0)^2 M$$

$$dY_1/d\tau = -3k_0/k_2^0 - \exp(-8380/T)\, Y_0Y_1 - k_6/k_2^0 MY_0Y_1 \qquad (5)$$

$$dT/d\tau = 1/(C_p\rho)[Q_1 k_6/k_2^0 MY_0Y_1 + Q_2 k_{11}/k_2^0 (Y_0)^2 M]$$

$$dY_3/d\tau = -k_5/k_2^0 Y_0Y_3$$

The equations of the set (5) were integrated using a Runge-Kutta fourth order method with an adaptive step of integration and the following initial conditions, $Y_0 = 1$, $Y_1 = 1$, $Y_3 = 0 \div 0.03$, $T_0 = 1000$ (K) is the measured temperature value in gas in a zone of spark ignition [12]. The values of other parameters were the following: $\rho = 10^{-3}$ g/cm^3 [13], $C_p = 0.88$ kal /g. grad [13], M= 750. 10 $^{19}/T_0$ cm^{-3} (atmospheric pressure), $k_2 = k_2^0 \exp(-8380/T)$ cm^3/ molec. s = 0.30.10^{-9}exp (-8380/T) cm^3/ molec. s [14], $k_{11} = 0.14.10^{-31}$ (T/300) $^{-0.4}$ cm^6/molec^{2}s [15], $k_6 = 10^{-32}$ cm^6/ molec^{2}s [16], $k_5 = 10^{-11}$ exp (-1500/ T) cm^3/molec. s [8], $k_0 = 0.33.10^{-9}$ exp (-22000/T) cm^3/ molec. s [17], $Q_1 = 45$ kcal/ mol [1], $Q_2 = 100$ kcal/mol [1], $[O_2]_0 = 760\ (0.13\ 10^{19}/T_0)$ cm^3.

The results of calculations are presented in Fig. 3. For estimation of the value of temperature increase at the expense of recombination of hydrogen atoms introduced into an initial mix calculations for lack of chain branching ($k_2 = 0$, the reaction of hydrogen oxidation doesn't occur, Fig. 3 a, b) were carried out. It follows from the calculations that due to heat which is released in recombination of hydrogen atoms introduced into initial mix, the temperature of gas mix increases (Fig. 3a). The additive of propene to the same mix leads to reduction of the maximum temperature (Fig. 3b). Propene influence for lack of the branching reaction shows itself as warming- up reduction. This is reached at the expense of smaller thermal emission in reaction of the active center with propene in comparison with recombination of hydrogen atoms with each other and with oxygen molecules.

From Fig. 3c, in which change in time of concentration of hydrogen atoms, oxygen and propene ($k_2 \neq 0$) molecules is given for absence and for presence of propene, it is seen that propene additive provides increase in τ_{del}. In calculations the delay period was estimated as the time of achievement of maximum concentration of hydrogen atoms.

We will apply the results obtained to the explanation of influence of active chemical additives on the process of spark initiation. As in the area of discharge not only temperature increases, but also super equilibrium concentration of active particles [7] is attained, then at the expense of their recombination (after discharge) temperature will additionally increase, and τ_{del} will respectively decrease (see Fig. 3c - calculation for dimensionless initial concentration of atoms of hydrogen 0.1, Fig. 3d - 0.017).

Propene additive leads, on the contrary, to increase in τ_{del}; as the active centers of combustion including those formed at an initiating impulse, are terminated on propene molecules and don't lead to chain branching until propene is consumed. In addition, influence of propene on the value of τ_{del} shows itself also in warming-up reduction. It is due to smaller heat release in reaction of the active center with propylene in comparison with recombination of hydrogen atoms with each other and with oxygen molecules.

It is necessary to tell apart two cases. If initial concentration of active particles is more than concentration of additive, the additive is quickly consumed due to interaction with these active particles and has no impact on the further development of ignition process. In this case τ_{del} slightly depends on additive concentration (see Fig. 3d) and is determined by the time of the development of ignition process without additive.

If initial concentration of active particles is less than concentration of additive, the delay period strongly depends on concentration of additive (see Fig. 3 d, e). This result is a consequence of slow consumption of additive in the reaction of chain origination.

It is known from literature on ignition and combustion that the velocity of oxidation reaction is a sharp function of initial temperature [1-4, 7]. Such dependence is determined by the high activation energy of the chain branching reaction. This fact is a necessary condition of occurrence of critical phenomena of local ignition and application of the approach developed above for their calculation. To estimate the critical size of the primary center we can use analytical expression for τ_{del} in hydrogen-air mix, obtained in *Appendix* (equation (11)).

Let us substitute the following values of parameters in the equation (4) for the critical size of the primary ignition center: Tn = 300K, E = 16.7 kcal/mol, $a \approx 0.8$ cm^2/s (for rich H_2-air mix [13]). Its solution for t_{del} is:

$$t_{del} = \frac{1.56\left(r_0^{cr}\right)^2}{1 + 2\Omega^2} \qquad (6)$$

Where Ω is the root of the equation- $4175T_0 \operatorname{erfc}\Omega + 1252500 \operatorname{erfc}\Omega + T_0^2 = 0$, and T_0 is the temperature of the primary center. Dependencies of τ_{del} on the critical radius of the primary center for temperatures of the center 800K, 1000K, 1500K, 2000K, calculated by (6), are shown in Fig. 4.

We will apply the obtained results to estimate the value of initial concentration of hydrogen atoms in the primary center. We will use for this purpose both the experimental data shown in Fig. 2e, and expressions for calculation of τ_{del}, obtained in the *Appendix* (equations (9), (11)), which describe well experimental data from literature. Experimental values of t_{del} given in Fig. 5 are taken from [19] and calculated by equation (11). As is seen the results of calculations by eq. (11) for temperatures <1500K adequately agree with experimental data [19] even for the mix H_2: O_2 = 1: 1.

The smallest diameter of the primary center from which a combustion wave develops, makes up 0.3 cm according to Fig. 2e. The value of $\tau_{del} \approx 0.02$ s at T_0=1000 K (experimental value of gas temperature in spark ignition zone [12]) corresponds to this critical radius according to Fig. 4.

On the other hand the delay period τ_{del} can be calculated directly by equation (9) for various initial concentrations of hydrogen atoms and in=2 %. Results of the calculations are shown in Fig. 6a. In this case the delay period was considered as time interval for which the warming up of mix becomes equal to a characteristic interval $\frac{RT_0{}^2}{E}$. This interval for E = 16.7 kcal/mol and T_0=1000K equals 120^0. As follows from Fig. 6a the delay period (t_{del} = 0.02 c) corresponds to initial concentration of hydrogen atoms ~ 7.10^{17} cm^3, i.e. the value has a reasonable order. This result is evidence that the developed approach for the analysis of critical conditions of local ignition is applicable.

As is seen in Fig. 6a, it is possible to allocate two stages at initial concentration of hydrogen atoms more than 10^{16} cm^3 in the course of warming-up: the fast stage when the velocity of heat release is determined by recombination with participation of hydrogen atoms in initial mix, and the slow one, related to heat release in the reaction of hydrogen oxidation.

For investigation of influence of initial concentration of additive on the critical size of the primary center and, respectively, on the value of critical energy of ignition, the calculation of change of a warming up in time by equation (9) was carried out at various initial concentration of additive (*In*) and given concentration of hydrogen atoms $[H]_0$ $=10^{14}$ cm^3. Concentration of the additive was chosen in such a way that the inequality [*In*] > $[H]_0$ was fulfilled. Results of these calculations are shown in Fig. 6b. As well as for Fig. 6a t_{del} was considered as the time interval for which the warming up of mix becomes equal to one characteristic interval.

As is seen in Fig. 6b, increase in concentration of an additive from 0.5% to 1% leads to increase in t_{del} from 0.02 s to 0.12 s, and from 1% to 2% from 0.12 s to 0.32 s. However such small amouns of additive (from 0.5% to 2%) correspond to change of the critical size of the center and respectively, the minimum energy of ignition by ~ 6.25 times.

We summarize shortly the results obtained.

The approximate analytical method is applied for analysis of the problem on local chain- thermal explosion by the example of the branched chain reaction of hydrogen oxidation in the presence of chemically active additive. It is shown that key parameters defining the critical size of the primary center of ignition, are the temperature in the local ignition center; quantity of the active centers of combustion created with the local source; and the presence of active chemical additives in combustible mixture. Comparison to the experiment has shown applicability of the developed approach for the analysis of critical conditions of local ignition in combustible gas mixtures.

APPENDIX

Analytical definition of τ_{del} *of hydrogen-air mix at atmospheric pressure*

We will consider the branched chain mechanism of hydrogen oxidation, described above. We will neglect consumption of initial reagents during τ_{del}. Then we have:

$$\frac{dH(t)}{dt} = l_0 + l_1 H(t) - 2k_{11}MH(t)^2$$

$$C_p\rho\frac{dT(t)}{dt} = Q_1k_6O_{20}MH(t) + Q_2k_{11}MH(t)^2 \qquad (7)$$

where $l_0 = k_iH_{20}O_{20}$ и $l_1 = 2k_2O_{20} - k_5In_0 - k_6O_{20}M$, H_{20}, O_{20} и In_0 – initial concentration of initial components and an additive, C_p is molar thermal capacity at a constant pressure, ρ - density. Into the first equation of system (7) we will put *H (t)* = $\frac{1}{k_{11}My(t)^2}\frac{dy(t)}{dt}$, then we get:

$$\frac{d^2y(t)}{dt^2} = l_0k_{11}My(t) + l_1\frac{dy(t)}{dt}$$

Its solution under initial condition H (0) = H_0 (the local source generates only hydrogen atoms) is:

$$H(t)=\frac{-\xi_1\exp(\xi_1 t)m+n\xi_2\exp(\xi_2 t)}{k_{11}M(-\exp(\xi_1 t)m+n\exp(\xi_2 t))}$$ Where

$$\xi_1=\frac{1}{2}l_1+\sqrt{l_1^{\,2}+4k_{11}Ml_0},\ \xi_2=\frac{1}{2}l_1-\sqrt{l_1^{\,2}+4k_{11}Ml_0},\quad m=\xi_1-k_{11}HoM,\ \ n=\xi_2-k_{11}HoM$$

Integration of the second equation of the set for T (0) = T_0 gives:

$$T(t)=To+\left(\frac{(\xi_1+\xi_2)\beta}{2\xi_1^{\,2}\xi_2^{\,2}}+\frac{Q_1k_6O_2}{k_{11}M\rho C_P}\right)\ln\left(\frac{-\exp(\xi_1 t)m+n\exp(\xi_2 t)}{n-m}\right)$$

-

$$\frac{\beta t}{2\xi_1\xi_2}-\frac{\beta mn(\xi_2-\xi_1)(\exp(\xi_1 t)+\exp(\xi_2 t))}{2(n-m)\xi_1^{\,2}\xi_2^{\,2}(-\exp(\xi_1 t)m+n\exp(\xi_2 t))}\quad \text{where}\quad \beta=\frac{Q_2}{C_P\rho k_{11}M} \tag{8}$$

According to [20] we will consider that the delay period expires when self-heating exceeds one characteristic interval, namely $\Delta T=T(t)-To=\frac{RTo^2}{E}$. We consider activation energy of the linear branching reaction (k_2, a limiting stage) as activation energy.

During the delay period it is possible to neglect concentration of accumulated hydrogen atoms. In addition, direct calculation shows that it is possible to ignore also the term $\frac{\beta t}{2\xi_1\xi_2}$. The equation (5) after substituting the values ξ_1 and ξ_2 takes a form:

$$\frac{RTo^2}{E}=\Delta T=$$

$$\left(\frac{\beta l_1}{2k_{11}^{\,2}M^2l_0^{\,2}}+\frac{Q_1k_6O_2}{k_{11}M\rho C_P}\right)\ln\left(-\frac{-\exp((l_1+\frac{k_{11}Ml_0}{l_1})t)(-\xi_2+k_{11}HoM)+(-\xi_1+k_{11}HoM)\exp(\xi_2 t)}{(l_1+\frac{2k_{11}Ml_0}{l_1})}\right) \tag{9}$$

We will simplify the equation (9) in order to get the equation for the delay period in an explicit form

$$:\ \frac{RTo^2}{E}=\Delta T=\left(\frac{\beta l_1}{2k_{11}^{\,2}M^2l_0^{\,2}}+\frac{Q_1k_6O_2}{k_{11}M\rho C_P}\right)\ln\left(\frac{\exp(l_1t)k_{11}M(Hol_1+l_0)}{l_1^{\,2}}+1-\frac{k_{11}MH_0}{l_1}-\frac{k_{11}Ml_0t}{l_1}\right) \tag{10}$$

Further we will calculate the value RT_0^2/E for the given conditions (T_0=1000K, E = 16.7 kcal/mol): $RT_0^2/E \approx$ 120. The point of intersection of the dependence (11) with a line y=120 also will give the required value of the delay period τ_{del} (Fig. 6 a, b). As is seen the value of the delay period depends both on the amount of the active centers introduced into gas mixture at initiation and on the concentration of additive in gas mixture. We solve the equation (10) for t, substituting $\frac{RTo^2}{E}$ instead of ΔT. Then by definition t = τ_{del} the value of the delay period. We get:

$$\tau_{del}=\frac{1}{k_{11}Ml_0l_1}\left(LambertW\left(-\frac{Hol_1+l_0}{l_0}\exp\left(\frac{-l_1\left(l_1\exp\left(\frac{RTo^2}{E\alpha}\right)-l_1-k_{11}MHo\right)}{k_{11}Ml_0}\right)\right)k_{11}Ml_0+l_1^{\,2}(\exp\left(\frac{RTo^2}{E\alpha}\right)-1)+k_{11}MHol_1\right) \tag{11}$$

In the equation (11) Lambert W (x) +exp (Lamber tW (x)) = x by definition,

$$\alpha = \left(\frac{\beta l_1}{2k_{11}{}^2 M^2 l_0{}^2} + \frac{Q_1 k_6 O_2}{k_{11} M \rho C_P} \right)$$

It is possible to show that the results of calculation by equations (9) - (11) practically coincide.

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FIGURES

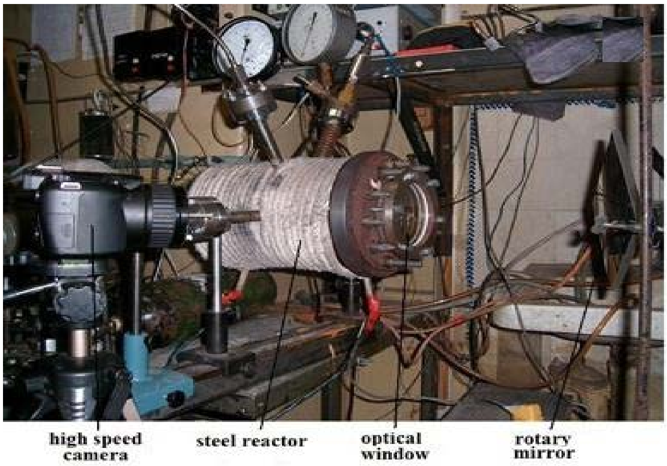

Figure 1 : Experimental installation

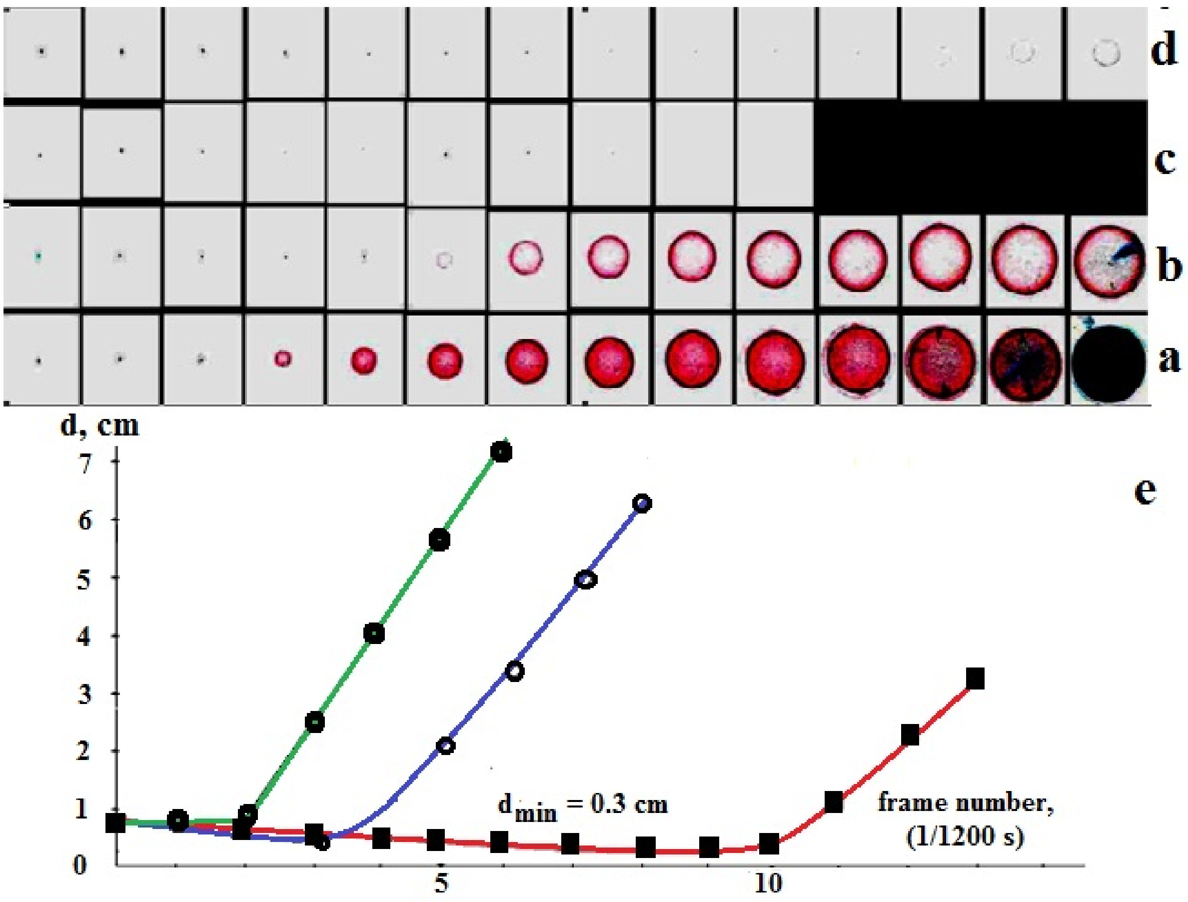

Figure 2 : Speed filming of propagation of the spherical flame front in the mix H_2 – air at atmospheric pressure in the presence of propene. The flame front is illuminated by 2% CCl_4 additive. Speed of filming is 1200 frames/s. Colors are inverted. The first frames to the left in the in the picture are the first frames after spark discharge.

a) 2% of propene, 6th initiation,
b) 2% of propene, 3rd initiation,
c) 1.5 % of propene,
d) 1% of propene,
e) Dependencies of the diameter of flame zone on time for Fig. 1a (points), b (circles), d (squares).

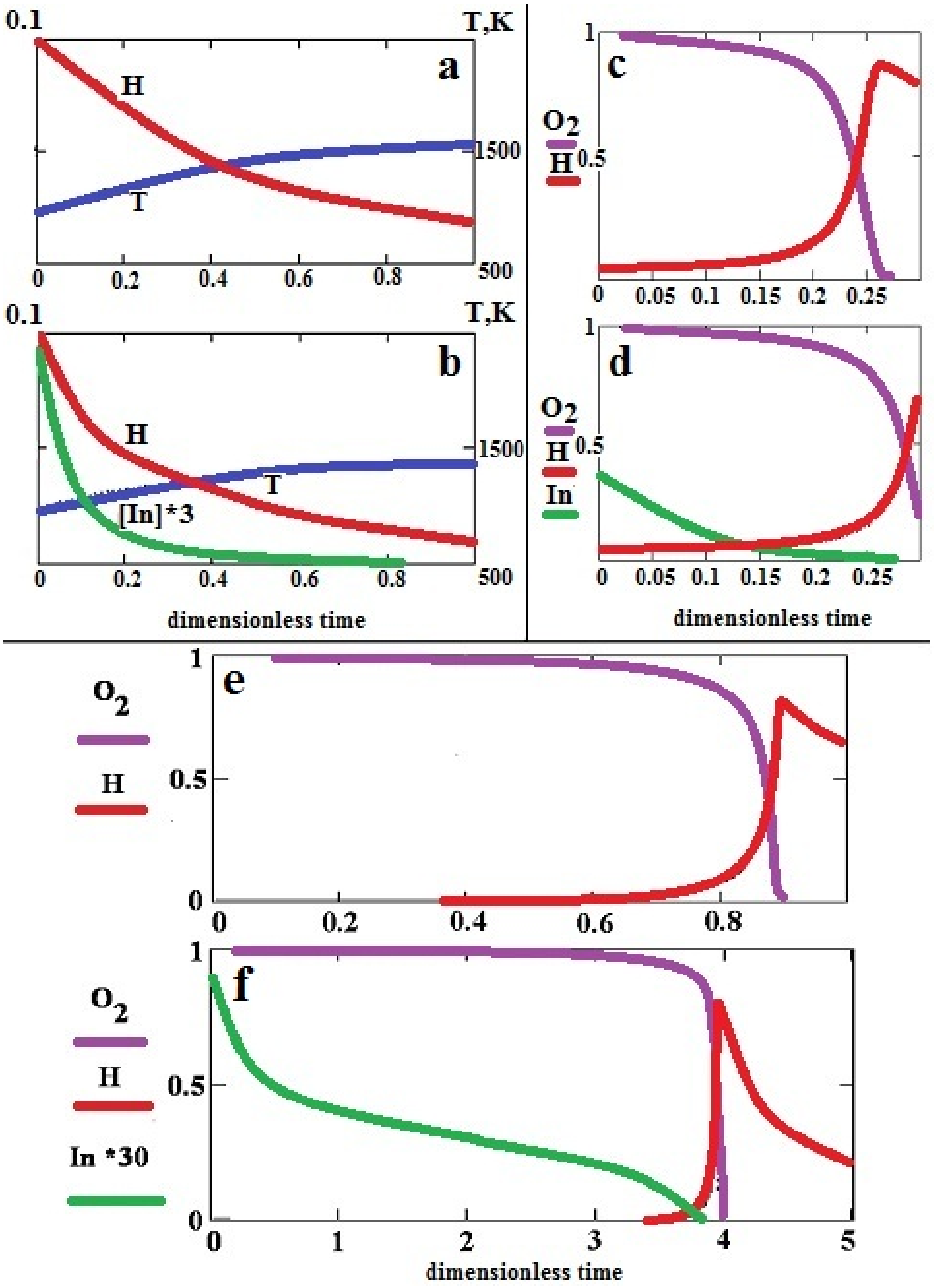

Figure 3 : Calculated dependencies of concentration of hydrogen atoms, molecular oxygen, temperature and additive at initiated combustion of hydrogen in air at atmospheric pressure.

a) $k_2 = 0$, the additive in the mix is missing;
b) $k_2 = 0$, concentration of additive in the mix is 3%;
c) the additive in the mix is missing, dimensionless concentration $[H]_0 = 0.1$;
d) concentration of additive in the mix is 3%, dimensionless concentration $[H]_0 = 0.1$;
e) the additive in the mix is missing, dimensionless concentration $[H]_0 = 0.017$;
f) Concentration of an the additive in mix is 3%, dimensionless concentration $[H]_0 = 0.017$.

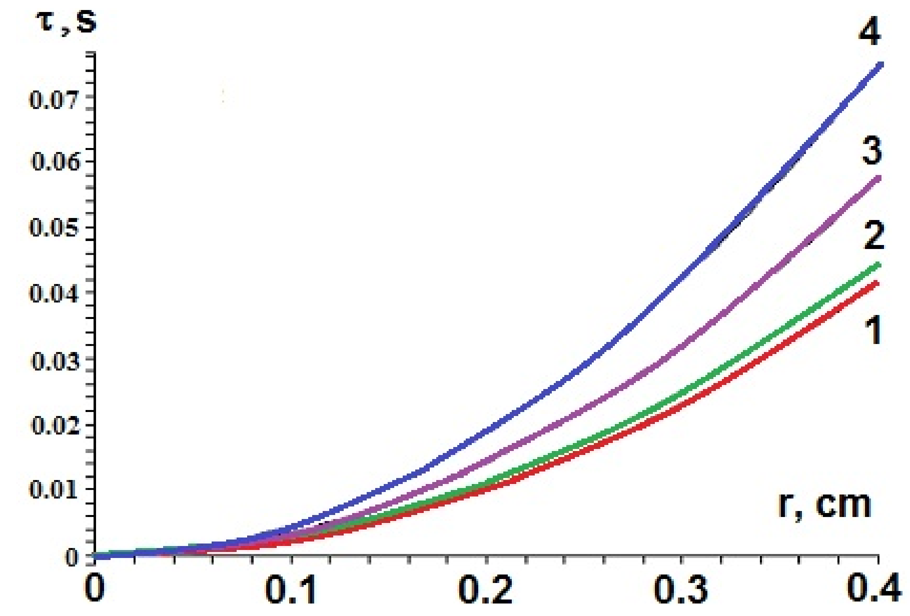

Figure 4 : Values of critical radius calculated by equation (6) depending on the delay period τ_{del} for various temperatures of the primary center: 1 – 800K, 2 - 1000K, 3 - 1500K, 4 - 2000K.

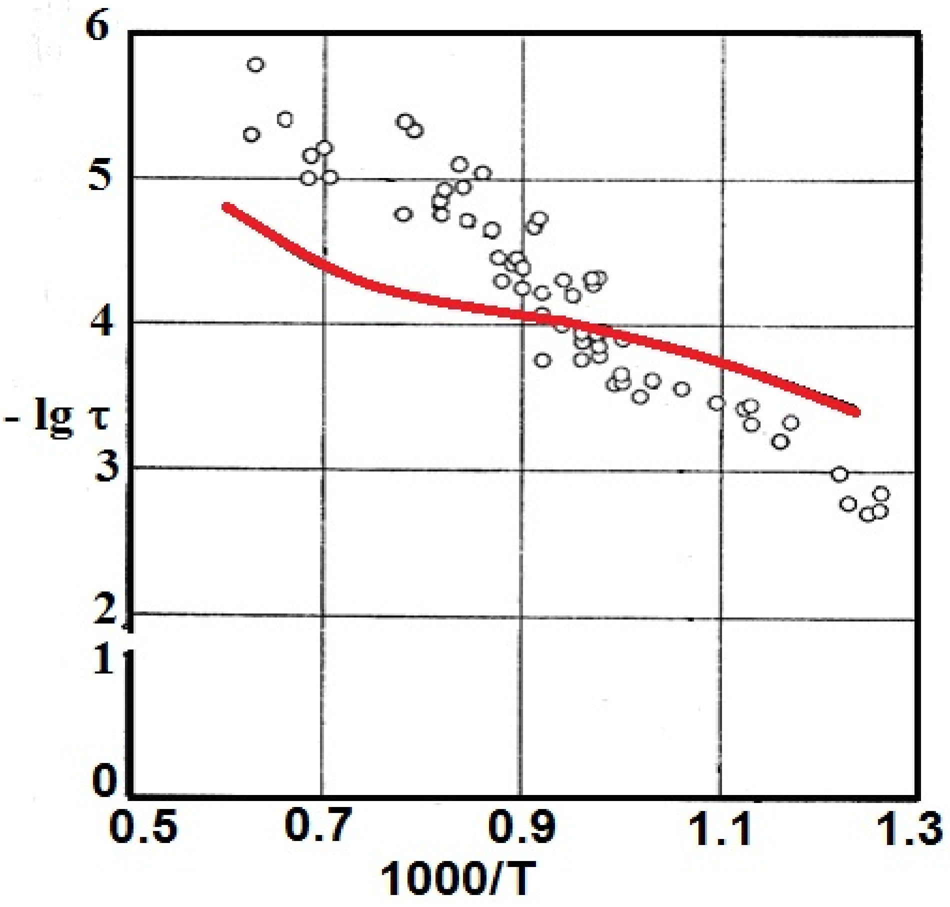

Figure 5 : Comparison of experimental data [19] on the periods of a delay (points) for the mix $H_2 + O_2$ (1:1, 1 atm) and calculated delay periods by equation (11) (a continuous curve) for $[H]_0=0$, $In_0=0$, $O_2 = 750.10^{19} / (2 T_0)$ cm $^{-3}$, other parameters are specified in the text.

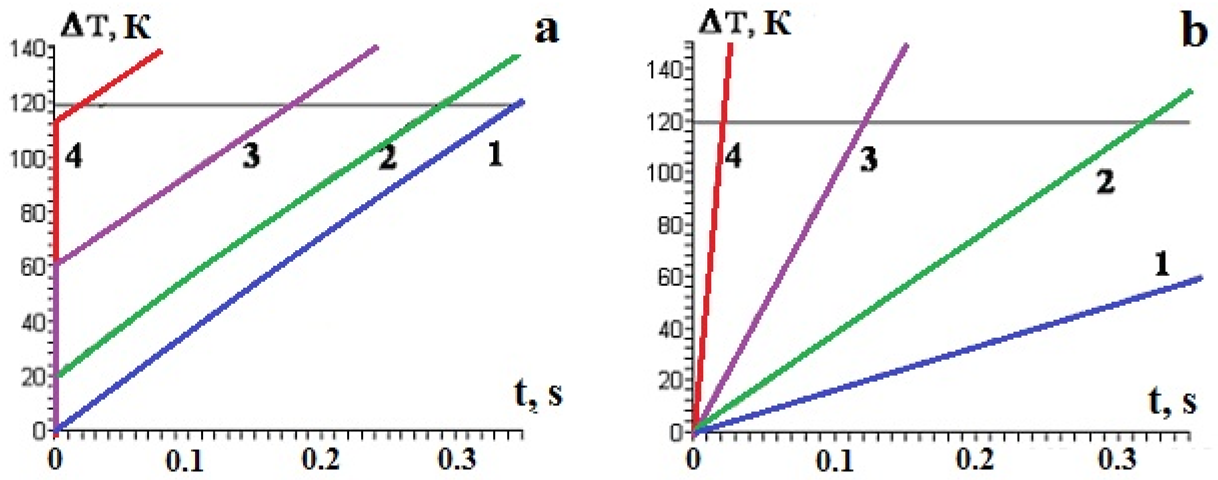

Figure 6 : The calculated values of the delay period from crossing of the graphics of the equation (9) and a straight line of $\frac{RTo^2}{E} \cong 120$

a) for various values $[H]_0$ at given concentration of additive of In=2%, 1 – $[H]_0$ =0, 2 – $[H]_0$ =10^{17} cm^3, 3 – $[H]_0$ =3.101^7 cm^3, 4 - $[H]_0$ =7.10 ^{17} cm^3;

b) For various In values at a given value $[H]_0$ =10^{14} cm^3 and concentration of additive 4 –In=0.5, 3 –In=1%, 2 In=2%, 1 - In=4%.

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New Approach for Synthesis of Hexa (Allylamino) Cyclotriphosphazene Catalysed by an Ecologic and Friendly Catalyst Layered Called Maghnite-H^+ (Algerian MMT)

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Abstract- Cyclic and linear phosphazenes are characterized by a repeating unit $[-N{=}PR_{2-}]n$ in which nitrogen is trivalent and phosphorus pentavalent. Ring sizes for the cyclic derivatives vary from three to about forty repeating units whereas for the linear polyphosphazenes derivatives are known which contain up to 15000 repeating units.

Algerien (MMT) called “Maghnite” a montmorillonite sheet silicate clay, exchanged with protons to produce “H-Maghnite” is an efficient catalyst for cationic polymerisation of many heterocyclic and vinylic monomers [1]. The structural compositions of “Maghnite” have already been determined. A phosphazenes derivative, hexa-allylamino-cyclotriphos-phazene (HACTP) reaction was performed under optimum conditions at 20°C. Experiments revealed that the reaction induced by “H-Maghnite” proceeds in bulk.

Keywords: *1H-NMR spectroscopy, dsc, nucleophilic substitution, cyclic structure, maghnite-h^+, phosphazene, hexa-allylamino-cyclotriphosphazene, allylamine, maldi-tof.*

GJSFR-B Classification : *FOR Code: 250102, 250504*

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The prepared samples were subsequently characterized by FTIR spectroscopy, 1H-NMR spectroscopy and. It should be noted that the product coating containing 1wt. %, 3wt. % and 5wt. % of clay loading was found to exhibit an observable structure, physicochemical properties and controlled molecular weight.

Keywords: 1H-NMR spectroscopy, dsc, nucleophilic substitution, cyclic structure, maghnite-h^+, phosphazene, hexa-allylamino-cyclotriphosphazene, allylamine, maldi-tof.

I. INTRODUCTION

Phosphazenes (or phosphonitrile or azaphosphorine) are compounds inorganics sub- stances which belong to the most important class of cyclic or linear structure general formula ($R_2P=N$)n. The degree of polymerization may vary from 3 to more thousands and (R) may be halogen, alkyl, aryl, amino, alkoxy and other groups[2]. Most of the structures of phosphazenes are easily synthesized by aminolysis of phosphorus pentachloride, PCl_5. The chlorophosphazenes (Cl_2P = N) n are the starting compounds for the preparation of almost wholes phosphazenes. *Christova et al* [3] have prepared cyclophosphazènes allyl-substituted for use as cross linking agents in the polymerization of 2-hydro- xyethyl methacrylate (HEMA) or in the synthesis of composites with good optical transparency and good flame resistance, compared to poly (dichlorophosphazene. A phosphazenes derivative, hexa-allylamino-cyclotriphosphazene (HACTP) was synthesized through the aminolysis of hexa-chloro-cyclo-triphosphazene with excess allylamine [4].Their potential applications included polymer electrolytes [5], biodegradable materials [6].

Montmorillonite have both Bronsted and Lewis acid sites and when es the catalytic activity of Algerian proton exchanged montmorillonite clay (Maghnite-exchanged with cations having a high charge density, as protons, they produce highly active catalysts for acid-catalysed reactions[7]. It has been demonstrated that intercalated organic molecules on the surface of Montmorillonite are mobile and can be highly polarize when situated in the space between the charged clay layers [8-9]). This study examinH^+). It was demonstrated that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite) [10].

The originality of this study is to obtain organophosphazenes compounds under very mild operating conditions using an ecologic and friendly catalyst layered called Maghnite-H^+ (Algerian MMT). Hesa (hallylamino) cyclotriphosphazene was prepared in the first place by the monomers organophophazènes nucleophilic substitution on hexa-chloro-cyclo-phosphazène by the allylamine using the same method as that used by D.Christova et al. [11] , secondly this monomer was prepared by a new method using Maghnite-H^+ and changing the solvent benzene with diethyl ether.

II. MATERIALS AND TESTING METHODS

a) Materials

Maghnite (MMT) used in this work comes from a quarry located in Maghnia (North West of Algeria) and was supplied by company "ENOF" (Algerian manufacture specialized in the production of nonferric products and useful substances). Allylamine CH_2 = CH-CH_2NH_2 (98 %) GC, laboratory FLUKA AG (Buchs) SG. Benzene (99%), boiling point: 80°C, mp: 5.50°C.

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b) *Testing methods*

^{1}H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl3. Tetramethylsilane (TMS) was used as the internal standard in these cases.

The thermo grams obtained have been made in the laboratory institute molecular chemistry, university of Burgundy (ICMUB) DIJON 1 option unit 500 MT GA^{TM} Hi Res^{TM} MFC STD.DSC measurements were carried out on a TA instrument, according to the following program: the specimens were first heated from ambient temperature to 250°C at 10°C/mn maintained at this temperature during 5 min then cooled to 25°C at 20°C/mn. The tests were performed on a TA instrument (TGA Q500) by heating the samples from 20 to 550°C at 20°C/mn. DTG thermo grams gave the variations of the weight loss derivative as a function of temperature.

The MALDI-TOF spectra have been carried out in a Bruker Ultra flex; the samples were prepared in methanol with DHBA as matrix or with CHCl3 Ditranol as template.

c) *Preparation of catalyst*

Maghnite-H$^+$ were prepared by a method similar to that described by Belbachir et al [12]. Raw maghnite (20 g) was crushed for 20 min using a Prolabo ceramic ball grinder. It was then dried by baking at 105°C for 2 h. The maghnite was then weighed and placed in an Erlenmeyer flask together with distilled water (500mL) and magnetically stirred maghnite/water mixture was combined with H_2SO_4 until saturation was achieved. After 2 days at room temperature the mineral was washed with water until it became sulfate free and then dried at 150°C. H_2SO_4 solutions of 0.25M concentration was used to prepare Maghnite-H$^+$.

d) *Thermal stability of Catalyst*

The thermal characterizations of the composites include thermo gravimetric analysis TGA. Figure-2. Show the weight losses (%) versus temperature (°C) curves for pure Maghnite-Na, The TGA of pure Maghnite-Na$^+$ show two stages of weight loss. The first weight loss in Na$^+$ Mag below 100 °C is a result of the release of free water. The second weight loss around 600 °C is associated with the dehydroxylation of silicate structure [13-14]. The total weight loss is only 13.94% up to 800 °C. As can be expected, Maghnite-Na+ shows a

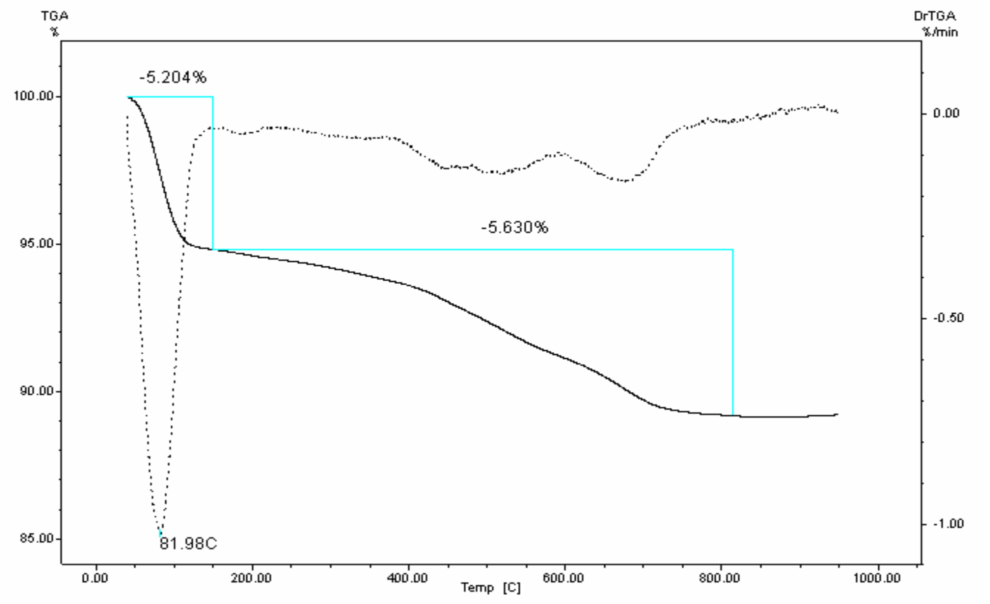


Figure 1 : TGA curves of a Maghnite-Na$^+$ obtained in nitrogen atmosphere at heating rate of 10 °C/min

e) *Procedures of synthesis*

Synthesis of hexa (allylamino) cyclotriphosphazene was conducted from the hexa (chlorocyclotriphosphazene) and allylamine as starting material and use benzene as solvent at 20° C and in 24 hours. The substitution on the nucéophilic hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) by allylamine (NH_2-CH_2 CH = CH_2) was performed, as was described by Christoval et al [15]:

3.03 ml of allylamine were diluted in 3.33 ml of benzene and in the other hand, 1g (0.0028 mol) of $N_3P_3Cl_6$ was dissolved in 5 ml of benzene after these two solutions were mixed and left under stirring for 24h at room temperature. The solvent was evaporated in a rot vapor, the resulting solid was extracted several times with diethyl ether and the product was then cooled to 20 °C and recrystallized from cyclohexane. Material obtained as white crystal and in the yield was (64%).The product is characterized by: ^{1}H-NMR: 3.5 ppm (CH_2-NH), 5.8 ppm (CH = CH_2), 5.0, 5.1 ppm (CH = CH_2), IR: 3232 cm^{-1} (NH), 1248 cm^{-1} (P = N), 1644 cm^{-1} (C = C).The reaction conditions are described as following:

Table 1 : Synthesis of hexa (allylamino) cyclotriphosphazene in benzene induced by Maghnite-H^{+} (0.25M)

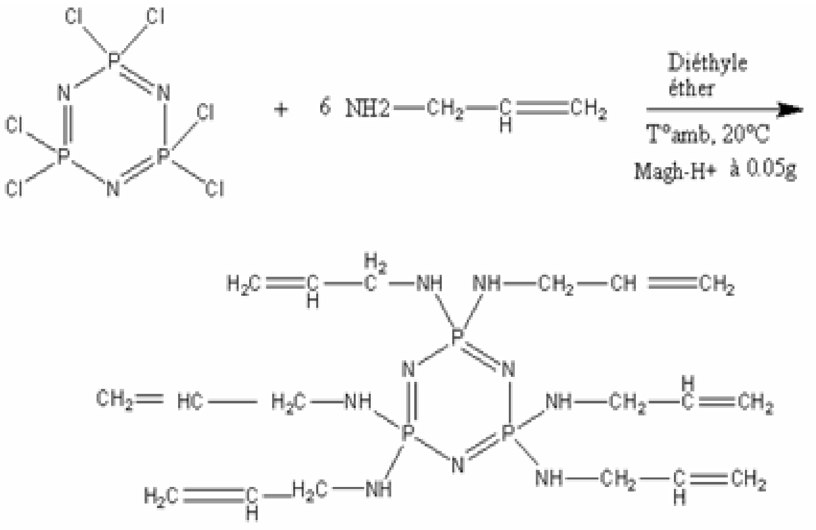
Product	Catalyst (Mag-H^{+})	solvent	yield	Time(h)	Temperature (°C)
1	_	Benzène	64%	24	20

Another synthesis of hexa (allylamino) cyclotriphosphazene was carried out by a new method: from the hexachlorocyclotriphosphazene of allylamine at 20°C using diethyl ether as solvent and a Mag-H^{+} (5%) an ecologic catalyst layered (Algerian MMT), finally the reaction lasted for 12 hours. Nucleophilic substitution on the allylamine by hexachlorocyclotriphosphazene was performed according to the same procedure as that used for precedent reaction except that we added (0.05 g) Mag-H^{+} clay catalyst layered and the solvent used is diethyl ether, the reaction time was reduced to 12 h, the solution was then filtered after adding $CDCl_3$ and recovered Mag-H^{+}, then the filtration was purified as for the precedent product, the product obtained is white crystals in the yield was 74%. Finally, the product is characterized by: ^{1}H-NMR: 1.2 ppm (NH), 3.5 ppm (CH2-NH), 5.8 ppm (CH = CH_2), 5.1, 5.0 ppm (CH = CH_2), IR: 3450 cm-1 (NH), 1254 cm-1 (P = N), 1644 cm 1 (C = C), RMN ^{31}P: 12 ppm (three phosphors). MALDI TOF: 471g/mol.

Table 2 : Synthesis of hexa (allylamino) cyclotriphosphazene in diethyl ether induced by Maghnite-H^{+} (0.25M).

Product	Catalyst (Mag-H^{+}	solvent	yield	Time (h)	Temperature (°C)
2	5%	Diethyl ether	74%	12	20

To complete the synthesis of hexa (allylamino) cyclotriphosphazene, can be avoided hazards of benzene (carcirogen solvent), using his place diethyl ether in the presence of Maghnite-H^{+} where achieving this synthesis under conditions sweet. The reaction taking place is shown in the following scheme:



Scheme 1 : Representation schematic of the synthesis of hexa (allylamino) cyclotriphosphazene catalysed by Maghnite-H^{+} (0.25M).

III. Results and Discussion

Figure 2. Shows the FTIR spectra of HACTP. The characteristic IR peaks of the resulting HACTP has characteristic peaks appear edat 3194.32 cm-^{1} for NOH groups, and at 1642.28 and 909.38 cm-^{1} for CAC bonds. The IR peak of PAN bonds were shifted to 1176.19 cm-^{1} as shown in Figure2.

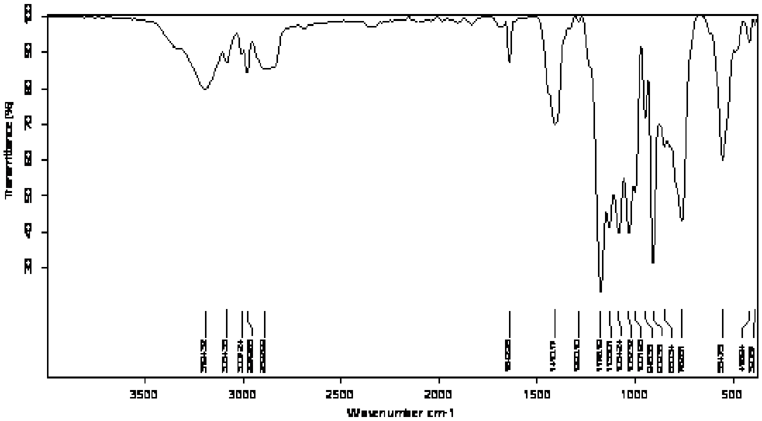


Figure 2 : FTIR spectrum of hexa (allylamino) cyclotriphosphazene induced by Maghnite-H^+ (0.25M) at room temperature

The ^{1}H-NMR spectra was complicated, but the integrated ratios of aliphatic to aromatic protons were consistent with structure of hexa (ally amino) cyclotriphosphazene (HACTP). ^{1}H-NMR spectroscopy at 300 MHz (solvent $CDCl_3$). Fig 3. Showed different peaks of hexa (allylamino) cyclotriphosphazene, ^{1}H-NMR: 1.2 (s , H_a), 3.4 (s, H_b), 5.8(m, H_c, J_{dc}=17.1, $J_{d'c}$=10.1, J_{cb}=4.8), 5.1, 5.2 (d, H_d , $J_{dd'}$=1.5 , $J_{d'c}$=10.1) , 7.2 (s, $CDCl_3$) .

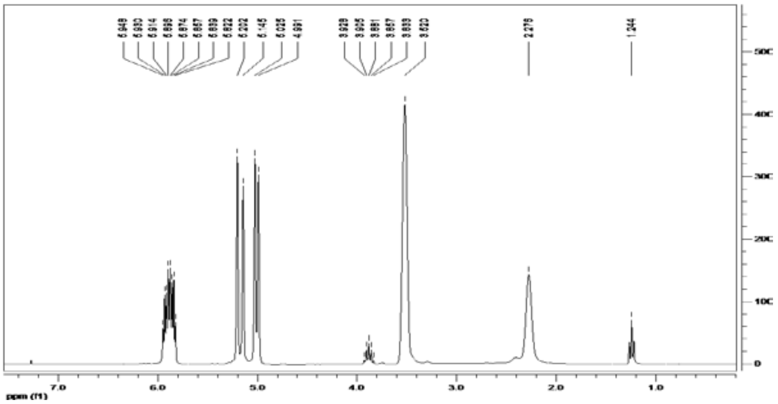


Figure 3 : ^{1}H-NMR spectrum of hexa (allylamino) cyclotriphosphazene induced by Maghnite-H^+ at room temperature in $CDCl_3$

The chemical structure of HACTP was further supported by ^{13}C-NMR .The ^{13}C-NMR spectrum clearly shows three resonance peaks with their carbons assigned in Figure 3.

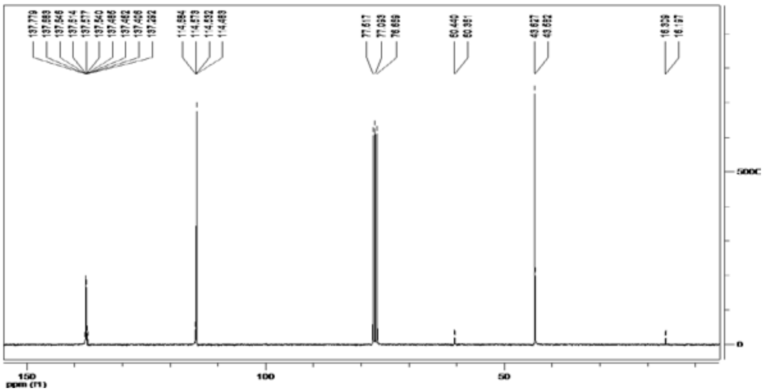


Figure 4 : ^{13}C-NMR spectrum of hexa (allylamino) cyclotriphosphazene (HACTP) induced by Maghnite-H^+(0.25M).

The TGA data of HACTP shown in Figure 5, indicates a two-stage degradation behavior. By comparing to the mass spectrometry of HACTP, it's possible that the first stage of degradation at around

230-320°C was proceeded by the cleavage of two allylamine groups remaining 56.89 wt % residue, and then proceeded with the cleavage of another two allylamine groups after 450°C[16].

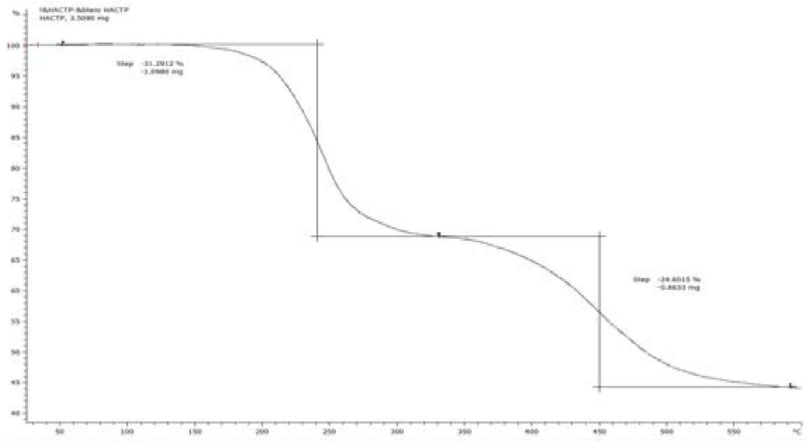


Figure 5 : TGA curves of hexa (allylamino) cyclotriphosphazene obtained in nitrogen atmosphere at heating rate of 10 °C/min

The molecular weight of HACTP determined from the mass spectrometry is 701 (see Fig. 4). Other significant observation on the mass spectrum of HACTP is its fragmentation to 488, 486, 472, and 461. The major peaks are contributed by the sequential cleavages of allylamine groups from HACTP and were contributed by the former fragments plus one [-NH] + group [17].

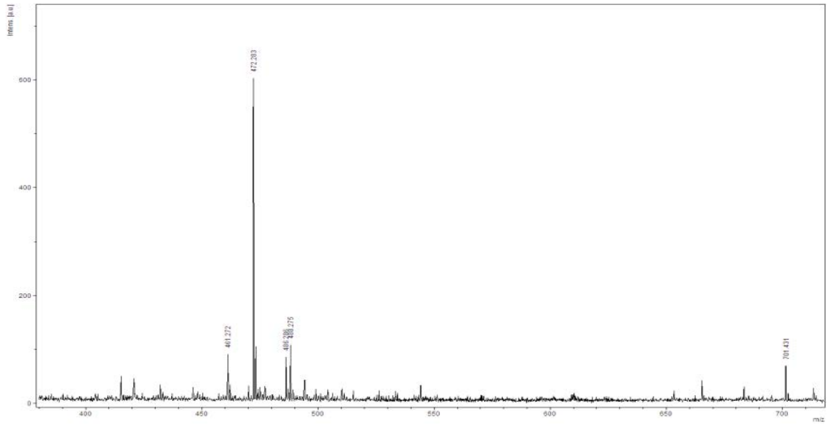


Figure 6 : Mass spectrum of hexa (allylamino) cyclotriphosphazene (HACTP) induced by Maghnite-H⁺(0.25M).

The DSC result shown in Figure 6 indicates that HACTP is a highly crystalline material with a melting temperature of 88.1°C. It is mildly reactive after melt with the maximum reaction temperature at 198, 9°C [18].

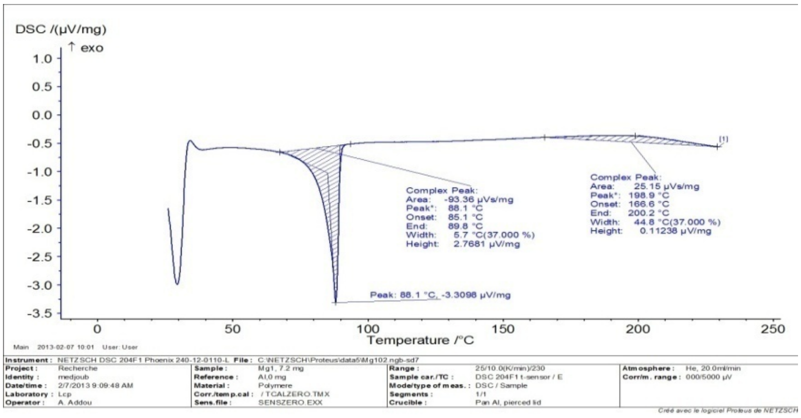


Figure 7 : DSC curves of obtained in nitrogen atmosphere at heating rate of 10 °C/min

IV. CONCLUSION

We have developed a new synthetic method to produce hexa allylamino cyclotriphosphazene, which does not use inorganic acid but friendly, green, ecologic and non toxic catalyst clay as proton source. To complete the synthesis of hexa (allylamino) cyclotriphosphazene, can be avoided hazards of benzene (carci- nogen solvent), using his place diethyl ether in the presence of Maghnite-H^{+} where achieving this synthesis under conditions sweet. The simplicity of the methods, good properties catalytic of the support catalyst solid super acid (Maghnite-H^{+}) and non toxic solvent make this an attractive method for the synthesis of hexa (allyl- amino) cyclotriphosphazene.

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Flame Propagation Regimes at Combustion of Lean Hydrogen-Air Mixtures in the Presence of Additives at Central Spark Initiation at Atmospheric Pressure

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Abstract- By means of high-speed color cinematography it is shown that the flames in lean H_2- air mixtures at an initial stage propagate symmetrically and the flame radius can be estimated from the frames of speed filming. It is shown that sufficiently strict calculation of cellular structure flame front of lean hydrogen mixes requires consideration of a 3D problem however thermal diffusion instabilities at the initial stage of combustion have no effect on the velocity of flame which can be estimated assuming unperturbed flame front in the range of $8\%<H_2<15\%$. It is shown that the analysis of experimental data on flame propagation in lean mixtures does not allow taking apart results of calculation by two-dimensional model with regard to convection and without convection. It is experimentally shown, that isobutene additives in quantities below a concentration limit (up to 1.5 %) tend to increase, and CO_2 additives up to 15 % - to reduce the flame propagation velocity in lean H_2-air mixtures. The reasons for acceleration of combustion in the presence of hydrocarbon additive are considered.

For lack of special conditions the processes of gas-phase combustion occur under non-stationary currents, density and pressure fluctuations, i.e. have non-steady character [1-3]. For example a cellular combustion front is characteristic of lean hydrogen-air mixes, caused by thermal diffusion instability [3-5].

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Abstract- By means of high-speed color cinematography it is shown that the flames in lean H_2- air mixtures at an initial stage propagate symmetrically and the flame radius can be estimated from the frames of speed filming. It is shown that sufficiently strict calculation of cellular structure flame front of lean hydrogen mixes requires consideration of a 3D problem however thermal diffusion instabilities at the initial stage of combustion have no effect on the velocity of flame which can be estimated assuming unperturbed flame front in the range of $8\%<H_2<15\%$. It is shown that the analysis of experimental data on flame propagation in lean mixtures does not allow taking apart results of calculation by two-dimensional model with regard to convection and without convection. It is experimentally shown, that isobutene additives in quantities below a concentration limit (up to 1.5 %) tend to increase, and CO_2 additives up to 15 % - to reduce the flame propagation velocity in lean H_2-air mixtures. The reasons for acceleration of combustion in the presence of hydrocarbon additive are considered.

For lack of special conditions the processes of gas-phase combustion occur under non-stationary currents, density and pressure fluctuations, i.e. have non-steady character [1-3]. For example a cellular combustion front is characteristic of lean hydrogen-air mixes, caused by thermal diffusion instability [3-5]. For the first time flame cells in combustion of lean H_2-air mixes were observed in [6]. In [1,7] it was shown that flame cells in lean H_2-air mixes can be obtained also in microgravity conditions, i.e. the gravity field isn't essential for occurrence of cellular flames.

Investigations of flame propagation in lean H_2-air mixes in narrow vertical pipes showed that flame propagation "upwards" is accompanied by the partial consumption of fuel; in this case the fuel content at concentration limit of flame propagation is less than that in a "downwards" direction [4,8].

In a 2D model of combustion of lean H_2 -air mixes in [9] convection and gravity were not taken into account. However, calculated velocities of flame fronts were close to their experimental values. The analytical theory of cellular flames based on representation of a flame as a dense flat structure of hexagonally packed flame balls [2], also gives a good consent with experiment at successful selection of parameters. It is important to find out limits of applicability of the models of the hydrogen flame which do not consider convection and compressibility of the environment for calculation of flame velocities [2,4,5,7,9,10] in comparison with the models considering convection and compressibility of the environment [2, 11]. Understanding combustion of lean H_2 -air mixes is critical to the design of efficient, clean-burning combustion engines as well as to provide explosion safety in mines, chemical plants and engines operation.

The work is aimed at investigation of the flame structure in lean hydrogen-air mixes in a bomb of constant volume at atmospheric pressure by means of a method of high-speed cinematography; the results obtained are compared with numerical calculations and experimental data including these reported in literature.

I. EXPERIMENTAL

Experiments were performed with lean (5.8-15%) hydrogen-air mixes at initial atmospheric pressure and temperature T = 298K in a horizontally located stainless steel cylindrical reactor 13 cm in diameter and 15 cm long supplied with an optical quartz window at a butt-end. Spark electrodes were placed at the reactor centre; the distance between them was 0.5 mm. Experiments were performed as following. The reactor was pumped out to 10-2 Torr, than filled with CCl_4 (~ 4%), then with hydrogen and air up to the atmospheric pressure. The gas was maintained for 15 min for completeness of mixing, then spark initiation (1.5 J) was carried out. Notice that that the additive of CCl_4 is necessary for visualization of a hydrogen flame; 4% CCl_4 in H_2 -air mixture can be considered as an inert additive [12]. Speed filming of ignition dynamics and flame front (FF) propagation was carried out through an optical window by means of a color high-speed digital camera Casio Exilim F1 Pro (frames frequency, 60–1200 s–1). The video file was stored in computer memory and its time-lapse processing was performed. The pressure change in the course of combustion was recorded by means of a piezoelectric gage synchronized with the discharge. Gases were chemically pure.

The degree of expansion of combustion products ε_T was determined as follows [4] (P_b is the maximum pressure developed in the course of combustion):

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$$P_b/P_o = 1 + \gamma\,(\varepsilon_T - 1) \qquad (1)$$

The normal velocity Un of FF was calculated from the equation [4]:

$$U_n = V_v/\varepsilon_T \qquad (2)$$

In equations (1), (2) P0 – initial pressure, $\gamma = 1.4$ - the ratio of specific heats, Vv - visible flame velocity.

II. Results and Discussion

As is seen in Fig. 1 (a-c), FF in lean burning mixture has a spherical form. The cells are well visualized, thus diameter of the sphere can be measured experimentally. For mixes containing < 10% of H2 FF has a spherical form only at an initial stage after initiation (Fig. 1a). Further in the course of combustion the action of gravity force is shown, and FF gets a form of the hemispherical segment moving upwards (Fig. 1 a, b). For the mixes containing > 10% H2 FF velocity increases so that gravity doesn't manage to be shown, and the flame propagates spherically symmetrically (Fig. 1c, d). The front of a flame remains cellular, thus with increase in hydrogen content to 15% in air the size of flame cells markedly decreases.

As is seen in Fig. 1a at an initial stage the sphericity of the combustion front (Fig. 1a, shots 2-6) is characteristic even for 8% of H2 in air. High-speed filming of flame propagation in 10% H2 + air is presented in Fig. 1b, also illustrating FF sphericity. The visible flame velocity Vv measured for 4% CCl4 + 10%H2 + 86% air mix (Fig. 1a) makes up 36 cm/s, thus the normal flame velocity Un calculated by means of eq.(2), makes up 21 cm/s taking into account that experimental value of εT is 1.6 for this mix. Visible flame velocity Vv for mix 4% CCl4 + 15%H2 + 81% air (Fig. 1c) makes up 2.4 m/s, thus the normal velocity Un calculated by means of eq.(2) makes up 60 cm/s taking into account the experimental value of εT = 4. These values of normal velocity are in good agreement with literature data, and also are close to results of numerical calculation of Un obtained using a model of a laminar flame without convection [9], i.e. without taking into account the cellular flame structure. It means that perturbations of thermal diffusion nature observed on FF at the initial stage of combustion have no essential impact on the velocity of flame propagation of lean H2-air mixes.

We specify concentration boundaries of various modes of a cellular flame propagation in lean H2-air mixes on a basis of Fig. 1 and [1, 4, 8]:

a) "anisotropic" at H2 <10% that corresponds to different velocities of flame propagation "upwards" and "downwards" in vertical pipes [4,8] and spherically-symmetric on an initial stage of combustion;

b) Spherically - symmetric at 10%< H2 <15%, thus distinction between propagation "upwards" and "downwards" is missing.

A spherically symmetric mode of cellular flame propagation in microgravity conditions at H2 concentration less than 10% is also known [1, 7]. We will note also that in the conditions of zero gravity there exists a mode of occurrence of separate isolated motionless cells of combustion [1]. Such "flame balls" can be observed in mixtures that are well outside the conventionally defined extinction limits, e.g. In 3.85% H2 - 96.15% air mixture [1].

We will specify that experimental values of the lower concentration limit of flame propagation in microgravity conditions ($C_{\mu g}$) have noticeable dispersion that doesn't allow reliable establishing whether the limit value is closer to a propagation limit "upwards" or "downwards". According to [7] the limit is close to "upwards" limit value in the gravity field and makes up 5.5% H2 in air, however from [1] $C_{\mu g}$ makes up 7% H2 and from [5] $C_{\mu g}$ makes up 7% H2 in the presence of 2.5% of CF3Br.

It is possible to conclude that the spherical form is inherent to cellular flames propagation in lean H2 -air mixes at an initial stage. The gravity field only then distorts a shape of FF for mixes in the vicinity of the lower concentration limit of the flame propagation (Fig. 1 a, b).

We will consider some results obtained at numerical modeling of cellular flames. A flat 2D problem and the model of thermal convection in Boussinesque approximation were used to analyze FF propagation in lean H2-air mixes in [10, 11, 14]. The reduced kinetic scheme of reaction of hydrogen oxidation including 13 reactions as well as thermo chemical parameters, were taken from [8]. However, for lack of gravity the cellular mode at calculation was missing. Thus, a 2D calculation in Boussinesque approximation doesn't allow modeling experimentally observed mode of the cellular flame propagation in microgravity conditions.

To establish physical processes to be considered for a 2D modeling of the cellular FF in the microgravity conditions a numerical analysis by finite elements method with use of a software package FlexPde 6.0 [15] was carried out. Thus, because it was shown in [11,14] that within Boussinesque approximation features of lean hydrogen flames do not depend on the chemical nature of the most quickly diffusing intermediate, but the features are determined by the value of diffusion coefficient of the insufficient initial component [4,8], a chemical reaction was set by a single equation in Arrhenius form (see Appendix).

In Fig. 2 results of calculation of FF propagation are presented in Boussinesque approximation a) g=0 (g is acceleration of gravity); b) g=980 cm2/c. The calculation of FF propagation at g=0 on the basis of

Navier-Stokes equations for a viscous compressible environment [16] is shown in Fig. 2c. As is seen in Fig. 2 (a,b,c) a 2D consideration of the convection caused by expansion of gas in the course of combustion for lack of gravity in weakly compressible environment doesn't lead to occurrence of a cellular combustion; thus taking into account of compressibility in Navier-Stokes equations provides a way to obtain a 2D cellular combustion mode. Thus, for a 2D modeling of cells at "anisotropic" (H2 <10%) mode of FF propagation Boussinesque approximation is applicable [11]; for the description of a 2D-symmetric mode in the absence of external forces compressible Navier-Stokes equations should be used.

We now turn to a 3D problem. It should be noted that it was earlier shown [4] that the steady heat and mass conservation equations admit a solution corresponding to a stationary spherical flame, though the same equations in planar geometry provide a solution in the form of a propagating wave. Indeed in the simplest case of spherical geometry, the solution to steady, free convection diffusion equations for temperature T and chemical species C, $\nabla^2 T = 0$ and $\nabla^2 C$, has the form c1 + c2/r, where c1 and c2 are some constants. This form reflects the fact that T and Y are bounded as $r \to \infty$. For cylindrical and planar geometry the forms are c1 + c2ln(r) and c1 + c2r, respectively, which are unbounded as $r \to \infty$. Therefore a spherical flame is admitted, but not (say) a “flame cylinder” solution. On the basis of this simple consideration illustrated below (see also Appendix) one should expect occurrence of cellular FF in a 3D modeling within Boussinesque approximation. The result is shown in Fig. 2d where the section of a 3D structure of the flame front is specified in the XZ plane (a 3D mesh structure is shown in Fig.2e). As is seen in Fig.2d a 3D flame front shows a cellular structure in relation to a 2D modeling (Fig.2a) which provides completely undisturbed FF.

It follows from aforesaid that sufficiently strict calculation of cellular FF structure of lean hydrogen mixes requires consideration of a 3D problem however on the other side thermal diffusion instabilities at the initial stage of combustion have no effect on FF velocity which can be estimated assuming unperturbed flame front in the range of 8%<H2<15%.

It is of interest in this connection to find out the limits of applicability of the models of hydrogen flame, which do not account for convection and compressibility of the environment, for calculation of FF velocities observed experimentally [2,4,5,7,9,10,13] in comparison with the models considering convection and compressibility of the environment [2, 11]. We will examine the data on measurement and calculation of FF normal velocities of lean H2-air mixes available in literature along with our results. A considerable set of literary data is presented in [2, 13] in which results of several groups of authors are given. Comparison of experimental and calculated normal FF velocities in lean H2 - air mixes at 1 atm and initial temperature 298 K in relation to the content of fuel in mix (equivalence ratio θ is a fraction of fuel in a mix with air: $\theta H_2 + 0.5(O_2 + 3.76N_2)$) is shown in Fig. 3. In Fig. 3 a thick curve represents results of modeling within a 1D problem [2], a thin curve shows calculated values with the use of an analytical formula [2]. Points represent experimental data cited in [2] (see Fig.1 [2]), crosses represent experimental data [10], thin circles – the data of a 2D calculation without convection (Fig.2, [9]), thick circles - the data of a 2D calculation with convection taken into account (Fig 3 and Fig.4 [10]), triangles – experimental data for lack of gravity [7]. The area filled with grey color relates to a number of sets of experimental values of FF normal velocities of lean H2- air mixes [13]. Notice that there were no reasons to choose any of the data sets as the most reliable one.

As is seen in Fig.3 the results obtained in [9] with use of a 2D model without convection (crosses), lie in the area of experimental values of FF normal velocities [13]. It is evident from Fig. 3 that the experimental errors of the data on FF propagation do not allow establishing the kinetic mechanism of H2 oxidation necessary for the description of lean H2-air combustion in detail; and even taking apart the results of calculation for the 2D models including convection and without it. In other words, only successful selection of parameters allows obtaining quantitative agreement with experiment. Notice that even calculations for a 1D model (a thick curve in Fig. 3) which agrees with the experimental data in the worst way also fit with experimental data.

It means from aforesaid that at the current state of experiment any comparison of experimental data on FF propagation in lean H2-air mixes with the results of numerical modeling is credible only in qualitative aspect e.g. on velocity change of movement of the boundary between initial and actively reacting gas, as well as on the shape of this border and on the degree of its "smoothness" or pertubations of its structure. Obviously, the consideration of detailed kinetic mechanism introduces additional uncertainty into calculations. The vast majority of kinetic parameters is not accurate enough to draw reliable conclusions on the basis of modeling. The question of completeness of the kinetic mechanism used is always an open question, i.e. whether any important reaction is overlooked. Moreover as there are no unicity theorems on reactive Navier-Stokes equations, the agreement between calculated quantities and experimental ones does not argue for accord between calculation and experiment as there can be other sets of the governing parameters describing the same profiles.

We will note that the discussion carried out above refers only to H2-air mixes in the absence of other reactive additives, for example, hydrocarbons. It is known that addition of hydrogen to hydrocarbon fuels holds much promise for providing ecological safety of combustion products e.g. in engines [1]. The results of high-speed filming of FF propagation in lean H_2 - air mixes in the presence of isobutene (C_4H_8) additive (CCl_4 additive was not used in the experiments) are presented in Fig. 4 (a-f); the concentration of additive in all cases doesn't exceed the lower concentration limit of C_4H_8 ignition being equal 1.8% [12]. Notice that C_4H_8 additive in stoichiometric and rich H_2 - oxygen mixtures act as combustion inhibitor [16].

Combustion of lean H_2 mixes is considerably accelerated in the presence of C_4H_8 additive in agreement with [17] as is evident from comparison of sequences of the video images shown in Fig. 4 (a-f); though C_4H_8 additive in such quantities isn't combustible. Indeed as is shown in Fig. 4 (a, b) 1.5% of C_4H_8 additive accelerates combustion of 10% H_2 in air several times in comparison with 10% H_2 - air without additive; as is seen in Fig. 4 (c, d) the increase in additive content by a factor of three accelerates combustion of 7.5% H_2 with air also approximately by the same factor. Even near a combustion limit isobutene additive considerably accelerates hydrogen combustion (see Fig. 4 (d- f)).

In addition (Fig. 4 (b, c, e)), gasdynamic features of FF propagation in lean H_2-air mixes in the presence of a hydrocarbon additive also qualitatively change; with increase in the content of the additive flame instabilities are no longer shown in the form of cells, but in the form of "folds" on FF surface. Such instabilities aren't observed in combustion of lean H_2-air mixes in the absence of the additive. It means that FF stability in the presence of hydrocarbon additive increases.

We will note that the chemical mechanism of combustion of combined fuels on the basis of lean H_2 - air mixes in the presence of hydrocarbons isn't considered in literature in detail. However the solution of this problem is necessary for correct numerical modeling of combustion of lean binary mixes of hydrogen and hydrocarbon with air. Dependencies of normal velocities of FF propagation in lean H_2 -air mixes in the presence of the isobutene and CO_2 additives on H_2 content are shown in Fig. 5. Visible velocities were measured at an initial stage of combustion process (from the very first frames of video filming when the flame front still keeps a spherical form) with use of the equations (1) and (2).

Normal combustion velocities of H_2-air mixes in the absence of additives obtained in the work are in agreement with [12]. As is seen in Fig. 2 1.5% isobutene additive is the most effective; it provides increase in the normal flame velocity of combined fuel in comparison with that of lean H_2 -air mix more than by a factor of 5. Chemically inert CO_2 additive [12] causes reduction of FF velocity (Fig. 5).

As is seen in Fig.5, 1% of C_4H_8 or 2% of H_2 is required to attain the same FF velocity e.g. for 5.8% of hydrogen in air (dotted straight lines in Fig. 5). One of the reasons of observed efficiency of a hydrocarbon additive can result from the fact that thermal effect of isobutene oxidation makes up 2549, 7 kJ/mol, and hydrogen - 242, 9 kJ/mol [12], therefore heat release in combustion of isobutene is ten times greater than in hydrogen combustion. It provides increase in FF velocity at the expense of increase in adiabatic temperature of combustion. The other reason can comprise the change in kinetic mechanism of combustion in the presence of hydrocarbon additive particularly at a stage of initiation of FF propagation. By this means in lean H_2-air mixes, unlike rich ones [17] hydrocarbon additive burns down completely in an excess of oxidizer (that is accompanied by luminescence, see Fig. 4 (b-d)) therefore calculation of FF velocity in the presence of hydrocarbon additive requires a consideration of the major elementary reactions of hydrocarbon oxidation along with the mechanism of hydrogen oxidation however in doing so all difficulties mentioned above are shown in full.

We summarize shortly the results obtained. It is established that cellular flames of lean H_2-air mixtures at an initial stage propagate spherically symmetrically. Therefore combustion velocity can be estimated from the change of visible radius of a flame front. It is shown that Boussinesque approximation is applicable for the description of cells occurrence in the field of gravity at $H_2 < 10\%$ within a 2D problem; in the conditions of microgravity it is necessary to invoke compressible Navier-Stokes equations within a 2D problem or Boussinesque approximation within a 3D problem. It is shown that the error of experimental data on FF propagation in lean H_2 -air mixes doesn't allow carrying out reliable verification of various numerical models as well as establishing the kinetic mechanism of H_2 oxidation necessary for the description of lean H_2-air combustion in detail. With use of a method of color high-speed filming it is shown that isobutene additives in quantities below lower concentration limit of ignition increase FF velocity of lean H_2-air mixes. The increase in adiabatic temperature of combustion can be one of the reasons of increase in flame propagation velocity; the other reason is change in kinetic mechanism of combustion in the presence of additive. It was shown that the most effective concentration of isobutene additive which provides increase in the normal flame velocity of the combined fuel in comparison with H_2-air mix more than by a factor of 5 amounts to 1.5%.

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APPENDIX

A qualiative 3D modeling for microgravity conditions was performed as follows. Chemical process is presented by a single reaction in Arrhenius form. In Boussinesque approximation, we assume that the fluid is almost incompressible, except for thermal expansion effects which generate a buoyant force. The incompressible form of the Navier-Stokes equations can be written:

$$\mathrm{grad}(U) = 0 \qquad (3)$$

$$\partial U / \partial t + U\,\mathrm{grad}\,(U) + \mathrm{grad}(p) = \nu\,\mathrm{div}\,(\mathrm{grad}\,(U)) + F \qquad (4)$$

Where U represents the velocity vector, p is the pressure, ν is the kinematic viscosity, F=0 - is the vector of body forces.

Eq. (3) is continuity equation while eq. (4) expresses the conservation of momentum. Dimensonless form of reactive Navier-Stokes equations (T-temperature, C-concentration) is according to [11]:

$$p=\rho T \text{ (state equation)}$$

$$\rho = \rho_0\,(1 - \alpha\ (T\text{-}T_0)) \quad \text{(Boussinesque approximation)}$$

$$\mathrm{grad}(U) = 0$$

$$\partial U / \partial t + U\,\mathrm{grad}\,(U) + \mathrm{grad}(p) = \nu/Re\,(\mathrm{div}\,(\mathrm{grad}\,(U)))$$

$$\partial T / \partial t + U\,\mathrm{grad}\,(T)) = 1/Re^*Pr_T\,(\mathrm{div}\,(\mathrm{grad}\,(T))) + \beta_2.RC$$

$$\partial C / \partial t + U\,\mathrm{grad}\,(C)) = 1/Re^*Pr_C\,(\mathrm{div}\,(\mathrm{grad}\,(C))) + \beta_1.RC$$

$Re = 10^5$, $Pr_T = \mu\ C_p /\lambda = 0.72$ [18] $Pr_C = \mu\ C_p / D= 0.5\ Pr_T$ (λ - heat conductivity, $D = 2\lambda$ – diffusivity in lean mixture, $D>\lambda$ for a lean H_2 mixture [8]). Reaction of the first order is set by Arrhenius's law RC (C, T) = (1-C) exp [ζ (1-1/T)], Temperature of walls of the external sphere is T_0, concentration C on the wall of the sphere is zero. The flame was initiated with a heated internal cube (Fig 2d). Temperature of flame initiation on an internal cube surface is $5T_0$, temperature in volume – T_0, initial concentration C_0 is 0; other parameters are put equal $T_0 =1$, $\alpha=9.10^{-3}$, $\rho_0 =6.10^{-3}$, $\zeta=10$, $\beta_2=0.3$, $\beta_1 = 0.2$. Software package of a finite elements method FlexPde 6.0 [15] was used.

For qualitative consideration of conditions of occurrence of cellular structures we followed BUOYANT.PDE example from FlexPde 6.0 [15] for the solution of a 2D problem. The reactor of circular section with ignition by a step on a horizontal axis was considered. Calculations were performed in the top half of area (Fig. 2 a-c). Using grad (U) =0 and grad (rot (U)) =0 ratios, and w definition = rot (U), we get the momentum conservation equation in the form:

$$\partial w/\partial t + u\ \partial w/\partial x + v\ \partial w/\partial y = \nu\ \mathrm{div}\ (\mathrm{grad}\ (w)) - g\ \partial\rho/\partial x$$

Taking into account that in two dimensions velocity has only two components, say u and v, and the vorticity has only one, which we shall write as w.

Let us consider now continuity equation. If we define a scalar function ϕ such that

That $u = \partial\phi / \partial y$, $v = - \partial\phi / \partial x$, then $\mathrm{grad}(U) = \partial^2 \phi/\partial x\partial y - \partial^2 \phi/\partial y\partial x = 0$, and the continuity equation is satisfied exactly, then $\mathrm{div}\ (\mathrm{grad}\ (\phi)) = - w$

If F is a gravitational force, then $F = (0, - g\ \rho)$ and $\mathrm{rot}\ (F) = - g\ \partial\rho/\partial x$ where ρ is the density, and g is the acceleration of gravity. If we assume linear expansion of the gas with temperature, then

$$\rho = \rho_0\ (1+\alpha\ (T\text{-}T_0)) \text{ and } \mathrm{rot}\ (F) = - g\ \rho_0\alpha\partial T/\partial x$$

For temperature we have $\mathrm{div}\ (\lambda \mathrm{grad}\ (T)) = \rho_0 Cp(\partial T/\partial t + u\ \partial T/\partial x + v\ \partial T/\partial y)$, Cp – the thermal capacity at a constant pressure.

Taking into account diffusion the system of the equations takes the form:

$$\partial w/\partial t + u\ \partial w/\partial x + v\ \partial w/\partial y = \nu\ \mathrm{div}\ (\mathrm{grad}\ (w)) - g\ \partial\rho/\partial x$$

$$\mathrm{div}\ (\mathrm{grad}\ (\phi)) = - w$$

$$\mathrm{div}\ (\lambda\ \mathrm{grad}\ (T)) + \beta_2 RC = \rho_0 Cp\ (\partial T/\partial t + u\ \partial T/\partial x + v\ \partial T/\partial y)$$

$$\mathrm{div}\ (D\ \mathrm{grad}\ (C)) + \beta_1 RC = \partial C/\partial t + u\ \partial C/\partial x + v\ \partial C/\partial y$$

and the equation of state $p = \rho T$

The temperature of the walls of the external cylinder is T_0, the concentration C on the wall is zero. Newmann's boundary condition for temperature, concentration and density are set on a part of abscissa axis dividing the top and bottom half of the cylinder. The initiation temperature of a flame on a step was $5T_0$, the temperature in volume is T_0, initial concentration is 0; other parameters are the following: $T_0 =1$, $D=2$, $\lambda =0.01$, $\alpha=0.009$, $\rho_0 =10^{-2}$, $\zeta=16$, $\nu=0.001$, $\beta_2=0.3$, $\beta_1 = 0.2$, g =0 (Fig. 2a), g=980 (Fig. 2b).

Compressible Navier-Stokes equations in the absence of gravity forces have the form [18]:

$$\partial U/\partial t + U\ \mathrm{grad}\ (U) + \mathrm{grad}\ (p) = \nu\ \mathrm{div}\ (\mathrm{grad}\ (U)) + \mu\ \sigma\ (\sigma\times U) + F \text{ (momentum conservation)}$$

$$\partial\rho/\partial t + \mathrm{grad}\ (\rho U) = 0 \text{ (continuity equation)}$$

We enter function w into the moment equation with regard to the identity

$\mathrm{rot}\ (\mathrm{rot}(w)) =\sigma\ (\sigma\times w) - \mathrm{div}\ (\mathrm{grad}(w))$ the equation takes the form :

$$\partial w/\partial t + u\ \partial w/\partial x + v\ \partial w/\partial y = \nu\ \mathrm{div}\ (\mathrm{grad}\ (w)) + \mu\ (\mathrm{rot}\ (\mathrm{rot}(w)) - \mathrm{div}\ (\mathrm{grad}(w)))$$

Along with the equations of continuity, temperature and concentration we have also:

$$\partial\rho/\partial t + \mathrm{grad}\ (\rho U) = 0$$

$$Cp/(\rho\ Re\ Pr)\ div\ (grad\ (T)) + \beta_2 RC - (\partial T/\partial t + u\ \partial T/\partial x + v\ \partial T/\partial y) = Cp(Cp\text{-}1)/(\rho Re)\ ((\partial u/\partial y + \partial v/\partial x)\ 2 + ⅔\ ((\partial u/\partial x + \partial v/\partial y)^2) + (\partial v/\partial y)^2 + (\partial u/\partial x)^2))\ div(D\ grad(C)) + \beta_1 RC = \partial C/\partial t + u\ \partial C/\partial x + v\ \partial C/\partial y$$

The initial and boundary conditions given above were used in calculations used. Dimentionless scales were chosen as follows [18]: L – length, T_0 – temperature, pressure – $R\rho_0T_0$, velocity – $(\gamma RT_0)^{1/2}$, time – $L/(\gamma RT_0)^{1/2}$. The dimensionless parameters $\gamma=Cp/Cv$, $Pr = \mu\ Cp / \lambda = 0.72$ [18], $Re = \rho_0 (\gamma RT_0)^{1/2} L/\nu$, $\mu=\nu/3$ (Fig. 2c).

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FIGURES

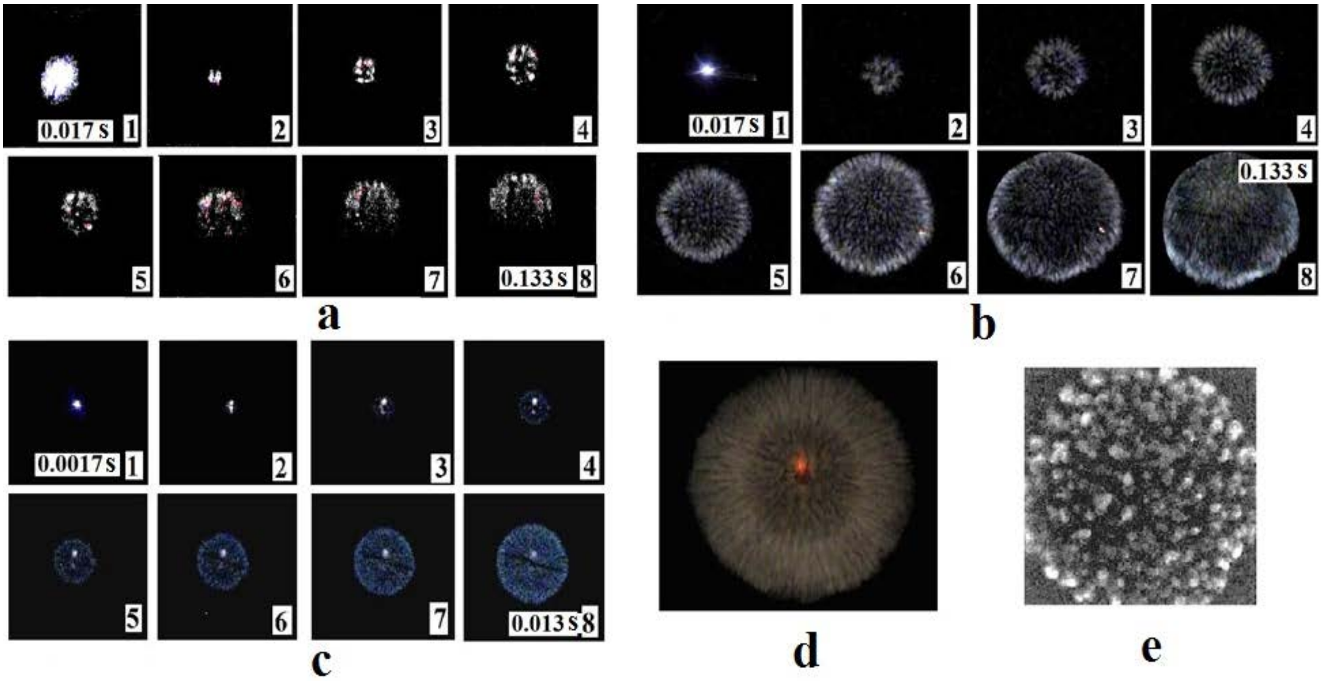

Figure 1 : High-speed filming

a) Of process of FF propagation illuminated with 4% CCl_4 + 8% H_2 + 88% air, T_0= 298K, Eo = 1.5 J. Speed of filming is 60 frames/s [9];

b) Of process of FF propagation illuminated with 4% CCl_4, in 10%H_2 + 86% air at initial pressure of 1 atm. Speed of filming is 60 frames/s;

c) Of process of FF propagation illuminated with 4% CCl_4, in 15%H_2 + 81% air at initial pressure of 1 atm. Speed of filming is 600 frames/s. The figure on a shot corresponds to a shot number when shooting. The first shot corresponds to occurrence of the spark discharge;

d) The shot from high-speed filming of FF propagation illuminated with 2% for CCl_4, in mix 12.5%H_2 + 87.5% air with an atmospheric pressure [8]. Speed of filming is 60 frames / s;

e) The shot from high-speed filming of FF propagation illuminated in the conditions of a microgravity, 7.0% of H_2 in air, an additive of 0.4% of CF_3Br, 1.18 s after initiation [7].

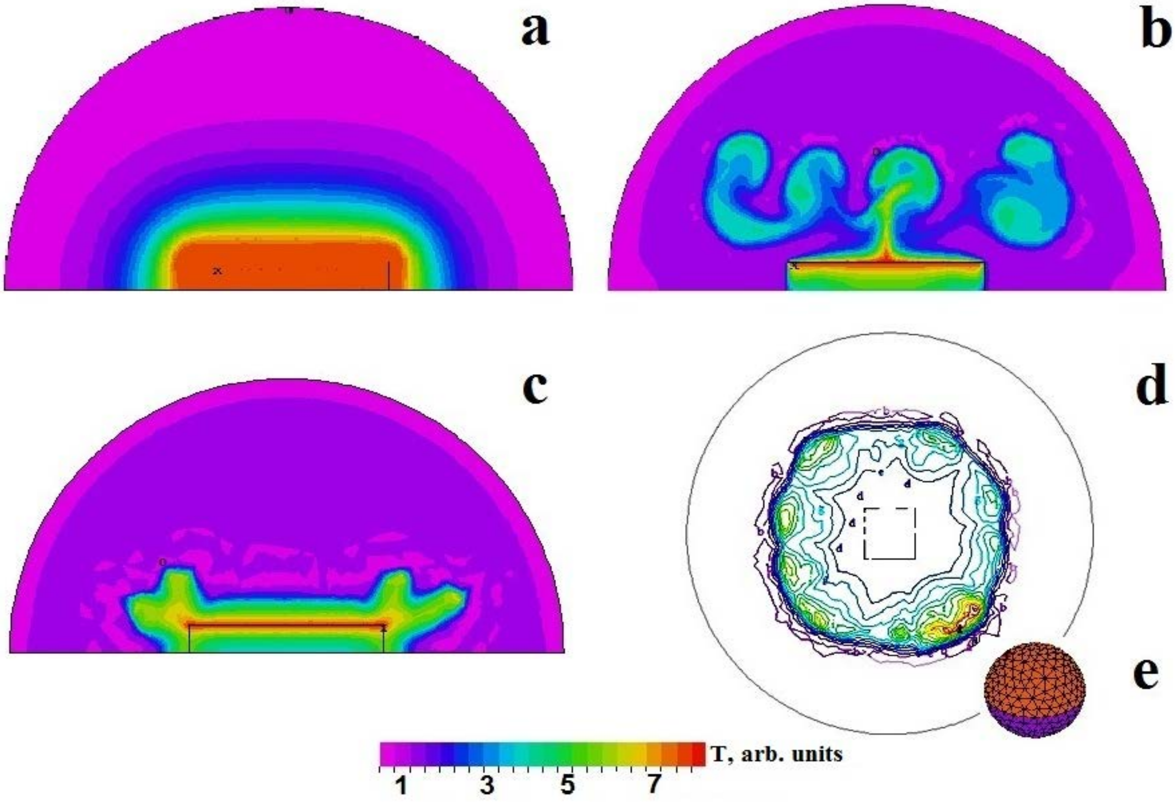

Figure 2 : Calculation by a finite elements method [15] (see Appendix) of a combustion zone propagation (temperature field) at a certain moment in a 2D Boussinesque approximation a) g=0, b) g=980 cm/s^2, c) of a combustion zone propagation (temperature field) at a certain moment at g=0, the solution of a 2D compressible Navier-Stokes equations; d) of a combustion zone propagation (temperature field) at a certain moment in a 3D Boussinesque approximation where the section of a 3D structure of the flame front is specified in the XZ plane, e) a 3D mesh structure. A scale of dimensionless T in arbitrary units is shown in the bottom

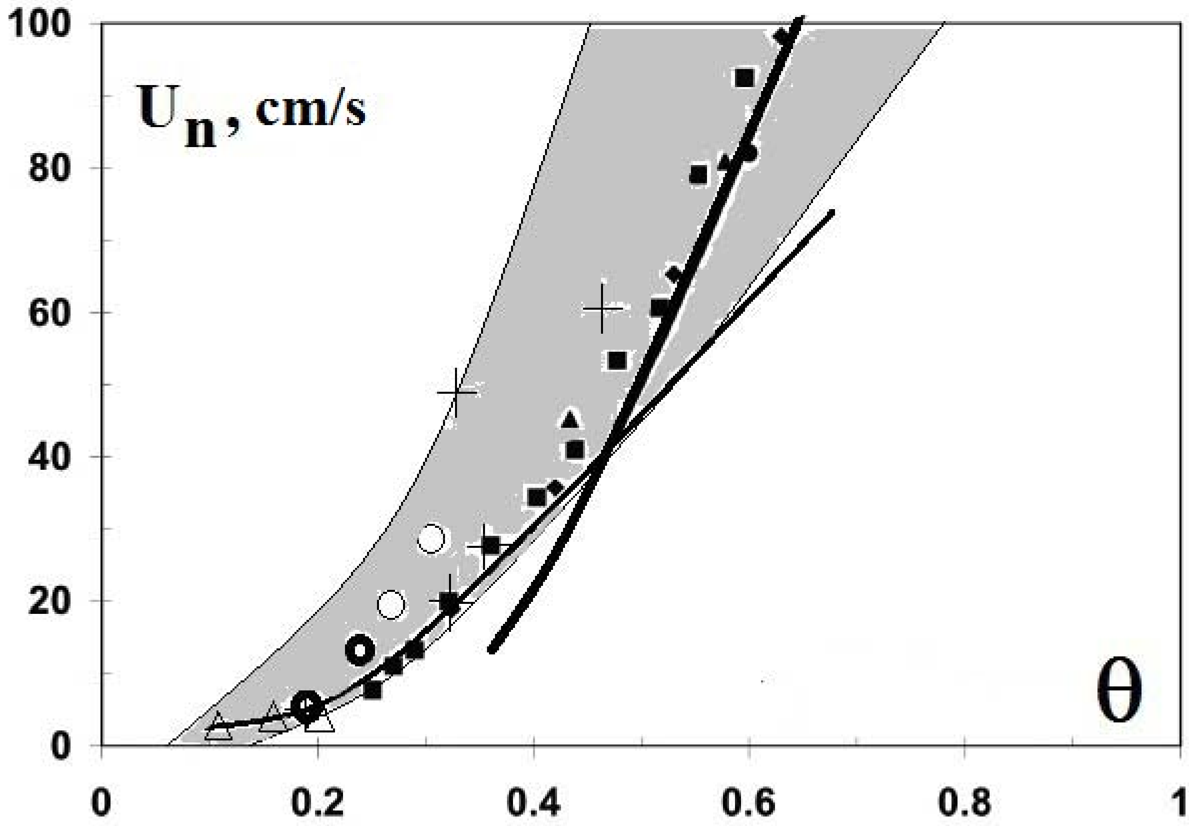

Figure 3 : Comparison of experimental and calculated normal FF velocities in lean H_2 - air mixes at 1 atm and initial temperature 298 K in relation to the content of fuel in mix (equivalence ratio θ is a fraction of fuel in mix with air: $\theta H_2 + 0.5(O_2 + 3.76N_2)$). Thick curve represents results of modeling within a 1D problem [2], a thin curve shows calculated values with the use of analytical formula [2]. Points represent experimental data cited in [2] (see Fig.1 [2]), crosses represent experimental data [10], thin circles – the data of a 2D calculation without convection (Fig.2, [9]), thick circles - the data of a 2D calculation with convection taken into account (Fig 3 and Fig.4 [10]), triangles – experimental data for lack of gravity [7]. The area filled with grey color relates to experimental values of FF normal velocities of lean H_2- air mixes [13]

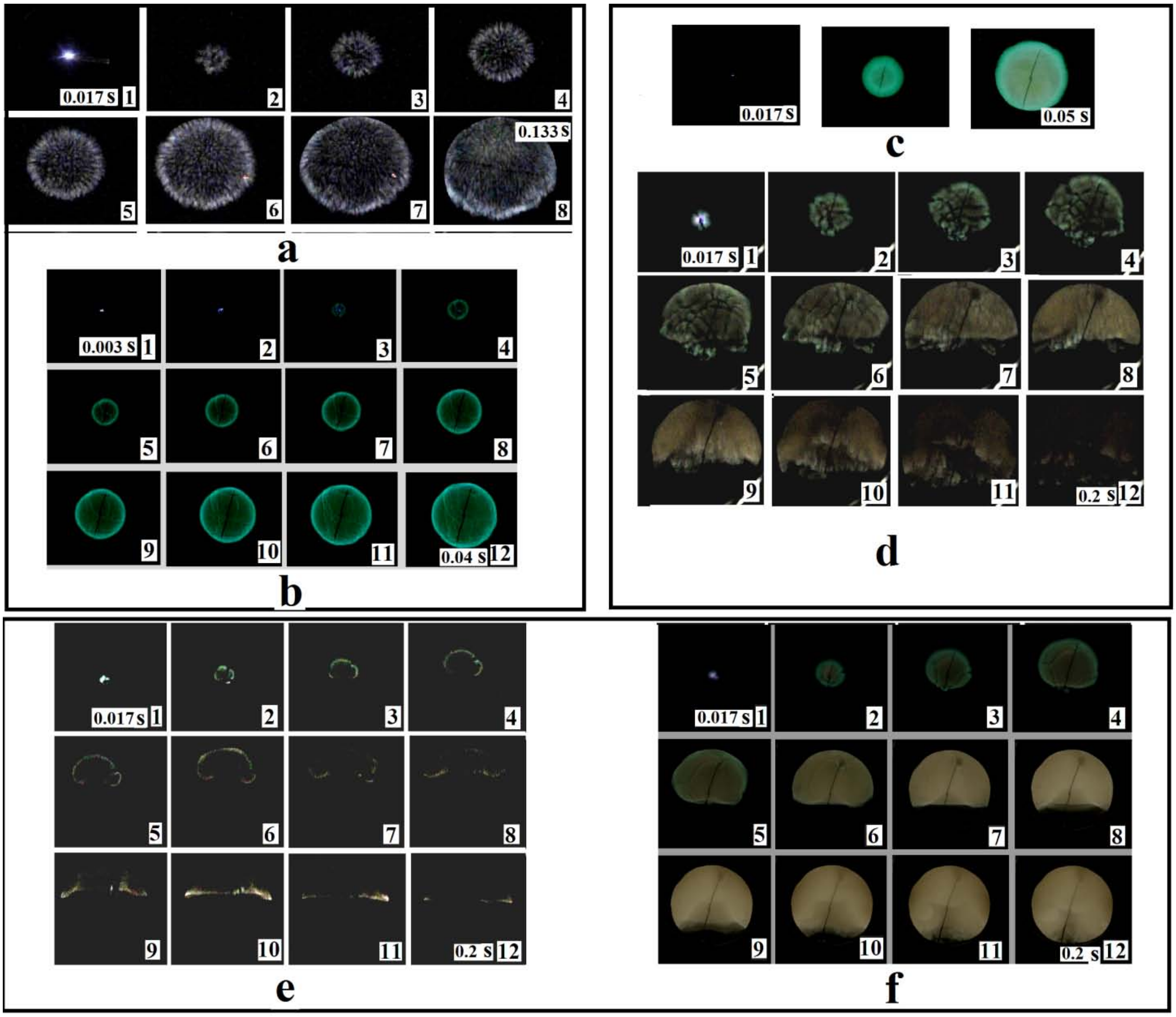

Figure 4 : High-speed filming

a) Of process of FF propagation illuminated with 4% CCl_4, in 10%H_2 + 86% air at initial atmospheric pressure. Speed of filming is 60 frames/s;

b) Of process of FF propagation in 1.5% C_4H_8 + 10%H_2 + 88.5% air at initial atmospheric pressure. Speed of filming is 300 frames/s.

c) Of process of FF propagation in 1.5% C_4H_8 + 7.5%H_2 + 91% air at initial atmospheric pressure. Speed of filming is 60 frames/s;

d) Of process of FF propagation in 0.5% C_4H_8 + 7.5%H_2 + 92% air at initial atmospheric pressure. Speed of filming is 60 frames/s

e) Of process of FF propagation in 1% C_4H_8 + 5.8%H_2 + 93.2% air at initial atmospheric pressure. Speed of filming is 60 frames/s.

f) Of process of FF propagation in 1% C_4H_8 + 6.5%H_2 + 92.5% air at initial atmospheric pressure. Speed of filming is 60 frames/s. The figure on a shot corresponds to a shot number when shooting. The first shot corresponds to occurrence of the spark discharge.

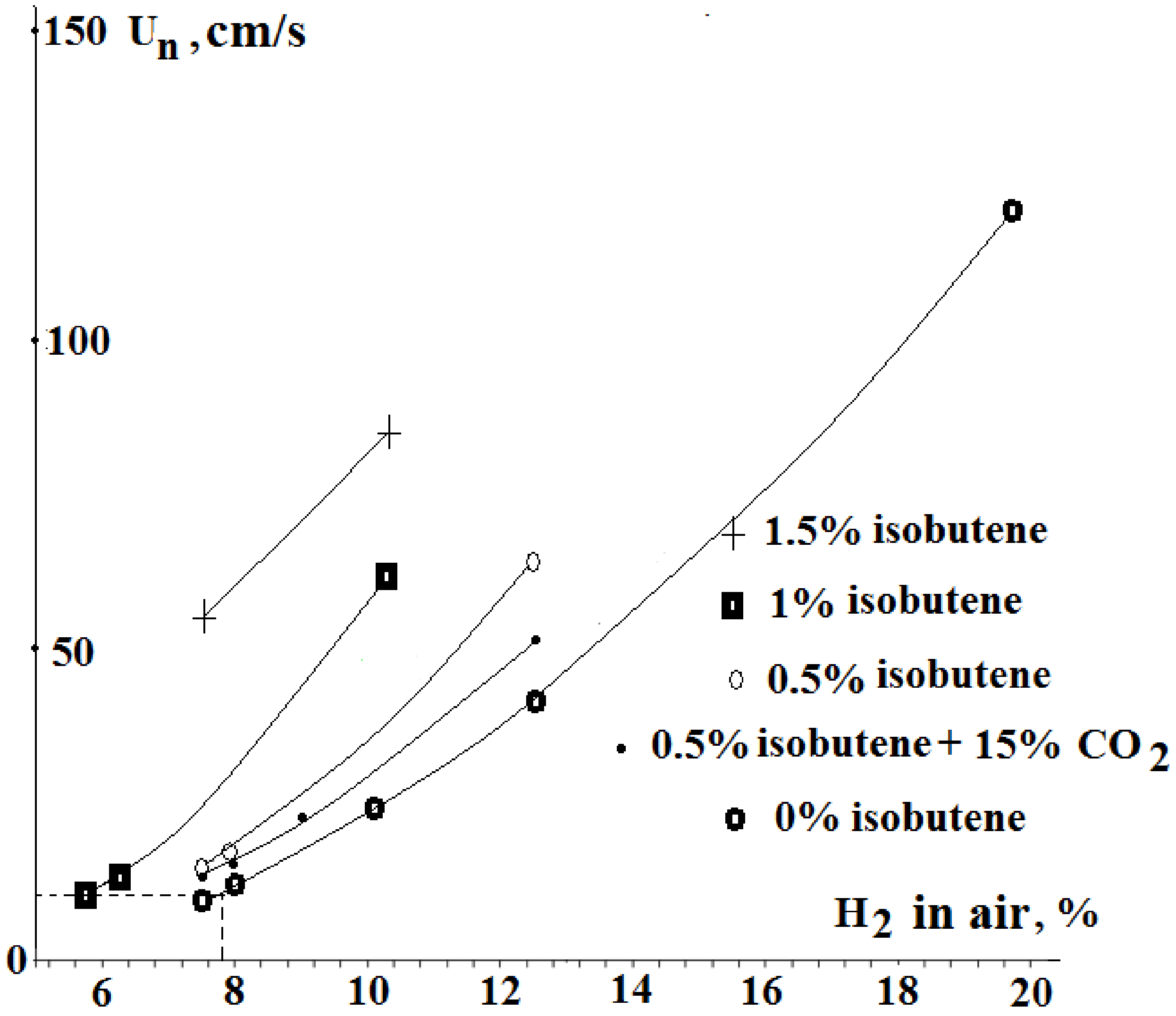

Figure 5 : Normal velocities of combustion of lean H_2-air mixes in the presence of isobutene and CO_2 additives

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Aloe Vera used as Inhibitor for Corrosion Protection of Beverage Containing Stainless Steel

By Rajesh Kumar Singh & Vikas Kumar
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Abstract- Beverage companies are used stainless steel in their manufacturing operations. Generally beverage companies make wine, beer and various types of soft drink. Their transportation and storage can be done in stainless steel containers. Beverage industries use different types of raw materials for the productions wine, beer and soft drink. They are acidic nature and their pH occur between5.5 to 6.5. Some preservatives are also added into these drinks for prevention of microorganism. These preservatives have acidic character. Wine, beer, soft drink and preservatives develop corrosion cell on the surface stainless steel thus corrosion reaction starts and harmful metal ions go into solution in this way these drinks contaminated. The contaminated drinks create several diseases. Corrosive effects are of remarkable consequence in beverage processing industry as wine, beer and soft drink contain corrosive substances, thereby causing significant impact on the degradation of constructional materials and the maintenance or replacement of products lost or contaminated as a result of corrosion reactions.

Keywords: aloevera, stainless steel, inhibitor, beverage, contaminated.

GJSFR-B Classification : FOR Code: 039999

ALOEVERA USEDASINHIBITORFORCORROSIONPROTECTION OFBEVERAGE CONTAININGSTAINLESSSTEEL

Strictly as per the compliance and regulations of :

Aloe Vera used as Inhibitor for Corrosion Protection of Beverage Containing Stainless Steel

Rajesh Kumar Singh [α] & Vikas Kumar [σ]

Abstract- Beverage companies are used stainless steel in their manufacturing operations. Generally beverage companies make wine, beer and various types of soft drink. Their transportation and storage can be done in stainless steel containers. Beverage industries use different types of raw materials for the productions wine, beer and soft drink. They are acidic nature and their pH occur between5.5 to 6.5. Some preservatives are also added into these drinks for prevention of microorganism. These preservatives have acidic character. Wine, beer, soft drink and preservatives develop corrosion cell on the surface stainless steel thus corrosion reaction starts and harmful metal ions go into solution in this way these drinks contaminated. The contaminated drinks create several diseases. Corrosive effects are of remarkable consequence in beverage processing industry as wine, beer and soft drink contain corrosive substances, thereby causing significant impact on the degradation of constructional materials and the maintenance or replacement of products lost or contaminated as a result of corrosion reactions.

For this work aloevera was taken as inhibitor. Aloevera was found to inhibit the corrosion of stainless steel in beverage. Its inhibition activities studied at different concentrations, temperatures and different intervals of times. The inhibition efficiencies and surface coverage area of aloevera increased as the concentration and temperature of aloevera increased. Inhibitive and adsorption properties of aloevera for the corrosion of stainless steel were investigated using weight loss and potentiostic methods. Test coupons dipped into drinks and the corrosion rate was determined by weight loss method. The corrosion current density absence and presence of inhibitor was studied by Potentiostic polarization technique.

The surface adsorption studied with help of Arrhenius equation, heat of adsorption, free energy, enthalpy and entropy. These thermo dynamical Para meters results produced the adsorption of the inhibitor on the surface of stainless steel was found to be exothermic, spontaneous and followed the mechanism of physical adsorption. Also Langmuir and Temkin adsorption isotherm was found to be the best isotherm that described the adsorption characteristics of the inhibitor. The result revealed that the corrosiveness of stainless steel mainly function of acidity of beverage.

Keywords: aloevera, stainless steel, inhibitor, beverage, contaminated.

I. INTRODUCTION

The material for most technical equipment are stainless steel which is selected because of its strength, ductility, weldability and it is amenable to heat treatment for varying mechanical properties. Metals and its alloys come in contact of acids during industrial processes which cause severe corrosion problems and economical losses. Beverage industry uses organic and inorganic substances for preservative purpose and they generate corrosive environment for constructional materials. These corrosive effects on different constructional materials in all phases of processing and packing of food which becomes basic need of life. Other factors affect the corrosion of metal like moist oxygen, oxide of nitrogen, oxide of sulphur, temperature, flow of liquid, pH and other factors all of which can alter the rate of corrosion.

Chemists and corrosion specialists have developed various types' corrosion protections methods. Generally organic and inorganic[1-3] substances used as inhibitors. Several works have been done with help of organic and inorganic materials for the corrosion protection of metal by coating[4-6]. Oxides of metals and phosphate of metals used as inhibitors[7, 8]. Sulpha drugs[9, 10] applied for corrosion control of stainless steel in sugar industry. Aromatic amine, fused aromatic amine and hetero cyclic aromatic amine[11] worked as inhibitors in phosphate inhibitors. Cyclic amine used for corrosion inhibition of metal in pulp and paper industry[12]. Nano coatings of organic and inorganic materials on surface of metal could produced good inhibition properties and improve the life of material[13]. Several types of nano coating can be done on the surface of materials like nano composite thin film coating, thermal barrier coating, Top layer coating, nano structural change and conversion coating. Thiourea and its derivates worked as inhibitors in petroleum industry in various operational units like production, storage and transportation. Recently natural products applied for corrosion protection of metal in acidic medium and these inhibitors were ecofriendly for environment. Polymeric coating also applied in highly corrosive environment. Organic compounds having nitrogen, oxygen and sulphur behave like anticorrosive inhibitors[14]. Electron rich organic compounds have good inhibition capability

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against acid. The corrosion is controlled by the application of aliphatic and aromatic amines. It is also observed that primary, secondary, tertiary and quaternary amine is produced good inhibitive effect against acidic medium. Several workers used heterocyclic compounds as inhibitors which possessed nitrogen, oxygen and sulphur. Rubber, polymer and silicon are used as coating material for protection of metal. For this work aloevera used as inhibitors for corrosion of protection of stainless in beverage.

II. METHODS AND METHODOLOGY

The sheets of stainless steel metal of 0.1 cm thickness was mechanically cut into coupons of sizes of 5cm length by 3cm width, perforated with hole of same diameter centrally to allow the passage of thread. These coupons were surface prepared using emery paper, acetone and water. The tested coupons were dipped into 40ml solution of beverage drink in 100ml beakers. The coupons, exposure periods were 24hrs, 48hrs, 72hrs and 96hrs. Tests were performed at different concentrations 2ml, 4ml and 6ml aloevera and at different temperatures 20°C, 25°C, 30°C and 35°C and temperature were maintained constant by keeping the solutions in a thermostat. The average corrosion rates of the in various concentrations and temperatures were determined by using weight loss method. The corrosion current measured with Potentiostatic polarization by using an EG & G Princeton Applied Research Model 173 Potentiostate. A platinum electrode used as an auxiliary electrode and a calomel electrode used as reference electrode with stainless steel coupons.

III. RESULTS AND DISCUSSION

The Corrosion rate of metal was calculated absence and presence aloevera by weight loss methods at different concentrations and temperatures with help of equation1.

$$K\ (\text{mmpy}) = 13.56\ W / D\ A\ t \qquad (1)$$

where W = weight loss of test coupon expressed in kg, A = Area of test coupon in square meter, D = Density of the material in kg. M^{-3}.

The inhibition efficiency of inhibitor was determined by using equation 2.

$$IE = (1 - K / K_o)\ 100 \qquad (2)$$

where K is the corrosion rate with inhibitor and K_o is the corrosion rate without inhibitor.

The surface coverage area of inhibitor was measured by equation 3.

$$\theta = (1 - K / K_o) \qquad (3)$$

where θ = Surface area, K = Corrosion rate with inhibitor, K_o = corrosion rate without inhibitor.

The Inhibition of Aloevera studied at 2ml, 4ml and 6ml concentrations and temperatures mention that concentrations were20°C, 25°C, 30°C and 35°C. The rate of corrosion of stainless steel with and without inhibitor at different concentrations and temperatures were recorded in Table 1, Table 2 and Table 3. Investigation of results of Table 1, Table2 and Table3 it observed that without inhibitor corrosion rate is high and addition of inhibitor corrosion rate is reduced. The results of Table1, Table 2 and Table 3 and Figure1indicated that at lower concentration of inhibitor, the inhibition efficiency and surface coverage area values were smaller and higher concentration the inhibition efficiency and surface coverage area values were bigger.

The recorded values of the rate of corrosion at different temperatures without and with inhibitor in Table 1, Table 2 and Table3 and Figure 2 were depicted that the corrosion rate increased without inhibitor and decreased without inhibitor. These results observed that use inhibitor active at high temperature and produces good inhibition efficiency.

Table 1 : Inhibition of Aloevera with beverage at different temperatures and 2ml concentration.

Inhibitor	Temp	20^0C	25^0C	30^0C	35^0C	C (ml)	logC
IH(0)	K_0	0.387	0.774	1.161	1.548	0.00	0.00
	$\log K_0$	-0.412	-0.111	-0.064	0.189		
IH(1)	K	0.301	0.512	0.713	0.965	2	-2.69
	logK	-0.521	-0.291	-0.147	-0.015		
	θ	0.22	0.34	0.39	0.38		
	(1- θ)	0.78	0.66	0.61	0.62		
	log(θ/1- θ)	-0.54	-0.28	-0.19	-0.21		
	(C/ θ)	-12.25	-7.91	-6.89	-7.07		
	log(C/ θ)	-0.602	-0.040	-0.051	-1.154		
	IE (%)	22	34	39	38		

Table 2 : Inhibition of Aloevera activities with beverage at different temperatures and 4ml concentration.

Inhibitor	Temp	20^{0}C	25^{0}C	30^{0}C	35^{0}C	C (Ml)	Logc
IH(0)	K_0	0.387	0.774	1.161	1.548	0.00	0.00
	$\log K_0$	-0.412	-0.111	-0.064	0.189		
IH(1)	K	0.214	0.512	0.713	0.665	4	-2.39
	logK	-0.669	-0.430	-0.301	-0.177		
	θ	0.45	0.52	0.56	0.58		
	(1- θ)	0.55	0.48	0.44	0.42		
	log(θ/1- θ)	-0.09	-0.04	-0.10	-0.14		
	(C/ θ)	-5.31	-4.59	-4.26	-4.12		
	log(C/ θ)	-0.508	-0.229	-0.585	-0.920		
	IE (%)	45	52	56	58		

Table 3 : Inhibitor Aloevera activities with beverage at different temperatures and 6ml concentration.

Inhibitor	Temp	20^{0}C	25^{0}C	30^{0}C	35^{0}C	C (Ml)	Logc
IH(0)	K_0	0.387	0.774	1.161	1.548	0.00	0.00
	$\log K_0$	-0.412	-0.111	-0.064	0.189		
IH(1)	K	0.195	0.201	0.319	0.413	6	-2.23
	logK	-0.709	-0.696	-0.496	-0.384		
	θ	0.49	0.74	0.72	0.73		
	(1- θ)	0.51	0.26	0.28	0.27		
	log(θ/1- θ)	-0.01	-0.28	-0.19	-0.21		
	(C/ θ)	-4.55	-3.01	-3.09	-3.05		
	log(C/ θ)	-0.259	-1.89	-1.04	-1.30		
	IE (%)	49	74	72	73		

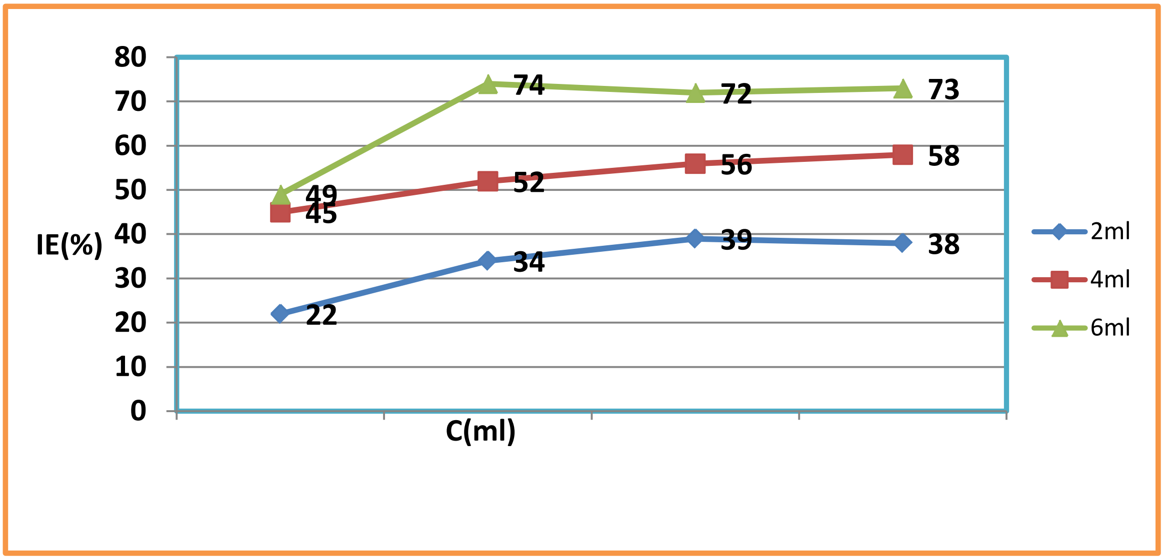

Figure 1 : Plot of IE(%) Vs. C(ml) for Stainless steel at different concentrations

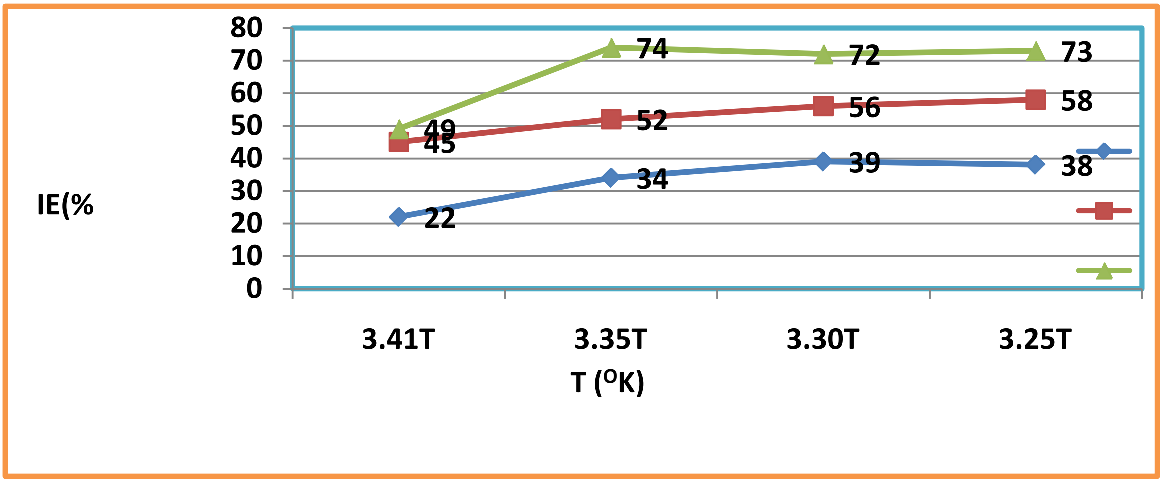

Figure 2 : Plot of IE (%) Vs. T (^{0}K) for Stainless steel at different temperatures

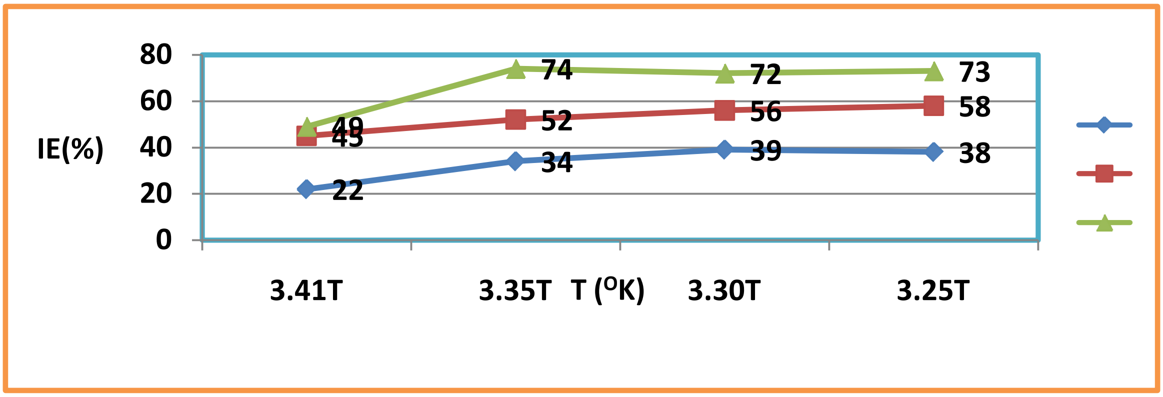

Figure 3 : Plot of IE (%) Vs. T (^{0}K) for Stainless steel at different temperatures

Activation energy was determined with help of Arrhenius equation 4

$$d /dt (\log K) = E_a / R T^2 \qquad (4)$$

where T is temperature in Kelvin and E_a is the activation energy of the reaction.

The values of activation energies were recorded in Table4, Table5 and Table6 absence and presence inhibitor by use of the plot between log K Vs. 1/T in Figure 3. It observed that without inhibitor activation energies decreased and with inhibitor activation energies increased. It indicated that physical adsorption occurred on the surface metal.

Table 4 : Thermo dynamical parameters for Aloevera at different temperatures

Thermodynamical Parameters	20^{0}C	25^{0}C	30^{0}C	35^{0}C
$E_{a(0)}$	26.87	7.11	4.04	11.75
E_a	33.98	18 .64	9.27	1.18
Q_{ads}	-35.81	-18.45	-12.24	-4.05
ΔG	-38.37	-21.14	-14.93	-6.72
ΔH	-68.75	-52.22	-41.98	-32.75
ΔS	-40.32	-31.17	-25.44	-20.15

Table 5 : Thermo dynamical parameters for Aloevera at different temperatures

Thermodynamical Parameters	20^{0}C	25^{0}C	30^{0}C	35^{0}C
$E_{a(0)}$	26.87	7.11	4.04	11.75
E_a	43.64	27 .55	19.01	12.18
Q_{ads}	-5.67	-2.17	-6.56	-8.70
ΔG	-8.06	-4.56	-8.95	-11.09
ΔH	-78.29	-61.20	-51.63	-43.89
ΔS	-45.91	-36.53	-31.29	-27.01

Table. 6 : Thermodynamical parameters for Aloevera at different temperatures

Thermodynamical Parameters	20^0C	25^0C	30^0C	35^0C
$E_{a(0)}$	26.87	7.11	4.04	11.75
E_a	46.25	44 .60	31.31	23.87
Q_{ads}	-1.10	-29.09	-25.88	-26.79
ΔG	-3.33	-31.32	-28.11	-29.02
ΔH	-80.88	-78.18	-63.76	-55.75
ΔS	-47.43	-46.67	-38.64	-34.25

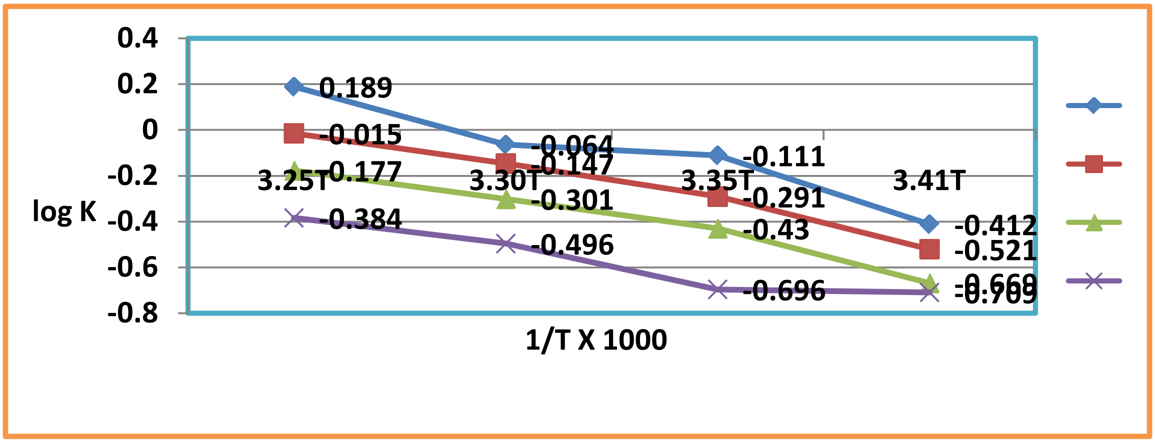

Figure 4 : Plot of log K Vs. 1/T for Stainless steel at different temperatures

The heat of adsorption was calculated by equation 5 with help of plot between log $(^{\theta}/1-^{\theta})$ vs. 1/T in Figure 4 and it values recorded in Table 4, Table 5 and Table 6.

$$\log (\theta/ 1-\theta) = \log (A .C) - (Q_{ads}/ R T) \qquad (5)$$

where T is temperature in Kelvin and Q_{ads} heat of adsorption

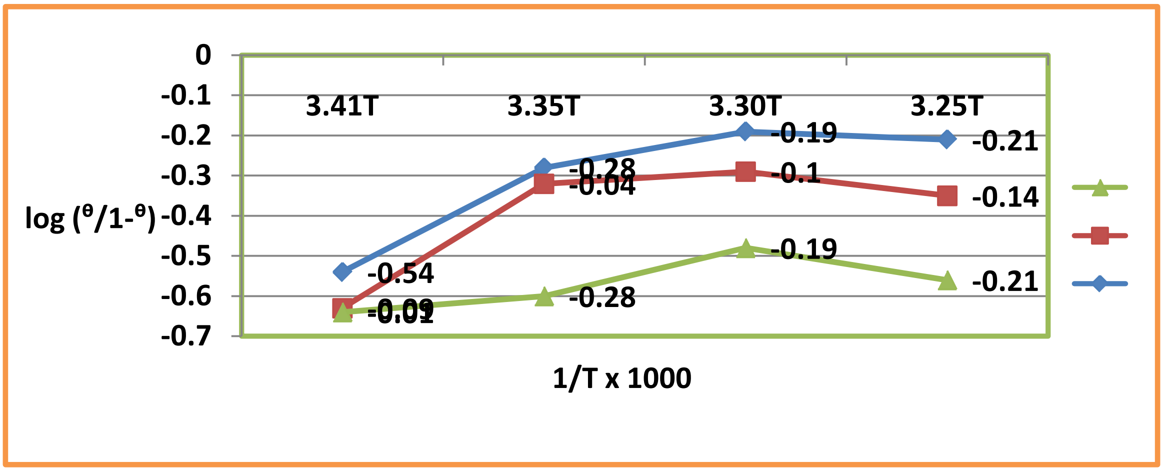

Figure 5 : Plot of log $(^{\theta}/1-^{\theta})$ Vs. 1/T for Stainless steel of different temperatures

The heat of adsorption found to be negative so it indicated that adsorption occurred on the metal surface. The values of heat of adsorption were shown that inhibitor was bounded with metal by physical adsorption. The plot between log $(^{\theta}/1-^{\theta})$ vs. log C found to be straight line in figure 5 which indicated Langmuir adsorption isotherm. It was a sign of adsorption. Temkin equation of isotherm for adsorption expressed as:

$$\log (C/ ^{\theta}) = \log C - \log K \qquad (6)$$

Where C is concentration of inhibitor, θ is surface coverage area and K be constant. The values of log $(C/ ^{\theta})$ were mentioned in Table1, Table 2 and Table 3. The plot against log $(C/ ^{\theta})$ vs. log C exhibited a straight line in figure 6 which indicates sign of adsorption.

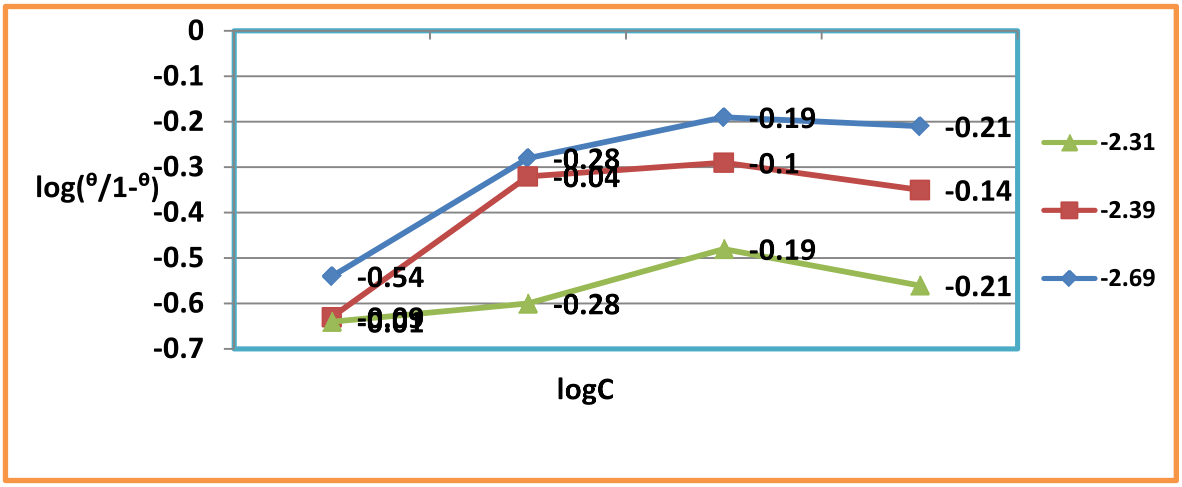

Figure 6 : Plot of log (θ/1-θ) Vs. log C for Stainless steel at different concentrations

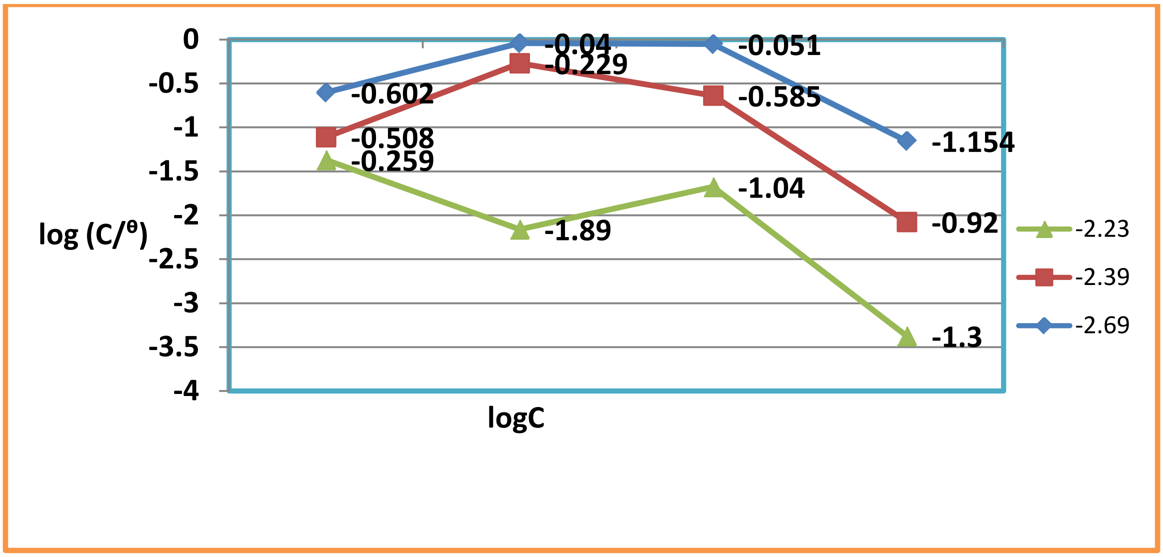

Figure 7 : Plot of log (C/θ) Vs. log C for Stainless steel at different concentrations

Free energy was determined by equation 7 and it values recorded in Table 4, Table 5 and Table 6 at different concentrations.

$$\Delta G=-2.303RT\ [\log C-\log(\theta/1-\theta)+1.72] \qquad (7)$$

Free energy results show that use inhibitor produces an exothermic reaction so it indicates sign of adsorption.

The energy of enthalpy and entropy were determined by transition state equation 8 and it values mentioned in Table 2.

$$K = RT/Nh \log(\Delta S^{\#}/R) \times \log(-\Delta H^{\#}/RT) \qquad (8)$$

Where N is Avogadro's constant, h is Planck's constant, $\Delta S^{\#}$ is the change of entropy activation and $\Delta H^{\#}$ is the change of enthalpy activation.

Enthalpy and entropy values are mentioned in Table 4, Table 5 and Table 6 which are found to be negative, it exhibited an exothermic reaction. The negative values of entropy indicated that inhibitors stable on surface adsorption of metal.

The corrosion current density determined absence and presence of inhibitor with help of equation 9 and values recorded in Table 7.

$$\Delta E/\Delta I=\beta_a\beta c/2.\ 303I_{corr}\ (\beta_a+\beta_c \qquad (9)$$

where ΔE/ΔI is the slope which linear polarization resistance (Rp), β_a and β_c are anodic and cathodic Tafel slope respectively and I_{corr} is the corrosion current density in mA/cm^2.

Looks the results of Table 7, it was noticed that corrosion current increases without inhibitor and its values reduced after addition of inhibitor.

The metal penetration rate (mmpy) is determined by

$$C.\ R\ (mmpy) = 0.1288I_{corr}\ (mA/cm^2) \times Eq.Wt\ (g)/\rho\ (g/cm^3) \qquad (9)$$

where I_{corr} is the corrosion current density ρ is specimen density and Eq. Wt is specimen equivalent weight.

Figure 7 indicates that Tafel graph has plotted between electrode potential and current density and absence and presence of inhibitors. Anodic potential, current density and corrosion rate increased without inhibitors but addition of inhibitors these values decreased and inhibition efficiency increased.

Table 7 : Potentiostatic Polarization values of Aloevera with different Concentrations at 30^{0}C.

Inhibitor	ΔE	ΔI	Ba	Bc	Icorr	K(Mmpy)	IE (%)	C(Ml)
IH(0)	-800	350	250	230	28.81	0.875	0.00	0
IH (1)	-475	190	115	135	10.78	0.327	62.62	2
	-465	175	100	125	9.10	0.276	68.45	4
	-450	160	50	115	7.80	0.237	72.91	6

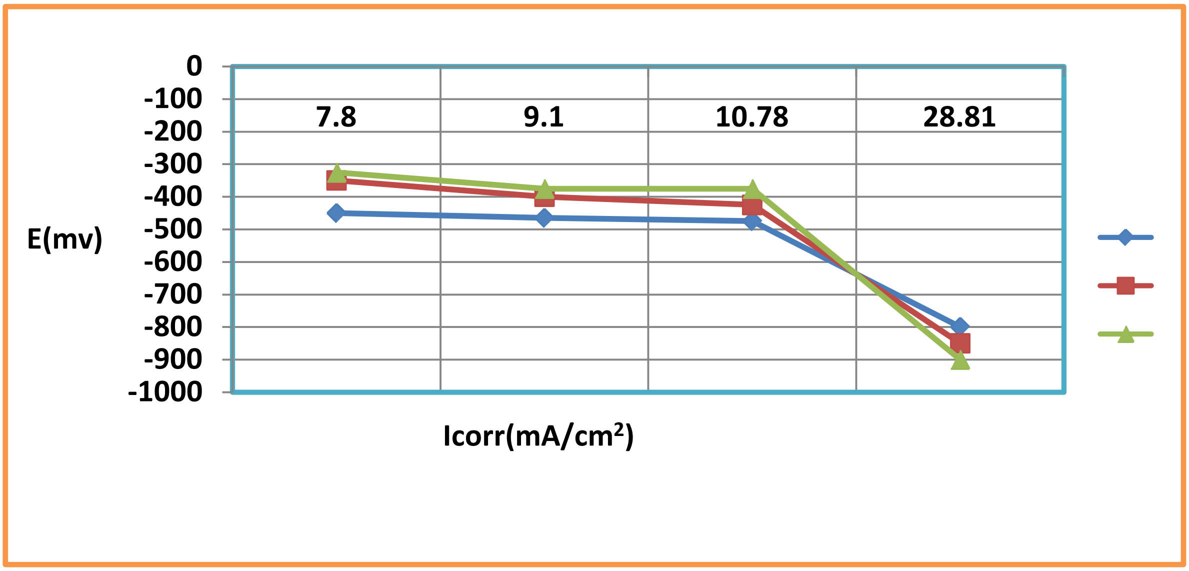

Figure 8 : Plot of E (mV) Vs. Icorr(mA/cm^2) for Stainlees steel at different concentrations

IV. Conclusion

Aloevera is a medicinal natural plant. It is eco friendly and it has no any side effect. Due to this character it is used as inhibitor in milk solution for protection of stainless steel. Its inhibition efficiency is low at lower concentration and its inhibition efficiency is high at higher concentration. The inhibition efficiency lies between 22 to 73% at different concentrations. It also produces good inhibitive effect at different temperatures. The results of activation energy, heat of adsorption, free energy, enthalpy and entropy show that aloevera bonded with metal surface physical adsorption. Potentiostatic polarization study results indicate that corrosion current decrease after addition of inhibitor.

V. Acknowledgement

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Synthesis Characterization and Antibacterial Activity of New Open and Macrocyclic Schiff Bases Ligands

By Hamid Hussein Eissa
University of Hajah, Yemen

Abstract- In this work we focused on the synthesis of two new macrocyclic Schiff bases: (III), (IV), (VI) containing nitrogen – oxygen donor atoms were synthesized by condensation of intermediate compounds: 1,6- bis (2- formylphenel) hexane (I)and **α**,**α**'-bis (2-carboxyaldehyde phenoxy) xylene(II) with 4,4'-Diamino-diphenylmethane and 4-Aminophenyl sulfone. Also new open Schiff bases (V) which were prepared by condensation of benzylhydrazidewith 1, 6- bis (2- formylphenel) hexane (I). Identification of these macrocyclic Schiff bases: 1,16-di aza-3,4,13,14-tri phenyl-17,25 -di phenyl methane-5,12-di oxacyclo penta-icozane-1,15-diene(III), 1,16- di aza-3,4, 7, 10, 13,14-tri phenyl-17,25 -di phenyl methan-5,8- di oxacyclo penta-icozane-1,15-diene. (IV).1,16-di aza- 3,4,13,14-tri phenyl-17,25 -di phenyl sulphide-5,12-di oxacyclo penta-icozane-1,15-diene(V), And N',N'-(2,2'-(hexane-1,6- bis(oxy))bis(2,1-phenylene)) bis(methanylidene) dibenzhydra-zide. (VI).The Schiff bases were checked by different spectral technique (LC-MS, 1H-NMR, IR, elemental analyses). The new Schiff Bases were studied for antibacterial activities against (Bacillus subtilis and Staphylococcus aureus) are Gram positive and (Salmonella typhi and Escherichia coli) are Gram negative. The ligands were exhibited a variable activity of inhibition on the growth of the bacteria.

Keywords: macrocyclic schiff bases, open schiff bases spectral technique, antibacterial activity.

GJSFR-B Classification : FOR: 039999

SYNTHESIS CHARACTERIZATION ANDANTBACTERIALACTIVITY OFNEW OPENANDMACROCYCLIC SCHIFFBASESLIGANDS

Strictly as per the compliance and regulations of :

Synthesis Characterization and Antibacterial Activity of New Open and Macrocyclic Schiff Bases Ligands

Hamid Hussein Eissa

Abstract- In this work we focused on the synthesis of two new macrocyclic Schiff bases: (III) , (IV), (VI) containing nitrogen – oxygen donor atoms were synthesized by condensation of intermediate compounds: 1,6- bis (2- formylphenel) hexane (I)and **α,α'**-bis (2-carboxyaldehyde phenoxy) xylene(II) with 4,4'-Diamino-diphenylmethane and 4-Aminophenyl sulfone. Also new open Schiff bases (V) which were prepared by condensation of benzylhydrazidewith 1, 6- bis (2-formylphenel) hexane (I). Identification of these macrocyclic Schiff bases: 1,16-di aza-3,4,13,14-tri phenyl-17,25 -di phenyl methane-5,12-di oxacyclo penta-icozane-1,15-diene(III), 1,16-di aza-3,4, 7, 10, 13,14-tri phenyl-17,25 -di phenyl methan-5,8-di oxacyclo penta-icozane-1,15-diene. (IV).1,16-di aza-3,4,13,14-tri phenyl-17,25 -di phenyl sulphide-5,12-di oxacyclo penta-icozane-1,15-diene(V), And N',N'-(2,2'-(hexane-1,6-bis(oxy))bis(2,1-phenylene))bis(methanylidene) dibenzhydrazide. (VI).The Schiff bases were checked by different spectral technique (LC-MS, 1H-NMR, IR, elemental analyses). The new Schiff Bases were studied for antibacterial activities against (Bacillus subtilis and Staphylococcus aureus) are Gram positive and (Salmonella typhi and Escherichia coli) are Gram negative. The ligands were exhibited a variable activity of inhibition on the growth of the bacteria.

Keywords: macrocyclic schiff bases, open schiff bases spectral technique, antibacterial activity.

I. INTRODUCTION

Polyazamacrocycles with large cavities have received recent interests as inorganic cation receptors[Kopolow et al,1973]. The cyclic arrangement of a large number of donor atoms and the flexibility of these ligands make them good hosts for ions [Lindoy et al., 1976]. They were also used as spectrophotometric analytical reagents [Lisowski et al., 1999]. Metal ions have enormous importance in many biological processes, especially heavy metal ions which are effective enzyme inhibitors exerting toxic effects on living system [Esteban et al., 1037]. Therefore, separation and determination of toxic metal ions such as mercury, lead, and cadmium in environmental sources play an important role for healthy life [Vance et al., 1997]. Although new paragraph macrocyclic compounds containing oxygen, sulfur, and nitrogen are knowing. Macrocyclic compounds used in solvent extraction were mostly the oxygen donor type [Ekstrom et al., 1980]. A number of methods for the preparation of the large polyazamacrocyclics have been reported. The most common synthetic procedure requires the use of N- tosyl groups to protect and activate the nitrogen atoms in the cyclization step [Ekstrom et al., 1979]. Ring closure occurs by a condensation reaction of N-tosylated polyamines with the appropriate ditosylate ester or dihalide in DMF in the presence of base [Anderegg et al., 1980]. These reactions allow the production of polyazamacrocycles in moderate yields [Adam et al., 1994], but removing the N- tosyl groups requires drastic conditions and is not always straightforward. Another cyclization process uses the template ring closure for formation of cyclic di- or tetra dentate Schiff bases. This is a simple process, but it is often difficult to choose the correct template metal ion or to predict certain ring contraction reactions were the template cation dose not coordinate with all of the ring nitrogen atoms [Fenton et al., 1981]. In some cases, reduction of the cyclic Schiff base and removal of the template ion have been difficult [Adam et al., 1981]. A non template method for the formation of macrocyclic poly Schiff bases has also been studied. This procedure often gave a polymeric material beside cyclization reaction, while there is no need to remove a metal ion [Henrick et al., 1984]. In the present work we used a non template method for the formation of four novel macrocyclic Schiff bases: (III), (IV), (V) and (V) then were used for removed of various metal ions from the aqueous phase into the organic phase in liquid – liquid extraction system.

II. EXPERIMENTAL

a) Materials and Method

Chloroform, dichloromethane, dimethylformamide, acetonitrile, methanol, K_2CO_3, were analytical grade reagents and were purchased from Merck. 4, 4' -Diaminodiphenylmethane, 4-Aminophenyl sulfone, benzylhydrazide, salicylaldehyde, 1,6- dibromohexane, **α,α'**-Dichlor-p-xylene were obtained from sigma- Aldrich. IR spectra were recorded on Jusco 300 FT-IR Spectrometer using KBr discs. Mass spectra of the ligands were carried out using a micro mass QuattroLC-MS/MS Spectrometer. NMR spectra were recorded at ambient BRUKERRAVANCE PX-400 Spectrometer.

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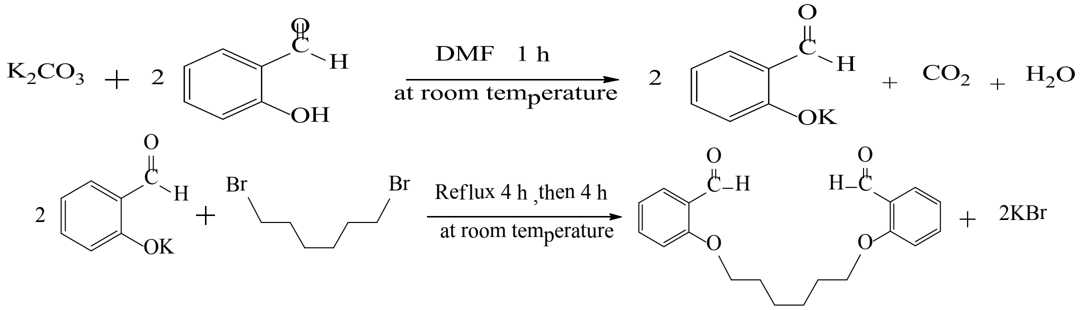
i. *Synthesis of 1,6- Bis (2- Formylphenel) Hexane (I)*

To a stirred solution of salicylaldehyde (2.44g, 0.02mol) and K2CO3 (1.38g, 0.01mol) in DMF (50ml) 1, 6-dibromohexane (2.24 g, 0.01mol) in DMF (10ml) was added dropwise. The reaction was heated for 4h at 150-155 0C and then stirred at room temperature for 4h [Kenneth et al., 1995]. After the reaction was completed, 100 ml distilled water was added, left in a refrigerator for 1h, the precipitate was filtered, washed by 50 ml water, dried in air and recrystallized from ethanol. (scheme No.1)- (I)

Yield: 80%, colour: White, m.p: 75 0C.

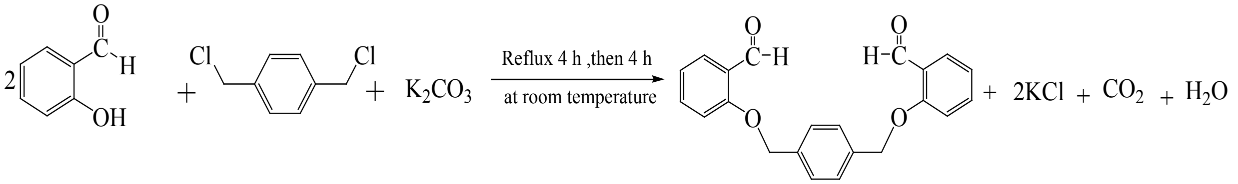


(Scheme No.1)- (I)

ii. *Synthesis of α,α'-Bis(2-Carboxyaldehyde Phenoxy) Xylene(II)*

To a stirred solution of salicylaldehyde (2.44g, 0.02mol) and K_2CO_3 (1.38 g, 0.01mol) in DMF (50ml) α,α'-Dichlor-p-xylene (1.39g , 0.01 mol) in DMF(10ml) was added dropwise. The reaction was heated for 4h at 150-1550C and then stirred at room temperature for 4h, after the reaction was completed, 100 ml distilled water was added, left in a refrigerator for 1h , the precipitate was filtered[Lindoy et al.,1976, Kenneth et al.,1995], washed by 50 ml water, dried in air and recrystallized from ethanol.(scheme No.2)

Yield: 85%, colour: White, m.p: 107 0C.



(Scheme No.2)- (II)

iii. *Synthesis of 1,16-Di Aza-3,4,13,14-Tri Phenyl-17,25 -Di Phenyl Methane-5,12-Di Oxacyclo Penta-Icozane-1,15-Diene(III).*

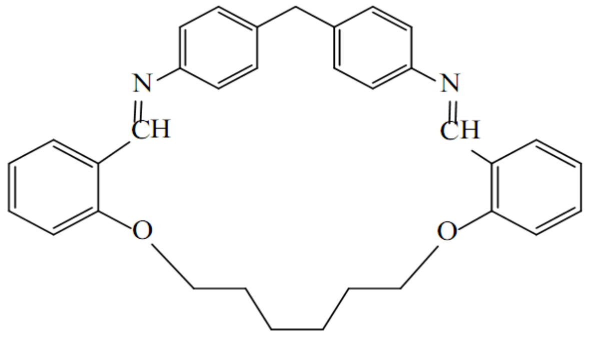
The macrocyclic compound (III) was prepared by dropwise addition of a solution of 4, 4'-Diaminodiphenylmethane (0.40g, 0.002 mol) in methanol (40 ml) to a stirred solution of compound (I) (0.652g, 0.002 mol) in methanol (60 ml). The stirring was continued for 12h, a white powder[Salih et al.,2007] was precipitated which was filtered and washed with cold diethyl ether, and recrystallized from mixed (DMF, ethanol9:1). (scheme No.3)

Yield: 80%, colour: Yellow, m.p= 284 0C. formula: (C33H32N2O2), M.Wt:(488g).

IR (KBr disk): 3041.8 - 3083.3 cm-1 ((C-H), aromatic), 2870.6-2946.7 cm-1 (C-H), aliphatic), 1660.4cm-1 (C=N), 1573.7-1593.3 cm-1 (C=C, aromatic), 1243.5cm-1 (C-O).

^{1}H-NMR(CDCl3-400MHz) δ = 8.512 (s,2H,CH=N) , 6.954 - 7.766 (m,16 H, Ar) , 4.087-4.119 (s,4H ,O-CH2-), 2.649 (s,2H, Ph-CH2-Ph), 1.625 – 1.927 (m, 8H,-CH2-).

Elemental analysis found % C : 81.07 , H: 6.72 , N: 5.69, O: 6.52 calculated for $(C_{33}H_{32}N_2O_2)$ % C: 81.12, H: 6.60, N: 5.73 ,O:6.55.



(Scheme No.3) (III)

iv. *Synthesis of 1,16-Di Aza-3,4,7,10,13,14-Tri Phenyl-17,25 -Di Phenyl Methan-5,8-Di Oxacyclo Penta-Icozane-1,15-Diene. (IV).*

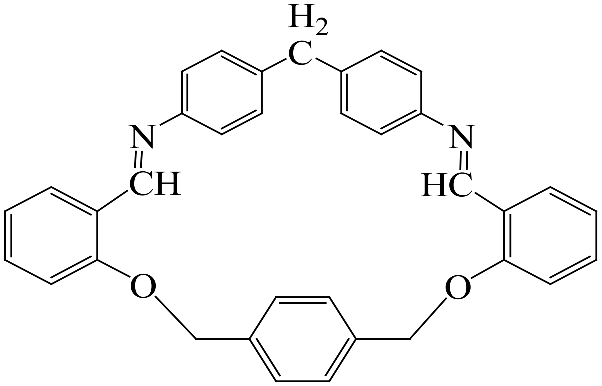
The macrocyclic compound (IV) was prepared by dropwise addition of a solution of 4, 4'-Diaminodiphenylmethane (0.40g, 0.002 mol) in methanol (40 ml) to a stirred solution of compound (II) (0.692g, 0.002 mol) in methanol (60 ml). The stirring was continued for 12h, a white powder[Salih et al.,2007]was precipitated which was filtered and washed with cold diethyl ether, and recrystallized from mixed (DMF, ethanol.9:1).(scheme No.4).

Yield: 80%, colour: White, m.p> 300 ^{0}C dec. formula:($C_{35}H_{28}N_2O_2$), M.Wt: (508g).

IR (KBr disk): 3056.6 cm^{-1} ((C-H), aromatic), 2870.7-2946.6 cm^{-1} ((C-H), aliphatic), 1660.8 cm^{-1} (C=N), 1575.2-1595.0 cm^{-1} (C=C, aromatic), 1243.2 cm^{-1} ((C-O).

^{1}H-NMR ($CDCl_3$-400MHz) δ=8.661 (s,2H,CH=N), 6.965-8.160 (m,20 H, Ar), 5.073 (s, 4H-O-CH_2-Ph-), 3.994 (s,2H,-Ph-CH_2-Ph).

Elemental analysis found % C: 82.71, H:5.48, N:6.42, O:5.39 calculated for ($C_{35}H_{28}N_2O_2$) % C: 82.65, H: 5.55, N: 5.51, O: 6.29.



(Scheme No.4)- (IV)

v. *Synthesis of 1,16-Di Aza-3,4,13,14-Tri Phenyl-17,25 - Di Phenyl Sulphide-5,12-Di Oxacyclo Penta-Icozane-1,15-Diene(V)*

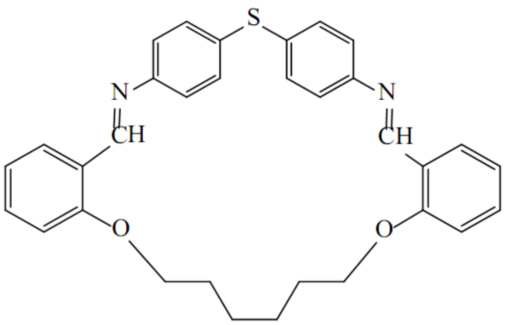
The macrocyclic compound (V) was prepared by dropwise addition of a solution of 4-Aminophenyl sulfone (0.432 g, 0.002 mol) in methanol (40 ml) to a stirred solution of compound (II) (0.692g, 0.002 mol) in methanol (60 ml). The stirring was continued for 12h, a white powder [Salih et al.,2007]was precipitated which was filtered and washed with cold diethyl ether, and recrystallized from mixed (DMF , ethanol. 9:1). (scheme No.5).

Yield: 65 %, colour: Yellow, m.p> 300 0C dec. formula: ($C_{32}H_{30}N_2O_2S$), M.Wt: (508g).

IR (KBr disk): 3047.6 cm^{-1} ((C-H), aromatic), 2864.7-2942.4 cm^{-1} (C-H), aliphatic), 1675.2cm^{-1} (C=N), 1594.2 cm^{-1} (C=C, aromatic), 1245.8cm^{-1} ((C-O).

^{1}H-NMR($CDCl_3$-400MHz)δ=8.140 (s,2H,CH=N) , 7.117-7.854 (m,16 H, Ar) , 3.729 (s,4H ,O-CH_2-), 1.164 - 1.642 (m, 8H,-CH_2-).

Elemental analysis found % C : 75.98 , H: 5.86 , N: 5.49 , O: 6.44 , S: 6.23 calculated for ($C_{32}H_{30}N_2O_2S$) % C: 75.86, H: 5.97 , N: 5.53 ,O:6.32 , S: 6.33.



(Scheme No.5)- (V)

vi. *Synthesis of N', N'-(2,2'-(Hexane-1,6-Bis (Oxy)) Bis (2,1-Phenylene)) Bis(Methanylidene) Dibenzhydrazide.(VI).*

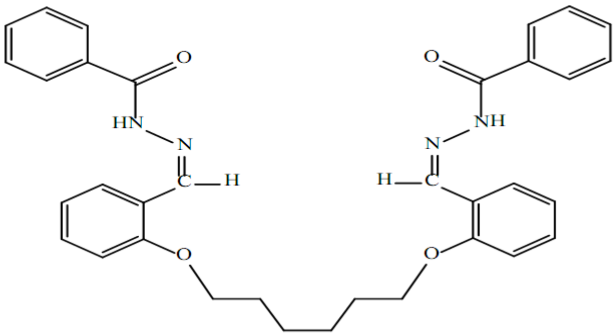
The open Schiff base (VI) was prepared by dropwise addition of a solution of the benzhylhyrazide (2.72 g, 0.02 mol) in DMF (40 mL) to a stirred solution of 1, 6-bis (2- formyl phenyl)-hexane (I) (3.26 g, 0.01mol) in DMF (60 mL) containing a few drops of concentrated HCl. The reaction mixture was heated to reflux for 5 hrs, where white precipitate was formed after cooling. On cooling, 200 ml distilled water was added and the mixture was kept in a refrigerator. After 2 hrs, the precipitate [Sultan et al., 2011] was filtered and washed with 200 mL water. The solid obtained was collected and recrystallized from mixture (DMF EtOH9:1) as yellow crystals. A white colored precipitate was washed with water, ethanol, CHCl3 and diethyl ether, respectively. Then dried in air. (scheme No.6).

Yield: 84%, colour: White, m.p= 263 0C dec. formula:($C_{35}H_{28}N_2O_2$), M.Wt: (562 g).

IR (KBr disk): 3217.27cm^{-1} (N-H), 3035.96 – 3062.96 cm^{-1}((C-H), aromatic, 2870.08 – 2939.52((C-H), aliphatic), 1647.21cm^{-1} (C=O), 1642.0 cm^{-1} (C=N).

^{1}H-NMR ($CDCl_3$-400MHz) δ =11.891 (s,2H, CO-NH-), 8.824 (s,2H,CH=N) , 7.007 - 8.479 (m,18H, Ar), 1.065 – 1.820(m,8H,-CH_2-CH_2-CH_2-CH_2-), 2.512 - 3.353 (DMSO,H2O).

Elemental analysis found % C: 72.81, H:5.98 ,N:10.04 , O: 11.17 calculated for (C34H34N4O4) % C: 72.58; H: 6.09; N: 9.96; O: 11.37.



(Scheme No.6) (VI)

b) Biological Activity

The prepared compounds were tested for their antimicrobial activity against four speices of bacteria (Bacillus subtilis, Escherichia coli, Staphylococcus aureus, Salmonella typhi) using filter paper disc method [Ibrahim et al., 2006] The screened compounds were dissolved individually in DMSO (dimethyl sulfoxide) in order to make up a solution of 50, 100, and 200 µg/ml concentration for each of these compounds. Filter paper discs (Whitman No.1 filter paper, 5mm diameter) were saturated with the solution of these compounds. The discs were placed on the surface of solidified Nutrient agar dishes seeded by the tested bacteria. The diameters of inhibition zones (mm) were measured at the end of an incubation period, which was 24 h at 37C for bacteria. Discs saturated with DMSO are used as solvent control. Ciprofloxacin 100 µg/ml was used as reference substance for bacteria.[Ibrahim et al.,2006]

III. Result and Discussion

a) Synthesis

The prepared macrocyclic (III, IV, V, VI) were synthesized by the condensation of by condensation of intermediate compounds 1,6- bis (2- formylphenel) hexane (I) and α,α'-bis(2-carboxyaldehyde phenoxy) xylene (II) with both 4,4'-Diaminodiphenylmethane and 4-Aminophenyl sulfonein the molar ratio 1:1 in absolute methanol. Also new open Schiff bases (VI) which was prepared by condensation of benzylhydrazidewith 1, 6-bis (2- formylphenel) hexane in the molar ratio 2:1 in DMF. The reactions proceeded smoothly, producing the corresponding Schiff bases ligands in good yield. The ligands are soluble in common organic solvent but insoluble in water. The structures of the ligands were elucidated by elemental analyses, MS, FTIR, electronic absorption, and 1-H- NMR spectra, which help in elucidating their empirical formulaTable 1.

Table 1 : Physical and Chemical Properties of the Synthesized Compounds [III]-[VI]

Schiff base	Color	M.Wt	Melting point ^{0}C	Yield %	Crystallization Solvent
III	White	448	248	80	DMF , EtOH (9:1)
IV	White	508	> 300	85	DMF , EtOH (9:1)
V	Yellow	506	> 300	65	DMF , EtOH (9:1)
VI	White	562	263 – 264	84	DMF , EtOH (9:1)

b) Elemental Analyses of Macrocyclic and Open (III, IV, V, VI).

The results of elemental analyses macrocyclic and open (III, IV, V, VI), as shown in Table 2, are in good agreement with those required by the proposed formulae.

Table 2 : Elemental Analysis Data of the Synthesized Compounds[III]-[VI].

Schiff base	Elemental analysis Calculated (Found %)				
	C	H	N	S	O
III	81.07 (81.12)	6.72 (6.60)	5.69 (5.73)	--------	6.52 (6.55)
IV	82.71 (82.65)	5.48 (5.55)	6.42 (6.51)	--------	5.39 (5.29)
V	75.98 (75.86)	5.86 (5.97)	5.49 (5.53)	6.23 (6.33)	6.44 (6.32)
VI	72.81 (72.58)	5.98 (6.09)	10.04 (9.96)	--------	11.17 (11.37)

c) IR Spectra Analysis of Macrocyclic Schiff Bases (III, IV, V, VI).

Compound (III): A strong band at 1660.4cm-1 in the IR spectrum of the macrocyclic Schiff base (Figure (1)) are assigned to υ(C=N) of azomethine vibrations. The band in the spectra at 1593.3 - 1573.7cm-1 is due to (C=C) of aromatic rings. The band in the spectra at 1243.5 cm-1 is due to (C-O). while the band at 2946.7 - 2870.6cm-1 is attributed to (C-H aliph). Also, the band at 3083.3 - 3041.8 cm-1 is attributed to (C-H ar). [Salih et al., 2007, Sultan et al., 2011].

Compound (IV): A strong band at 1660.8 cm-1 in the IR spectrum of the macrocyclic Schiff base (Figure (2)) are assigned to υ(C=N) of azomethine vibrations. The band in the spectra at 1595.0 - 1575.2 cm^{-1} is due to (C=C) of aromatic rings. The band in the spectra at 1243.2 cm^{-1} is due to (C-O). while the band at 2946.6 - 2870.7 cm^{-1} is attributed to (C-H aliph). Also, the band at 3056.6

cm^{-1} is attributed to (C-H ar). [Salih et al., 2007, Sultan et al., 2011].

Compound (V): A strong band at 1675.2 cm-1 in the IR spectrum of the macrocyclic Schiff base (Figure (3)) are assigned to υ(C=N) of azomethine vibrations. The band in the spectra at 1594.2 cm^{-1} is due to (C=C) of aromatic rings. The band in the spectra at 1245.8 cm^{-1} is due to (C-O). while the band at 2942.4 - 2864.7 cm^{-1} is attributed to (C-H aliph). Also, the band at 3047.6 cm^{-1} is attributed to (C-H ar). [Salih et al., 2007, Sultan et al., 2011].

Compound (VI): A strong band at 1600.92 and 1647.21cm-1 in the IR spectrum of the Schiff base (Figure (4)) are assigned to υ(C=N) of azomethine and carbonyl υ(C=O) vibrations, respectively. An intense band at 3217.27 cm-1 is due to the -NH- vibrations of the hydrazine group. The band in the spectra at 1554.83 cm-1 is due to (C=C) of aromatic rings. The band in the spectra at 1249.86 cm-1 is due to (C-O). while the band at 2870.08 – 2939.52 cm-1 is attributed to (C-H aliph). Also, the band at 3035.96 – 3062.96 cm-1 is attributed to (C-H ar). [Salih et al.,2007, Sultan et al.,2011].

However, in the IR spectra of Schiff bases this band (C=O) disappears and a new vibration band for azo methane (-HC=N-), indicating that complete condensation takes place. [17-18].

Table 3 : IR Spectral Data of the Synthesized Compounds[III]-[VI].

Schiff base	v(C-O)	v(C=C)	v(HC=N)	v(C=O)	v(C-H) aliph	v(C-H) arom	v(N-H)
III	1243.5	1593.3 - 1573.7	1660.4	---------	2946.7 - 2870.6	3083.3 - 3041.8	---------
IV	1243.2	1595.0 - 1575.2	1660.8	---------	2946.6 - 2870.7	3056.6	---------
V	1245.8	1594.2	1675.2		2942.4 - 2864.7	3047.6	
VI	1249.86	1554.83	1600.92	1647.21	2870.08 – 2939.52	3035.96 – 3062.96	3217.27

d) 1-H-NMR Spectra of Macrocyclic Schiff Bases (III, IV, V, VI).

Compound (III): The 1H NMR spectrum (Figure (5)) of the Schiff base (III), showed that in the signals at 8.512 ppm were assigned to the protons of imine -CH=N groups, The multiple signals in the region 1.927 - 1.625 ppm were assigned to protons of methylene groups in two different environments [Salih et al., 2007, Sultan et al.,2011].The multiple signals in the region 7.766 - 6.954 ppm were assigned to the aromatic protons. While The signals at 4.119 - 4.087 ppm were assigned to the protons of (-O-CH2-) group.

Compound (IV): The 1H NMR spectrum (Figure (6)) of the Schiff base (IV), showed that in the signals at 8.661 ppm were assigned to the protons of imine -CH=N groups[Salih et al.,2007, Sultan et al.,2011].The multiple signals in the region 8.160 - 6.965 ppm were assigned to the aromatic protons. While The signals at 5.073 ppm were assigned to the protons of (-O-CH2-) group.

Compound (V): The 1H NMR spectrum (Figure (7)) of the Schiff base (V), showed that in the signals at 8.140 ppm were assigned to the protons of imine -CH=N groups, The multiple signals in the region 1.642 - 1.164 ppm were assigned to protons of methylene groups in two different environments [Salih et al.,2007, Sultan et al.,2011].The multiple signals in the region 7.854 - 7.117 ppm were assigned to the aromatic protons. While the signals at 3.729 ppm were assigned to the protons of (-O-CH2-) group. Also the signal at 11.891 ppm were assigned to the protons of amide (-CO-NH-) groups.

Compound (VI): The 1H NMR spectrum (Figure (8)) of the Schiff base (VI), showed that in the signals at 8.824 ppm were assigned to the protons of imine -CH=N groups, The multiple signals in the region 1.065 – 1.820 ppm were assigned to protons of methylene groups in two different environments [Salih et al., 2007, Sultan et al.,2011].The multiple signals in the region 8.479 - 7.007 ppm were assigned to the aromatic protons. While the signals at 4.087 ppm were assigned to the protons of (-O-CH2-) group. Also the signal at 11.891 ppm were assigned to the protons of amide (-CO-NH-) groups.

The other obtained values for 1-H-NMR chemical shifts of the compounds are given in the experimental section. [Pathak et al., 2000, Rajaa.,2008].

Table 4 : ^{1}H-NMR Spectra of the Synthesized Compounds[III]-[VI]

Schiff base	Chemical Shifts δ ppm				
	C-H aromatic	CH=N	-CO-NH-	$-O-CH_2-$	$(-CH_2-CH_2-)_n$
III	7.766 - 6.954 (m,16 H)	8.512 (s,2H)	--------------	4.119 - 4.087 (s,4H)	1.927 - 1.625 (m,8H)
IV	8.160 - 6.965 (m,20 H)	8.661 (s,2H)	--------------	5.073	--------------
V	7.854 - 7.117 (m,16 H)	8.140 (s,2H)	11.891 (s,2H)	3.729 (m,8H)	1.642 - 1.164 (m,8H)
VI	8.479 - 7.007 (m,18H)	8.824 (s,2H)	11.891 (s,2H)	4.087 (s,2H)	1.065 – 1.820 (m,8H)

e) *Biological Activity*

During the last two or three decades, attention has been increasingly paid to the synthesis of macrocyclic and open (III, IV, V, VI) which exhibits various biological activities including antibacterial, fungicidal, tuberculostatic and plant growth regulative properties [19]. It was judicious to investigate the synthesis of various new types of Schiff base and studied their antibacterial activity against four strains of bacteria (Bacillus subtilis, Escherichia coli, Staphylococcus aureus, Salmonella typhi). The concentrations used for the screened compounds are 50, 100, and 200 µg/ml. Ciprofloxacin was used as reference standard while DMSO as control and inhibition zones are measured in mm. The new compounds were tested against one strain each of a gram positive and two gram negative. The test results presence in Table (3.11), a new compound was active against tested and another compounds are no active.

All compounds are no active where used 50, 100 µg/ml but active in the concentrations 200 µg/ml see table (3.4).

Table 5 : Antibacterial Activity of the Synthesized Compounds[III]-[VI]

Shiff base	Bacteria			
	Gram negative		Gram positive	
	B. subtilis	S. aureus	E.coli	S. typhi
III	17 mm	18 mm	15 mm	18 mm
IV	18 mm	16 mm	16 mm	19 mm
V	20 mm	18 mm	17 mm	18 mm
VI	20 mm	18 mm	17 mm	18 mm
Control	00 mm	00 mm	00 mm	00 mm
Ciprofloxacin	20 mm	20 mm	20 mm	20 mm

(-)No zones of inhibition were observed.
Moderately sensitive,(+)Inhibition zones of 7-10mm.
Sensitive,(++)Inhibition zones of 11-14mm.
High sensitive,(+++)Inhibition zones of 15-20mm

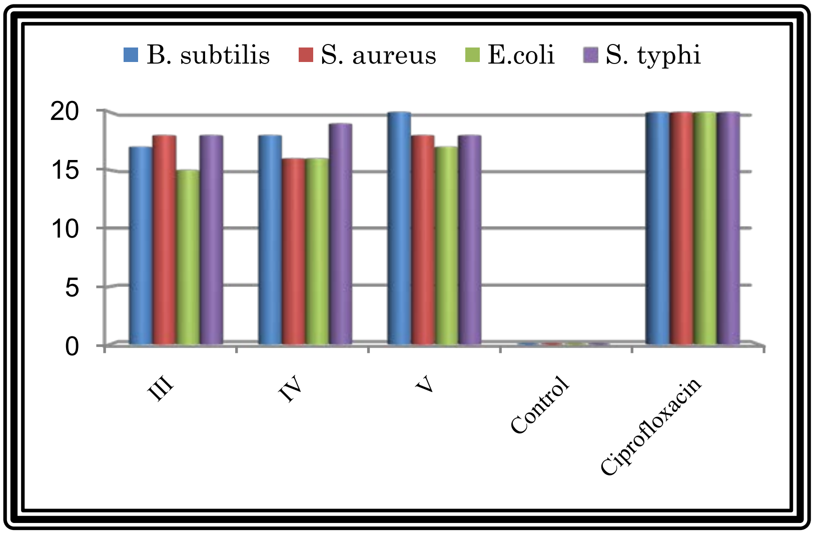


Figure 9 : Antibacterial Activity of Synthesized Compounds[III]-[VI].

IV. Conclusion

1. The compounds are new and were prepared for the first time.
2. The new compounds were identified by melting point, elemental analyses 1HNMR, IR, LC-MS, spectral methods.
3. The prepared compounds have been biologically screened i.e. studying their effects against two gram-positive, two gram-negative bacteria. The results show that their activities were found to vary from moderate to very strong.

V. Acknowledgement

The authors are grateful to the Department of Chemistry, Faculty of Science, University of Damascus, Damascus, Syria.

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V. Figures

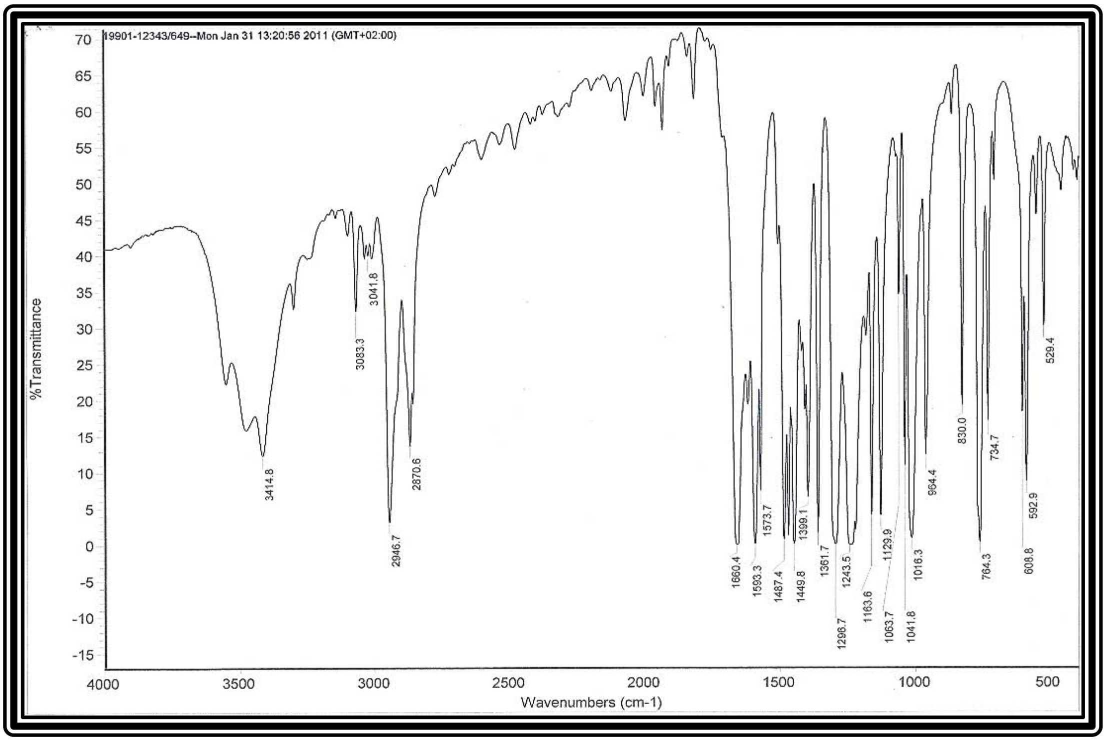

Figure 1 : IR Spectrum of Macrocyclic Schiff Base(III)

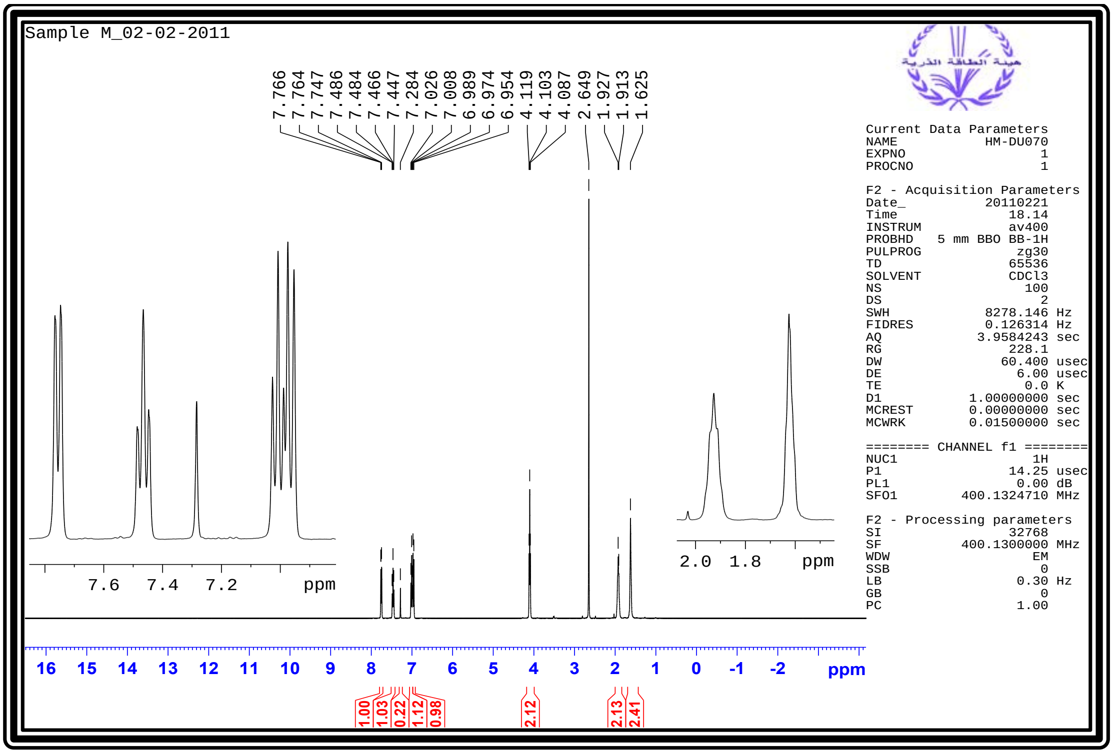

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Figure 5 : ^{1}-HNMR Spectrum of Macrocyclic Schiff Base(III)

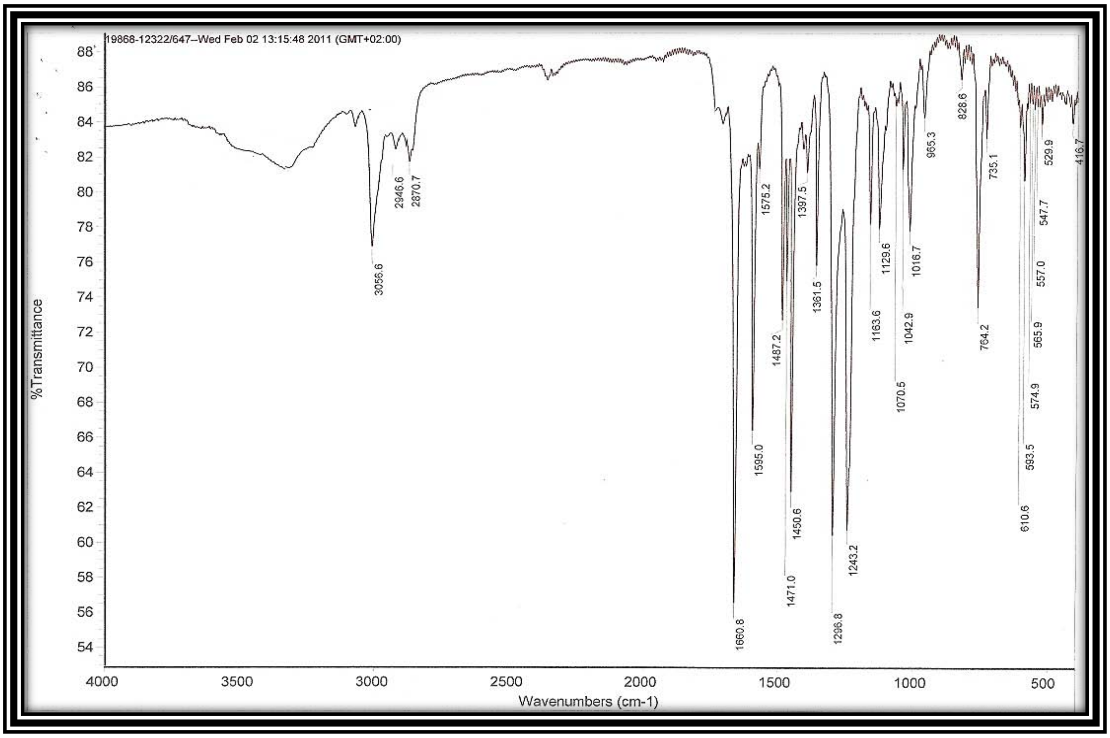
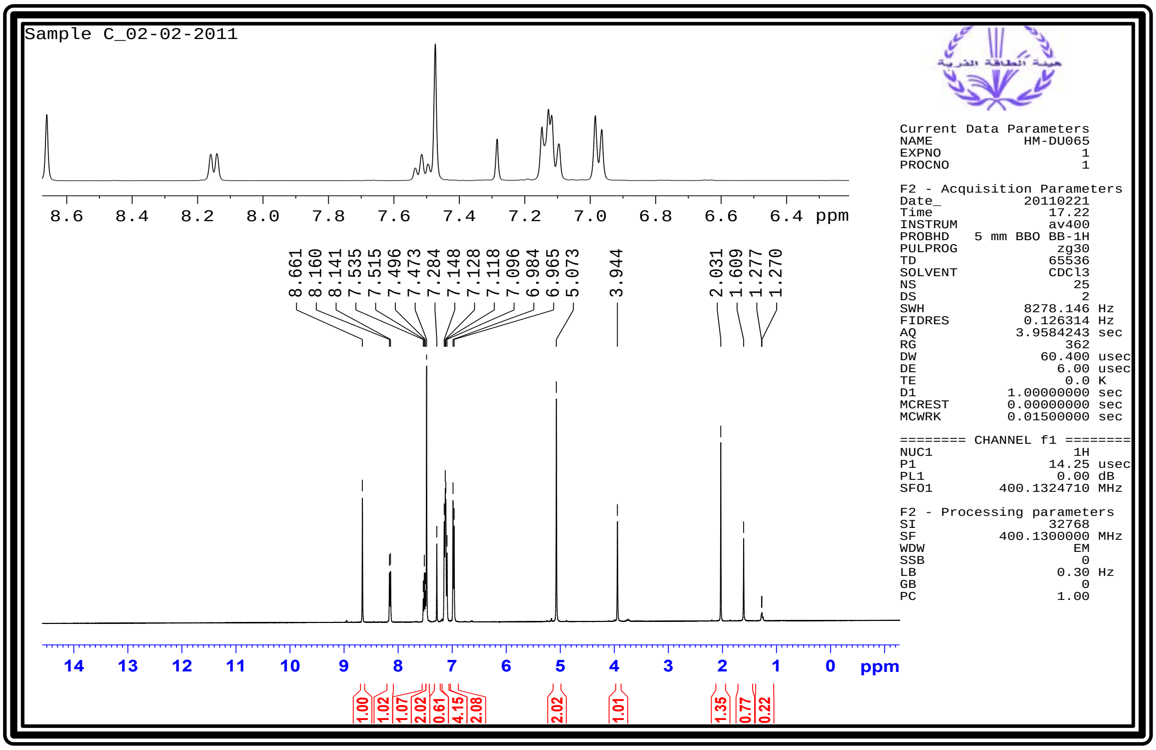


Figure 2 : IR of Macrocyclic Schiff Base(IV)



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F2 - Processing parameters
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Figure 6 : ^{1}-HNMR spectrum of Macrocyclic- Schiff base(IV)

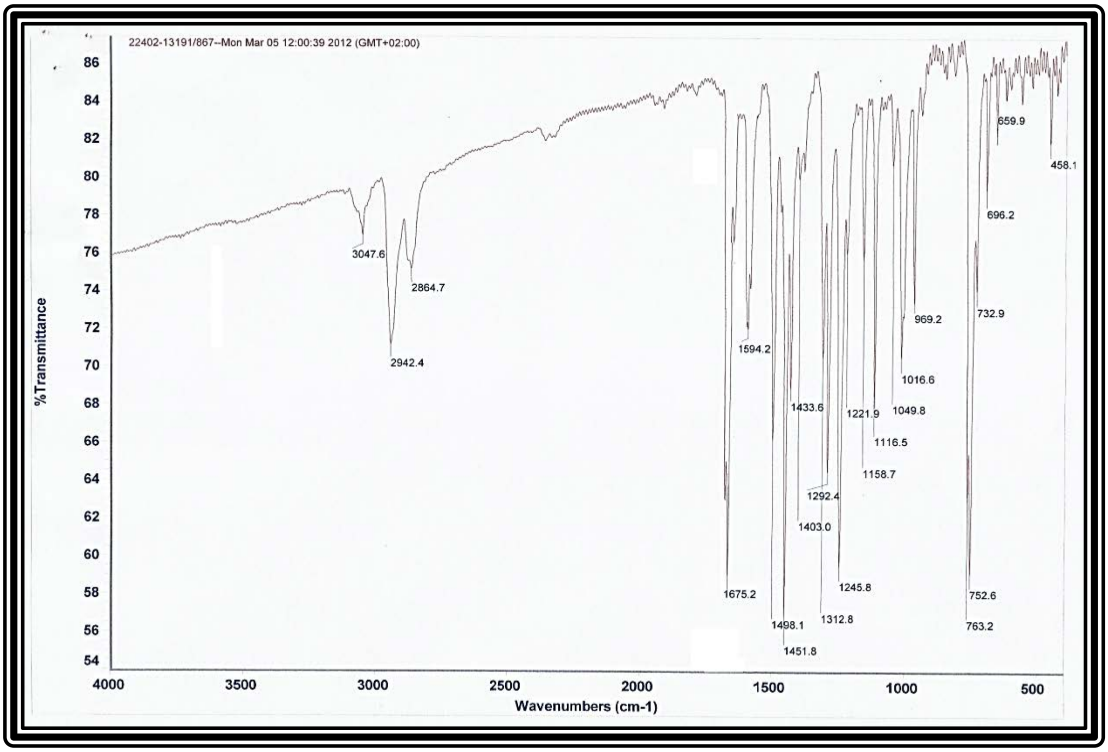
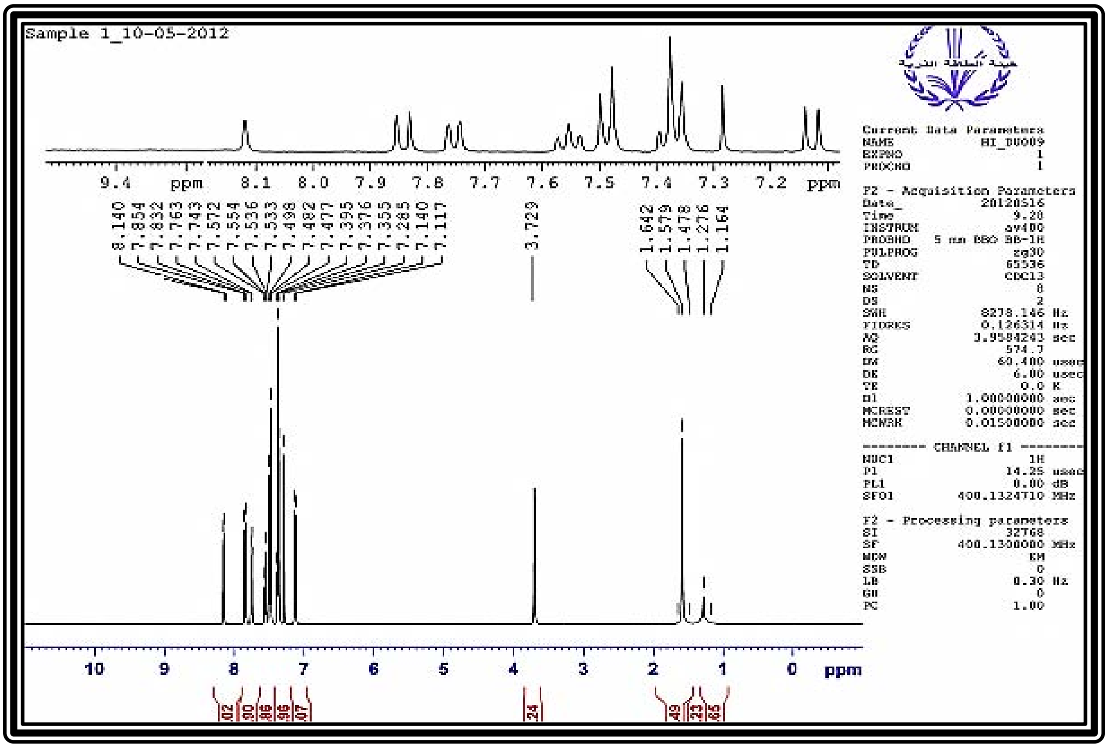


Figure 3 : IR of Macrocyclic Schiff base(IV)



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```

Figure 7 : $^{1-}$HNMR spectrum of Macrocyclic- Schiff base(IV)

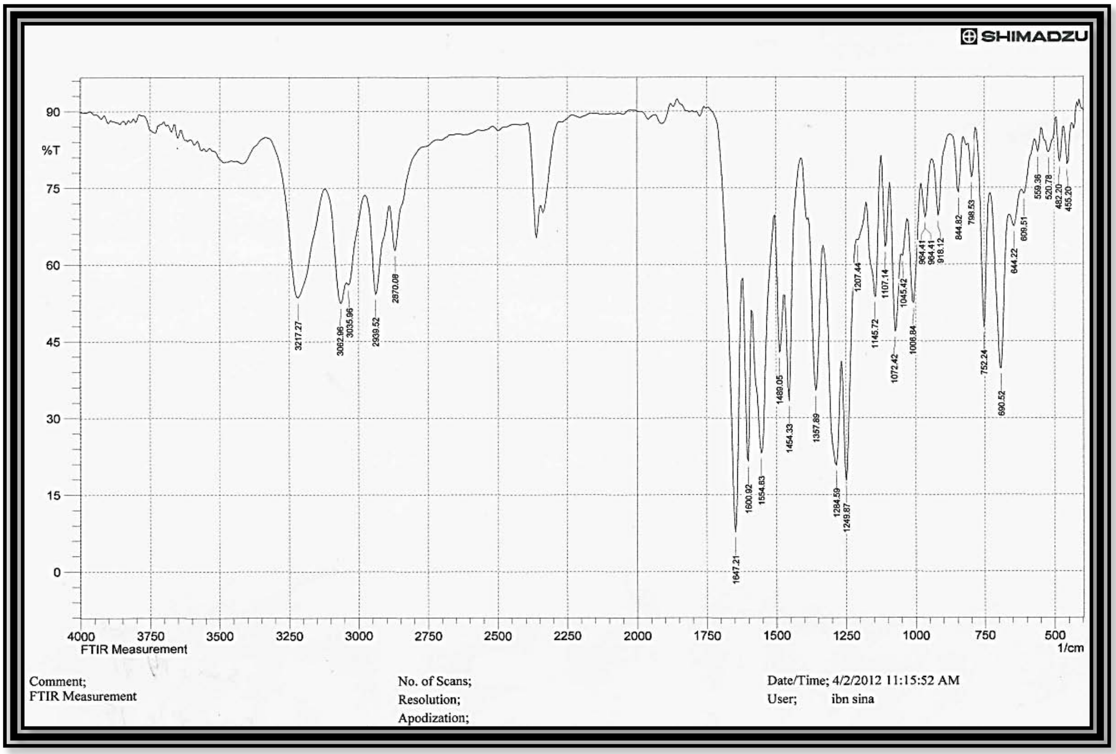

Figure 4 : IR spectrum of Schiff base(V)

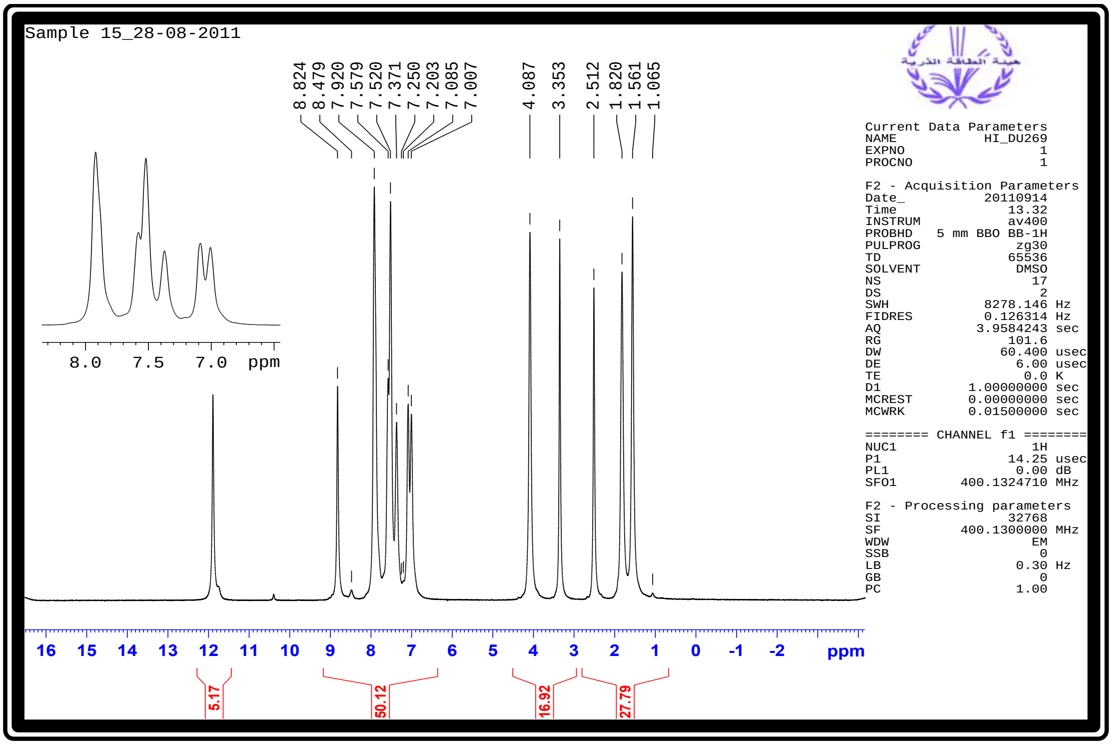

Figure 8 : 1-HNMR spectrum of Schiff base(V)

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Synthesis of 1-(2-(4-Substitutedphenylamino)- Imidazo [2, 1-B] Benzothiazole-3-Yl) Propan-1- One

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Islamic Azad University, Iran

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GJSFR-B Classification : FOR Code: 250301, 030599

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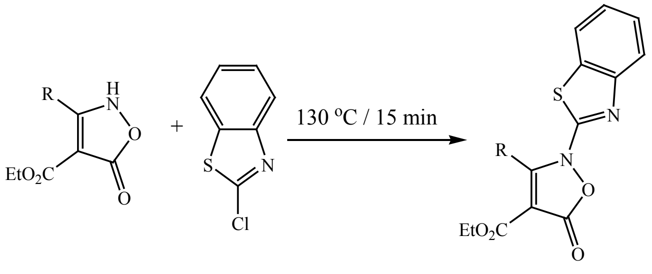
Chalak Azimi [α], Helal Tahazadeh [σ] & Rasol Kamari [ρ]

Abstract- **4-propionyl-3-(4-substitutedphenylamino) isoxazol-5(2H)-one, substituted on nitrogen with a 2-chlorobenzothiazole group, reacts with triethylamine (TEA) in ethanol under reflux conditions to provide a convenient synthesis of 1-(2-(4-substitutedphenyl amino) -imidazo [2,1-b] benzothiazole-3-yl) propan-1-one.**

Keywords: isoxazolones; 2-chlorobenzothiazole; imidazobenzothiazoles; triethylamine (tea).

I. INTRODUCTION

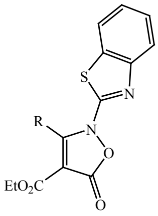
The synthesis of isoxazol-5(2H)-one with benzothiazole substituted on nitrogen **1a** has been reported by Prager and co-workers[1] as shown in Scheme I.



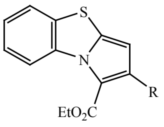
1a R=H

Scheme I

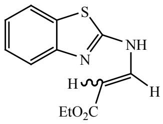
It has been reported[2] that the 2-benzothiazol-2-yl isoxazolones **1a** and **2b** gave the corresponding imidazobenzothiazoles **2a** and **2b** respectively on photolysis in ethyl acetate/ trifluoroacetic acid, and the acrylate **3** was obtained from the photolysis of **1a** in methanol.



1b R=Me



2a R=H
2b R=Me



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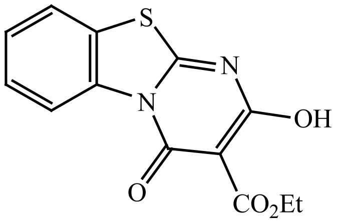
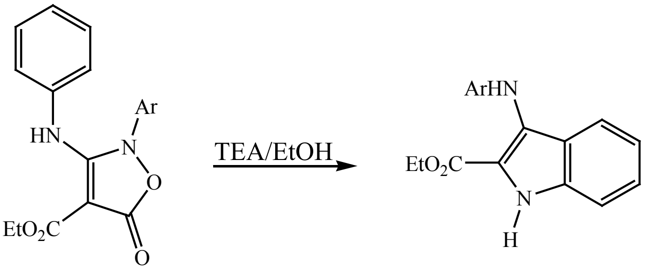
Base-catalysed rearrangement of isoxazolinyl heterocycle **1a** using a solution of sublimed potassium t-butoxide in dry tetrahydrofuran at 40 °C gave ethyl 2-hydroxy-4-oxo-4H-pyrimido [2, 1-b] benzothiazole-3-carboxylate **4**.[3]



4

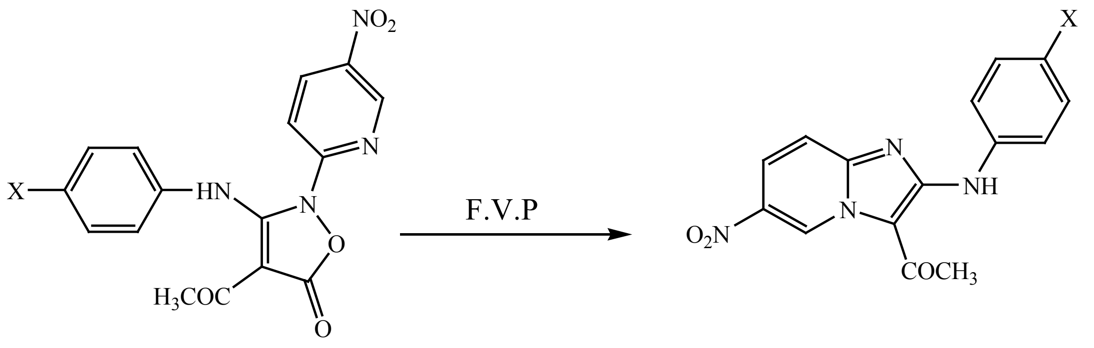
Khalafy et al. recently reported[4] that the reaction of certain 2-aryl-3-arylaminoisoxazolones **5** with triethylamine (TEA) leads to the formation of indoles **6** and carbon dioxide, an outcome that is formally the same as that achieved by photolysis or pyrolysis[5] (Scheme II).



5 6

Scheme II

We have recently reported[6] rearrangement of 4-acetyl-3-(4-substituted phenylamino)-2- (5-nitropyridin-2-yl) isoxazol-5(2H)-ones (**7**, X: Br, Me, OMe) to Imidazo [1, 2-a] pyridines (**8**, X: Br, Me, OMe) under Flash-Vacuum-Pyrolysis (F.V.P) conditions (Scheme III).

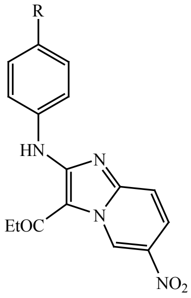


7, X: Br, Me, OMe

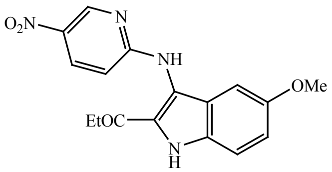
8, X: Br (90%), Me (93%), OMe (95%)

Scheme III

We have also reported[7] that 4-propionyl-3-(4-substituted phenylamino) isoxazole-5 (2H) -one, substituted on nitrogen with a nitropyridine group, react with triethylamine (TEA) to give imidazo [1,2- a]pyridines and indoles. With 4-bromophenyl and 4-methylphenyl group substituents only imidazopyridines **9a-b** are formed, but the 4-methoxyphenyl derivative gave a 3: 1 mixture of corresponding imidazo [2,1-a]pyridine **9c** and 2-pyridylaminoindole **10**, respectively.



9a R=Br
9b R=Me
9c R=OMe

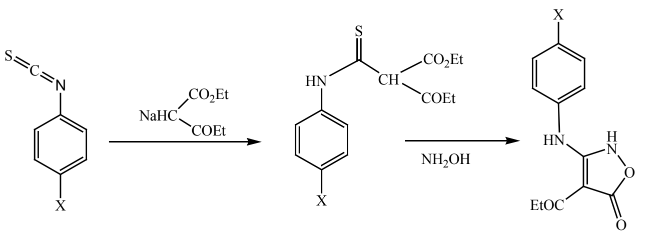


10

Here we describe the synthesis of new N-substituted derivatives of P-substituted 4-(phenylamino) isoxazol-5(2H)-ones **13** with a 2-chlorobenzothiazole group substituted on N-2 **14**, and their rearrangement in the presence of triethylamine to produce 1-(2-(4-substitutedphenylamino)-imidazo [2,1-b] benzothiazole-3-yl) propan-1-one **15**, as shown in (Scheme V).

II. RESULTS AND DISCUSSION

The required isoxazolones **14** were synthesized by reaction of 2-chlorobenzothiazole with 2H-isoxazolones **13**, which in turn were made by a modification of the procedure of Worrall.[8,9] Thus, the reaction of the sodium salt of ethyl-3-oxopentanoate in ethanol with 4-phenylisothiocyanates **11** gave the thiocarbamates **12** in high yield, and these were converted to the corresponding isoxazolone **13** by reaction with 3 equiv of hydroxylamine (Scheme IV).

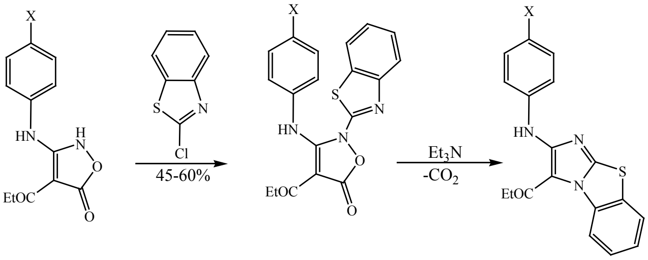


11 12 13

X: Br, Me, NO$_2$

Scheme IV

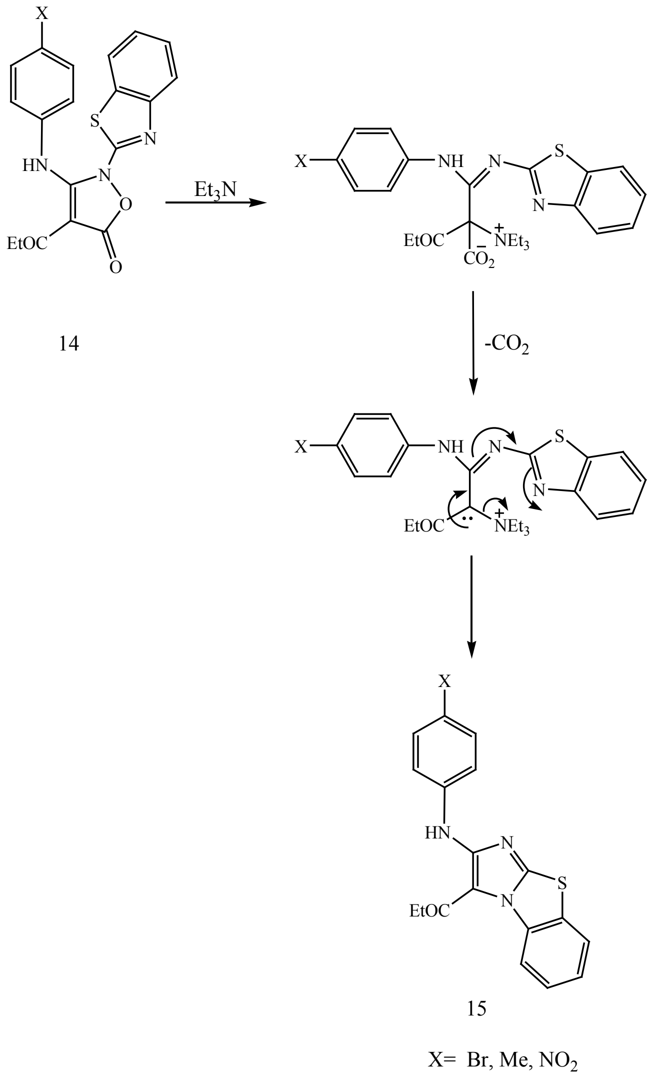
N-arylation of **13** with 2-chlorobenzothiazole in toluene under reflux conditions gave the corresponding N-substituted isoxazolones **14** in medium yield. The rearrangement of N-substituted isoxazolones **14**, as shown in (Scheme V), proceeded in 40-60% yield in refluxing ethanol for 48 h in the presence of triethylamine (TEA). The reaction pathway leading to the imidazobenzothiazole is consistent with our earlier suggestion for the formation of imidazopyridines, which is consistent with the electronic requirements of the reaction, as shown in (Scheme VI), or with the alternative pathway suggested by Prager and co-workers.[10]



13 14 15

Scheme V

X= Br, Me, NO$_2$



Scheme VI

III. EXPERIMENTAL

Freshly distilled solvents were used throughout, and anhydrous solvents were dried according to Perrin and Armarego.[11] Melting points were determined on a Philip Harris C4954718 apparatus and are uncorrected. Infrared spectra were recorded on a Thermonicolet (Nexus 670) FT-infrared spectrometer, using sodium chloride cells and measured as Nujol mulls or KBr. ^{1}H (300 MHz) and ^{13}C (300 MHz) NMR measurements were recorded on a Bruker 300 spectrometer in DMSO-d_6 or $CDCl_3$ using TMS as the internal reference. High resolution mass spectra were recorded on a Varian Matt 311 spectrometer. Mass spectra were registered in a HP 5973 MSD connected to HP 6890 GC interfaced by a Pentium PC and relative abundances of fragments are quoted in parentheses after the m/z values. Microanalyses were performed on a Leco Analyzer 932.

a) *Ethyl-2-((4-bromophenyl)carbamothioyl)-3-xopentanoate (12, X: Br)*

In a 100 mL round-bottomed flask, absolute ethanol (60 mL) was reacted with sodium (2.9 g, 0.126 mol) and after cooling to room temperature ethyl-3-oxopentanoate (20 g, 18.90 mL, 0.126 mol) was added. The reaction mixture was stirred at room temperature for 20 min; 4-bromophenyl isothiocyanate (26.82 g, 0.126 mol) was added and the stirring was continued for a further 6 h, during which a yellowish white precipitate of sodium ethyl-2- ((4-bromophenyl)carbamothioyl)-3-oxopentanoate salt was formed. The salt was collected and washed with light petroleum ether (b.p. 30-55 °C) (3 × 50 mL) to give yellow crystals m.p. 155-156 °C (31.18 g, 70%). The pure salt was dissolved in water (50 mL) and neutralized with dropwise addition of HCl (10%) to maintain the pH at 7. The product was extracted with dichloromethane (CH_2Cl_2) and the extract was washed with water (3 × 50 mL) and dried over anhydrous Na_2SO_4. Removal of solvent gave (10, X: Br) as a yellow oil (21.6g, 66%).

^{1}H-NMR($CDCl_3$)(δppm): 1.06 (t, J=7.1Hz, 3H), 1.3 (t, J=7.1Hz, 3H), 2.5 (q, J=7.1Hz, 2H), 4.32 (q, J=7.1Hz, 2H), 5.09 (s, 1H), 7.55 (d, J=8.6Hz, 2H), 7.73 (d, J=8.6Hz, 2H), 10.9 (bs, 1H, NH).

^{13}C-NMR($CDCl_3$)(δppm): 8.2, 14.34, 27.8, 63.63, 70.68, 120.37, 125.13, 132.37, 137.89, 166.08, 188.05.

FT-IR: 3285, 1759, 1723, 1548, 1431, 1285, 1146, 1023, 831 cm^{-1}.

b) *Ethyl-2-((4-methylphenyl)carbamothioyl)-3-oxopentanoate (12, X: Me)*

This compound was prepared as described above, using 4-methylphenyl isothiocyanate (1.34 g, 9 mmol) and stirring for a further 1.5 h after addition of 4-methylphenyl isothiocyanate to the ethyl-3-oxopentanoate salt to give ethyl-2-((4-methylphenyl) carbamothioyl)-3-oxopentanoate (1.92, 70.25%) as pale yellow solid, m.p. 52-53 °C.

^{1}H-NMR($CDCl_3$)(δppm): 1.06 (t, J=7.1Hz, 3H), 1.3 (t, J=7.1Hz, 3H), 2.35 (s, J=7.1Hz, 3H), 2.49 (q, J=7.1Hz, 2H), 4.32 (q, J=7.1Hz, 2H), 5.09 (s, 1H), 7.23 (d, J=8.3Hz, 2H), 7.66 (d, J=8.3Hz, 2H), 10.77 (bs, 1H, NH).

^{13}C-NMR($CDCl_3$)(δppm): 8.2, 14.35, 23.57, 34.3 63.47, 67.62, 123.64, 129.86, 136.41, 137.43, 166.16, 187.68.

FT-IR : 3284,1760, 1723, 1515, 1430, 1315, 1223, 1148, 1020, 831 cm^{-1}.

c) *Ethyl-2-((4-nitrophenyl)carbamothioyl)-3 oxopentanoate (12, X: NO_2)*

This compound was prepared as described above, using 4-nitrophenyl isothiocyanate (1.62 g, 9 mmol) and stirring for a further 1.5 h after addition of 4-nitrophenyl isothiocyanate to the ethyl-3-oxopentanoate salt to give ethyl-2-((4-nitrophenyl)carbamothioyl)-3-oxopentanoate (1.8, 68.20%) as pale yellow solid, m.p. 54-56 °C.

^{1}H-NMR($CDCl_3$) (δppm): 1.06 (t, J=7.1Hz, 3H), 1.3 (t, J=7.1Hz, 3H), 2.49 (q, J=7.1Hz, 2H), 4.32 (q, J=7.1Hz, 2H), 5.09 (s, 1H), 6.8 (d, J=8.3Hz, 2H), 7.89 (d, J=8.3Hz, 2H), 10.77 (bs, 1H, NH).

^{13}C-NMR ($CDCl_3$) (δppm): 8.2, 14.35, 34.3 63.47, 67.62, 123.64, 129.86, 136.41, 137.43, 166.16, 187.68, 199.

FT-IR: 3284, 1760, 1723, 1515, 1430, 1350, 1315, 1223, 1148, 1020, 831 cm^{-1}.

d) 4-propionyl-3-(4-bromophenylamino)isoxazole-5(2H)-one (13, X: Br)

To a solution of hydroxylamine hydrochloride (7.06 g, 102 mmol) in water (30 mL), sodium bicarbonate (10.17 g, 102 mmol) was added slowly. Ethanol (80 mL) was added and the resulting potassium chloride was filtered off. Ethyl-2-(4-bromophenyl) carbamothioyl-3-oxopentanoate (**10**, 12.13g, 34 mmol) was added to the filtrate and the mixture was stirred at room temperature for 24 h. The reaction mixture was acidified with dilute HCl and the white precipitate was collected and recrystallized from acetone to give the title product (8.78 g, 79%) as colourless crystals, m.p.= 201 ° C (dec.).

^{1}H-NMR (d_6-DMSO)(δppm): 1.11 (t, J=7.1Hz, 3H), 3.01 (q, J=7.1Hz, 2H), 7.37(d, J=8.4Hz, 2H), 7.57 (d, J=8.4Hz, 2H), 8.30 (bs, 1H, NH), 9.39 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO)(δppm): 7.9, 30.7, 59.96, 84, 118.02, 132.94, 137.10, 163.53, 164.74, 167.39.

FT-IR : 3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1398, 1316, 1183, 1018, 818 cm^{-1}.

e) 4-propionyl-3-(4-methylphenylamino)isoxazole-5(2H)-one (13, X: Me)

The compound was prepared as described above using Ethyl-2-(4-methylphenyl)carbamothioyl-3-oxopentanoate (1.17 g, 4 mmol) and refluxing for 24 h to give the desired product as colourless crystals (0.7 g,73%), m.p. 165-167 °C.

^{1}H-NMR (d_6-DMSO + $CDCl_3$) (δppm): 1.11 (t, J=7.1Hz, 3H), 2.35 (s, Me, 3H), 3.01 (q, J=7.1Hz, 2H), 6.78 (d, J=9.2Hz, 2H), 6.79(bs, 1H, NH), 6.80(d, J=9.2Hz, 2H), 8.85 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO+ $CDCl_3$)(δppm): 7.9, 24.52, 30.85, 84.2, 121.53, 130.13, 133.29, 135.64, 163.59, 165.51, 166.74.

FT-IR : 3669, 2979, 2746, 1705, 1669, 1615, 1331, 1208, 1115, 1023, 800 cm^{-1}.

f) 4-propionyl-3-(4-nitrophenylamino)isoxazole-5(2H)-one (13, X: NO_2)

The compound was prepared as described above using Ethyl-2-(4-nitrophenyl)carbamothioyl-3-oxopentanoate (1.3 g, 4 mmol) and refluxing for 24 h to give the desired product as colourless crystals (0.5 g,65%), m.p. 162-164 °C.

^{1}H-NMR (d_6-DMSO + $CDCl_3$) (δppm): 1.11 (t, J=7.1Hz, 3H), 3.01 (q, J=7.1Hz, 2H), 6.78 (d, J=9.2Hz, 2H), 6.79(bs, 1H, NH), 7.8 (d, J=9.2Hz, 2H), 8.85 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO+ $CDCl_3$) (δppm): 7.9, 30.85, 84.2, 121.53, 130.13, 133.29, 135.64, 163.59, 165.51, 166.74.

FT-IR: 3669, 2979, 2746, 1705, 1669, 1615, 1350, 1331, 1208, 1115, 1023, 800 cm^{-1}.

g) 4-propionyl-3-(4-bromophenylamino)-2-(benzothiazol-2-yl)-isoxazol-5(2H)-one (14, X: Br)

4-propionyl-3-(4-bromophenylamino) isoxazole-5(2H)-one (93 mg, 0.3 mmol) and 2-chlorobenzothiazole (51 mg, 0.3 mmol) were refluxed in toluene (6 mL) for 48 h. The solvent was removed under reduced pressure. On addition of n-hexane (10 mL) to the residue (colourless oil) a white precipitate was formed. The precipitate was filtered and recrystallized from ethanol to give 4-propionyl-3-(4-bromophenylamino)-2-(benzothiazol-2-yl)-isoxazol-5(2H)-one as white prisms (84.4 mg, 60%) m.p. 153-155 °C.

^{1}H-NMR (d_6-DMSO)(δppm): 1.11 (t, J=7.1Hz, 3H), 3.01 (q, J=7.1Hz, 2H), 6.37(d, J=8.4Hz, 2H), 7.3 (d, J=8.4Hz, 2H), 7.6 (t, J=8.4Hz, 2H), 8.3 (d, J=8.4Hz, 2H), 8.30 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO)(δppm): 7.9, 30.7, 59.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 163.53, 164.74, 167.39.

FT-IR: 3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.

MS ***m/z***: (%) 442.9 (M+, 12%), 440 (M+, 11%), 417 (82), 415 (71), 371 (48), 369 (40), 334 (25), 294 (28), 291 (27), 290 (100), 262 (30), 224 (27), 177 (33), 161 (34), 150 (40), 135 (26), 134 (33), 108 (29), 44 (65).

h) 4-propionyl-3-(4-methylphenylamino)-2-(benzothiazol-2-yl)-isoxazol-5(2H)-one (14, X: Me)

This compound was prepared as described above, using the corresponding isoxazolone (11, X: Me) (67 mg, 0.27 mmol) and 2-chlorobenzothiazole (45.8 mg, 0.27 mmol) to give the desired product as white prisms (48 mg, 50%) after recrystalization from ethanol, m.p. 158-160 °C.

^{1}H-NMR (d_6-DMSO)(δppm): 1.11 (t, J=7.1Hz, 3H), 2.35 (s, J=7.1Hz, 3H), 3.01 (q, J=7.1Hz, 2H), 6.37(d, J=8.4Hz, 2H), 7.3 (d, J=8.4Hz, 2H), 7.6 (t, J=8.4Hz, 2H), 8.3 (d, J=8.4Hz, 2H), 8.33 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO) (δppm): 7.9, 24.3, 30.7, 59.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 163.53, 164.74, 167.39.

FT-IR: 3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.

MS ***m/z***: (%) 379.1 (M+, 12%), 371 (48), 369 (40), 334 (25), 294 (28), 291 (27), 290 (100), 262 (30), 224 (27), 177 (33), 161 (34), 150 (40), 135 (26), 134 (33), 108 (29), 44 (65).

i) 4-propionyl-3-(4-nitrophenylamino)-2-(benzothiazol-2-yl)-isoxazol-5(2H)-one (14, X: NO_2)

This compound was prepared as described above, using the corresponding isoxazolone (11, X: NO_2) (94 mg, 0.34 mmol) and 2-chlorobenzothiazole (57.1 mg, 0.34 mmol) to give the desired product as white prisms (44 mg, 47%) after recrystalization from ethanol, m.p. 168-170 °C.

^{1}H-NMR (d_6-DMSO)(δppm): 1.11 (t, J=7.1Hz, 3H), 3.01 (q, J=7.1Hz, 2H), 6.7(d, J=8.4Hz, 2H), 7.6 (t, J=8.4Hz, 2H), 7.9 (d, J=8.4Hz, 2H), 8.3 (d, J=8.4Hz, 2H), 8.33 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO) (δppm): 7.9, 30.7, 59.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 163.53, 164.74, 167.39.

FT-IR : 3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1450, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.

MS ***m/z***: (%) 410.1 (M+, 12%), 402 (48), 370 (40), 334 (25), 294 (28), 291 (27), 290 (100), 262 (30), 224 (27), 177 (33), 161 (34), 150 (40), 135 (26), 134 (33), 108 (29), 44 (65).

j) 1-(2-(4-bromophenylamino)-imidazo[2,1-b] benzothiazole-3-yl) propan-1-one (15, X: Br)

The isoxazolone (12, X: Br) (97.2 mg, 0.22 mmol) and triethylamine (0.3 mL) were refluxed in ethanol (10 mL) for 24 hours. The reaction mixture was left to cool to room tempreture and resulting precipitate was colleted to afford 1-(2-(4-bromophenylamino)-imidazo [2, 1-b] benzothiazole-3-yl) propan-1-one as white needles (49 mg, 55%), mp 177-182 °C.

^{1}H-NMR (d_6-DMSO)(δppm): 1.18 (t, J=7.1Hz, 3H), 2.5 (q, J=7.1Hz, 2H), 6.6(d, J=8.4Hz, 2H), 7.2 (t, J=8.4Hz, 1H), 7.3 (t, J=8.4Hz, 1H), 7.5 (d, J=8.4Hz, 2H), 8.2 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO) (δppm): 7.6, 32.7, 59.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 143.53, 144.74, 147.39.

FT-IR: 3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1450, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.

MS ***m/z***: (%) 399.1 (M+, 12%), 387 (48), 370 (40), 334 (25), 298 (28), 295 (27), 293 (100), 262 (30), 224 (27), 179 (33), 161 (34), 153(40), 145 (26), 134 (33), 108 (29), 44 (65).

k) 1-(2-(4-methylphenylamino)-imidazo[2,1-b] benzothiazole-3-yl) propan-1-one (15, X: Me)

The isoxazolone (12, X: Me) (83.3 mg, 0.22 mmol) and triethylamine (0.3 mL) were refluxed in ethanol (10 mL) for 24 hours. The reaction mixture was left to cool to room tempreture and resulting precipitate was colleted to afford 1-(2-(4-methylphenylamino)-imidazo [2, 1-b] benzothiazole-3-yl) propan-1-one as white needles (43 mg, 50%), mp 151-156 °C.

^{1}H-NMR (d_6-DMSO)(δppm): 1.18 (t, J=7.1Hz, 3H), 2.3 (s, J=7.1Hz, 3H), 2.5 (q, J=7.1Hz, 2H), 6.6 (d, J=8.4Hz, 2H), 6.9 (d, J=8.4Hz, 2H), 7.3 (t, J=8.4Hz, 1H), 7.5 (t, J=8.4Hz, 1H), 7.7 (d, J=8.4Hz, 2H), 8.2 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO) (δppm): 7.6, 24.3, 32.7, 59.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 143.53, 144.74, 147.39.

FT-IR: 3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1450, 1402, 1398, 1301, 1183, 1018, 818 cm^{-1}.

MS ***m/z***: (%) 336.11 (M+, 12%), 330 (48), 310 (40), 304 (25), 298 (28), 295 (27), 293 (100), 262 (30), 224 (27), 179 (33), 161 (34), 153(40), 145 (26), 134 (33), 108 (29), 44 (65).

l) 1-(2-(4-nitrophenylamino)-imidazo[2,1-b] benzothiazole-3-yl) propan-1-one (15, X: NO_2)

The isoxazolone (12, X: NO_2) (90 mg, 0.22 mmol) and triethylamine (0.3 mL) were refluxed in ethanol (10 mL) for 24 hours. The reaction mixture was left to cool to room tempreture and resulting precipitate was colleted to afford 1-(2-(4-nitrophenylamino)-imidazo [2, 1-b] benzothiazole-3-yl) propan-1-one as white needles (41 mg, 49%), mp 199-200 °C.

^{1}H-NMR (d_6-DMSO)(δppm): 1.18 (t, J=7.1Hz, 3H), 2.5 (q, J=7.1Hz, 2H), 6.7 (d, J=8.4Hz, 2H), 7.3 (t, J=8.4Hz, 1H), 7.5 (t, J=8.4Hz, 1H), 7.7 (d, J=8.4Hz, 2H), 8.6 (bs, 1H, NH).

^{13}C-NMR (d_6-DMSO)(δppm): 7.6, 32.7, 70.96, 84, 118.02, 121, 125.3, 132.94, 137.10, 143.53, 144.74, 147.39.

FT-IR: 3250, 2950, 2740, 1723, 1696, 1666, 1607, 1563, 1456, 1450, 1402, 1398, 1353, 1301, 1183, 1018, 818 cm^{-1}.

MS ***m/z***: (%) 366.11 (M+, 11%), 353 (48), 310 (40), 304 (25), 298 (28), 295 (27), 293 (100), 262 (30), 224 (27), 179 (33), 171 (34), 153(40), 149 (26), 134 (33), 108 (29), 44 (65).

IV. CONCLUSION

In conclusion we have shown that a variety of N-substituted isoxazolones **14**, rearranged with Triethylamine to give imidazo [2, 1-b] benzothiazole.

V. ACKNOWLEDGMENTS

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Synthesis, Characterization, Antibacterial, and Extraction Studies of Dioxouranium (Uo22+) Ofn, N'-[(4, 4'-Biphenyl Bis (Methylidene))] Di Nicotinic Hydrazine

By Hamid Hussein Eissa

University of Hajah, Yemen

Abstract- New Hydrazonic Schiff base was synthesized by reaction Nicotinic hydrazidewith Biphenyl-4,4'-Dicarbal-dehydehave been characterized by elemental analyses IR, massand1H-NMR spectral data Hydrazoic Schiff base have been studied by liquid-liquid extraction towards the metal ion Uo(II) from aqueous phase to organic phase. behave as a good extractant ligand for uranyl ions Uo(II) from aqueous solution, and the study of conditions of extraction shows that the optimum pH values for extraction was (pH= 5.2), so the suitable concentration of Uo(II) ions in aqueous solution which is giving highest distribution ratio (D) was (1x10-4M), in addition the optimum shaking time to reach the equilibria was (60 min.), as well as the stoichiometric study by using three methods shows the structure of Uo(II) ions complex with ligand was 1 : 1 (metal : ligand), in addition the study of organic solvent effect appear there is no straight line relation between the distribution ratio for extraction of Uo(II) ions and dielectric constant for organic solvents but this study demonstrate there is an effect for the structure of organic solvent used, thermodynamic study shows the complexation reaction an endothermic.The new Schiff Bases was studied for antibacterial activities against (Bacillus subtilis and Staphylococcus aureus) are Gram positive and (Salmonella typhi and Escherichia coli) are Gram negative. The compound ligand was exhibited a variable activity of inhibition on the growth of the bacteria.

Keywords: nicotinic hydrazide, liquid-liquid extraction, uranyl ions, stoichiometric, thermodynamic.

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Keywords: nicotinic hydrazide, liquid-liquid extraction, uranyl ions, stoichiometric, thermodynamic.

I. INTRODUCTION

Schiff bases are widely studied and used in the fields of organic synthesis and metal ion complexation [1, 2] for a number of reasons: their physiological and pharmacological activities [3-5] their use in ion selective electrodes [6-11] in the determination of heavy metals ions in environmental samples [12] and in the extraction of metals ions [13,14] and their many catalytic applications (e.g. for epoxidation of olefins, alkene cyclopropanation [15,16] trimethylsily-lcyanation of ketones [17] asymmetric oxidation of methyl phenyl sulfide enantioselective-epoxidation of silylenol [18] and ring- opening Polymerization of lactide [19]. Hydrazones are special group of compounds in the Schiff bases family. They are characterized by the presence of (C=N-N=C). the presence of two inter-linked nitrogen atoms was separated from imines, oximes, etc. hydrazone Schiff bases of acyl, aroyl and heteroacroylcompounds have additional donor sites like C=O. The additional donor sites make them more flexible and versatile. This versatility has made hydrazones good polydentate chelating agents that can form a variety of complexes with various transition and inner transition metals and have attracted the attention of many researchers. Various hydrazones are obtained depending on the experimental conditions; which have application as biologically active compounds [20] and as analytical reagents [21]. As biologically active compounds, hydrazones find applications in the treatment of diseases such asanti-tumor [22] tuberculosis [22] leprosy and mental disorder [23]. Tuberculostatic activity is attributed to the formation of stable chelates with transition metals present in the cell. Thus many vital enzymatic reactions catalyzed by these transition metals cannot take place in the presence of hydrazones [24,25]. Hydrazones also act as herbicides, insecticides, nematocides, rodenticides and plant growth regulators.

Uranium exists in various concentrations in all parts of the environment, in certain types of rocks*e.g.* Some types of granites, and various mineral deposits. There are also some artificial contributions of uranium to the environment *e.g.* from mineral exploration, emissions from the nuclear industry, the combustion of coal and other fuels, and the use of phosphate fertilizers that contain uranium.[26].1 Natural uranium is one of the elements that can be transferred to the plants or accumulated under the influence of microbial processes including oxidoreduction, production of complexing compounds, and biosorption. In this way, plants and fungi are directly involved in the absorption, accumulation of major and trace elements including radionuclides. In natural and also in disturbed environments, accumulation of uranium has been observed in plants, mushrooms and fungal mycelium. [27] The contents have been observed in mycelia by

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coupling the microscopic and spectrometric methods. The complex compounds formed between uranyl ions and different complexing agents are of great interest due to their possibilities to be applied in extraction of metallic ions from ores, extraction of uranium from solutions of low concentration treatment of the radioactive waters and in environmental chemistry. It is known the fact that the uranylions have a big complexing capacity in the presence of different organic and inorganic compounds. Behavior of uranium in solution is very interesting. Usually, uranium is found in form of uranyl ions very stable in both solution and solid state. From the structural point of view, the uranyl ions has in its center the uranium atom with the oxidation state (VI), and the two atoms of oxygen form two double bonds O=U=O with an angle of 180° between them (linear, stable structure), fact demonstrated by Duval [28] and Frankuchen [29] (in his studies over the uranyl and sodium acetate). The ligands coordinate equatorially to the uranium atom and in a perpendicular plane on the plane of the O=U=O bonds, coordination numbers being between 4 and 7 depending on the chemical surrounding.[30-32] The Schiff bases are chelating agents used to get different complexes with transitional metals. They form complexes compounds with different metallic ions in the 1/1 ratio form 3 very stable chelate cycles. Taking into account the high capacity of the Schiff bases to coordinate metallic ions, these are the intensively utilized as complexing agents to extract some. Metals from various media. The uranyl ions form complex compounds with numerous Schiff bases showing a strong affinity for ligands with oxygen and nitrogen-bearing ligands, a series of such complexes being already studied. [33-36].

II. Experimental

a) *Reagents and Apparatus*

All the chemicals used were of AnalaR grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. Distilled water was used in the extraction experiments. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction. The C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. The IR spectrum was recorded on Jusco 300 instrument in KBr pellets. $^{1-}$H NMR spectra of ligands in CDCl3 solution were recorded on a Bruker DT-400 MHz spectrometer, and chemical shifts are indicated in ppm relative to tetra methyl silane. Mass spectra were recorded using a KRATOS MS50TC spectrometer.

AA 929 Unicam Spectrometer was used for FAAS measurements with an air-acetylene flame. A pH meter (Metrohm–691pH Meter) was also used. All extraction experiments were performed by using a mechanical flask agitator in 50 cm^{3} stoppered glass flasks, M.P Apparatus Digital (32-300 ^{0}C).The thermo gravimetric analysis (TGA) was carried out in a dynamic nitrogen atmosphere (20 mL.min−^{1}), with a heating rate of 10 ◦C min−1 using Shimadzu TGA-50H thermal analyzers.

c) *Synthesis of N,N'-[(4,4'-biphenyl bis (methylidene))] di nicotinic hydrazide*

The hot ethanolic solution (30mL), of 4, 4'-biphenyl aldehyde (1 mmol, 0.210 g), and a hot ethanolic solution (30mL), of nicotinic hydrazide (2mmol, 0.274 g), were mixed slowly with constant stirring. Containing a few drops of concentrated HCl. The reaction mixture was heated to reflux for 4hrs, where white precipitate was formed scheme (1). The solid obtained was collected and recrystallized from mixture DMF, EtOH (9: 1) as white crystals. A yellow colored precipitate was washed with water, ethanol, CHCl$_3$ and diethyl ether, respectively, and dried under vacuum over P2O5.

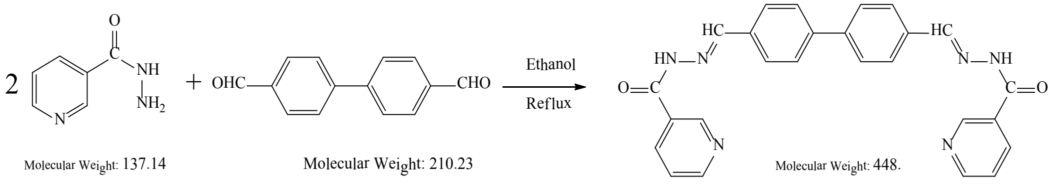
White; Yield: (80 %), m. p= 285 ^{0}C, Empirical formula ($C_{26}H_{20}N_6O_2$), M. Wt: (448 g)

Mass spectrum (m/z): 448. (Figure 1).

UV-Vis: ʎmax = 360 nm. . (Figure 4).

IR (KBr disk): 3248.13 cm^{-1} (N-H), 3062.96 cm^{-1}(C-H), aromatic, 1651.07 cm^{-1} (C=O), 1600.92 cm^{-1} (C=N). (Figure 2).

^{1}H-NMR (CDCl$_3$-400MHz) δ =12.0957(s, 2H, CO-NH-), 9.093 (s, 2H, CH=N), 7.591 - 8.979 (m,16H, Ar), 2.508 -2.677(DMSO,H$_2$O). (Figure 3).



Scheme (1) (I)

b) *Procedure of Extraction*

The extraction properties of the Schiff base ligand (I) was investigated under liquid–liquid phase and neutral condition using transition metal picrates Uo (II) as substrates and measuring by UV–vis measurements the amounts of metal picrate in the aqueous phase before and after treatment with the compounds. About 10 mm of 2×10^{-5} M aqueous picrate solution and 10 mm of 1×10^{-3} M solution of ligand in $CHCl_3$, CH_2Cl_2, C_6H_6 were vigorously agitated in a stoppered plastic tube with a mechanical shaker for 2 min, then magnetically stirred in a thermo stated water bath at 25 ^{0}C for 1 h, and finally left standing for an additional 30 min. The concentration of the picrate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of ligand. Transition metal picrate were prepared by successive addition of 1×10^{-2} M metal nitrate solution to 2×10^{-5}M aqueous picric acid solution and shaken at 25 ^{0}C for 1 h.This metal picrate Uo(II) was measured by UV–vis using maximum wavelength 352 nm. For each combination of host and metal picrate, the picrate extraction was conducted on three different samples and the average value of percent picrate extracted, with a standard deviation, was calculated. In the absence of host, a blank experiment, no metal ion picrate extraction was detected. The extractability was calculated by using the equation below:

$$\text{Extractability (\%)} = \left(\frac{A_0 - A}{A_0}\right) \text{ x } 100$$

Where A_0 is the absorbance in the absence of ligand. A denotes the absorbance in the aqueous phase after extraction. [37].

d) Biological Activity

The prepared compounds were tested for their antimicrobial activity against four speices of bacteria (Bacillus subtilis, Escherichia coli , Staphylococcus aureus, Salmonella typhi) using filter paper disc method [38]The screened compounds were dissolved individually in DMSO (dimethyl sulfoxide) in order to make up a solution of 50, 100, and 200 μg/ml concentration for each of these compounds. Filter paper discs (Whitman No.1 filter paper, 5mm diameter) were saturated with the solution of these compounds. The discs were placed on the surface of solidified Nutrient agar dishes seeded by the tested bacteria. The diameters of inhibition zones (mm) were measured at the end of an incubation period, which was 24 h at 37C for bacteria. Discs saturated with DMSO are used as solvent control. Ciprofloxacin 100 μg/ml was used as reference substance for bacteria**. [38].**

III. RESULT AND DISCUSSION

a) Synthesis

The prepared organic compound (I) was synthesized by the condensation of4,4'-biphenyl aldehyde with nicotinic hydrazide in the molar ratio 1:2 in absolute ethanol . The reaction proceeded smoothly, producing the corresponding Schiff bases in good yield. The ligand is soluble in common organic solvent but insoluble in water. The structures of the ligand was elucidated by elemental analyses, MS, FTIR, electronic absorption, and $^{1-}$H- NMR spectra, which help in elucidating their empirical formula (Table 3.1).

b) Elemental analyses of Schiff base

The results of elemental analyses Schiff base, as shown in Table (3.2), are in good agreement with those required by the proposed formulae

Table 3.1 : Color, molecular weight and melting point of Schiff base (I)

Schiff base	Color	M. Wt	Melting point ^{0}C	λ_{max} nm	Yield %	Crystallization Solvent
I	White	448	285	360	80	DMF , EtOH

Table 3.2 : Elemental analysis data of Schiff base (I)

Schiff base	Elemental analysis Calculated (Found %)				
	C	H	N	S	O
I	69.34 (69.63)	4.56 (4.49)	19.11 (18.74)	--------	6.99 (7.14)

c) IR Spectra

The IR Spectraldata are shown in table (3.3) of the prepared Schiff base. The band at 1600.92 cm^{-1}is attributed to imine group (-HC=N-) for (I) (Fig 2). The band in the spectra at 1579.8 - 1420.4cm^{-1}is due to (C=C) of aromatic rings. while the band at 2858.5-2933.5cm^{-1} are attributed to (C-H alkanes) for (I) .Also, the band at 3062.96cm^{-1} are attributed to (C-H ar) .While the band at 3248.13cm^{-1} are attributed to (N-H), and the band at 1651.07cm^{-1} are attributed to (C=O). However, in the IR spectra of Schiff bases this band (C=O) disappears and a new vibration band for azo methane (-HC=N-) is observed at 1600.92 cm^{-1}, indicating that complete condensation takes place. . [39-40].

Table 3.3 : IR spectral data (cm^{-1}) of Schiff base (I)

Schiff base	v(C=C)	v(HC=N)	v(C=O)	v(C-H) aliph	v(C-H) arom	v(N-H)
I	1579.8 - 1420.4	1600.92	1651.07	2858.5-2933.5	3062.96	3248.13

d) $^{1-}$H-NMR Spectra of Schiff base (I)

The data of $^{1-}$H-NMR Spectra of prepared Schiff base is shown in table (3.4). The $^{1-}$HNMR spectra of (I) ligand in d6-DMSO (Fig 3) shows a singlet signal at 9.093ppm assigned to the protons (HC=N-) groups of the ligand, while the singlet signal at 12.0957 ppm assigned to the protons (CO-NH) group of the ligand (I). The multiple signals 8.979 - 7.591 ppm are due to the aromatic protons. The other obtained values for $^{1-}$H-NMR chemical shifts of the compound is given in the experimental section.

The $^{1-}$HNMR spectral data of the new compound. These data are in good agreement with those previously reported for similar compound. These results strongly suggest that the proposed compound has been formed. [39-40].

Table 3.4 : $^{1-}$H-NMR Spectra of Schiff bases (I)

Schiff base	Chemical Shifts δ ppm		
	C-H aromatic	CH=N	-CO-NH-
I	8.979 - 7.591 (m,16H)	9.093 (s,2H)	12.0957 (s,2H)

IV. RESULTS AND DISCUSSION

The complexation reaction between the ligand (I) and Uo(II) ion to produce the ion pair complex have to extracted to the organic phase, this complexation reaction of necessity behave among many optimum condition to reach equilibria and giving stable ionpair complex .

a) Effect of pH

Extracted of 10 ml of Uo(II) ion in aqueous phase at different pH (3 –12) by using (10 ml) of (1×10^{-4} M) ligands dissolved in chloroform, after that shaking the two layers for suitable time and separate this two layers and determined the remainder of Uo (II) ion in aqueous phase and Uo (II) ion transfer to the organic phase as complex by stripping method or by difference method according to general procedure, afterward determine the distribution ratio (D) and percentage of extraction (E_{ex}%) at each pH, the results in Table (3.5), and Fig. (5) Shows the optimum of pH extraction was (pH_{ex} = 5.2). At pH less than optimum value effect to protonated ligand to occupy the pair of electron and then can't coordinate strongly with Uo (II) ion and give less stable ion pair complex and minimize the distribution ratio (D) and percentage of extraction (E_{ex}%), also atpH values more than optimum value effect to decrease distribution ratio (D) and percentage ofextraction (E_{ex}%) by reason of formation ion pair complex contain anion (OH) this complex more soluble in aqueous phase and less extracted to organic phase and sovereignty the dissociation equilibria.

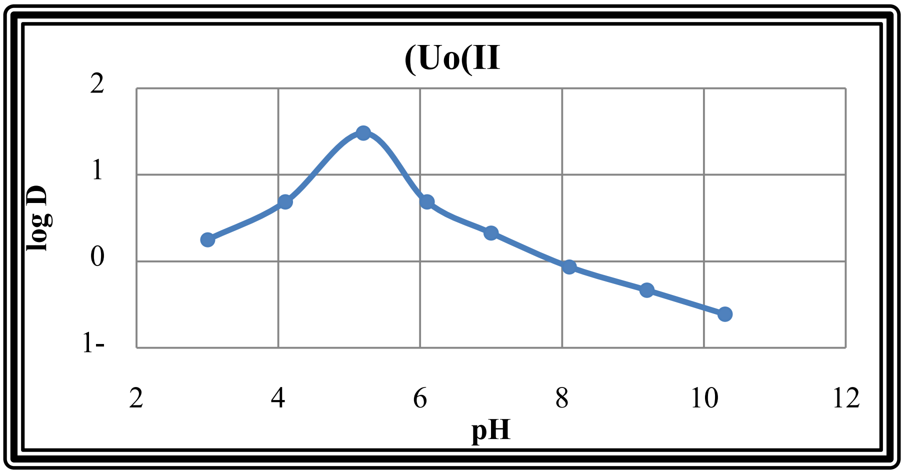


Figure 5 : pH effect on the extraction of Uo (II) ion

Table 3.5 : Effect of pH on the extraction of Uo (II) ion

pH	UO(II)		
	log D	D	E%
3	0.252	1.786	64.1
4.1	0.686	4.848	82.9
5.2	1.481	30.25	96.8
6.1	0.686	4.848	78.9
7	0.329	2.135	62.1
8.1	-0.063	0.866	46.4
9.2	-0.335	0.462	31.6
10.3	-0.613	0.244	19.6
11.1	0	0	0

b) Effect of Shaking Time

Extraction of Uo (II) ion from (10 ml) aqueous phase at (pH =5.2) by using (10 ml) of organic phase of (1×10^{-4} M) ligand dissolved in chloroform, after shaking the two phases at different times, separate the two phases and determine the concentration of Uo (II) ion remainder in aqueous phase and the concentration of Uo(II) ion transfer to organic phase as ion pair complex by previous spectrophotometric method and then determine distribution ratio (D) and percentage of extraction (E_{ex}%). The results in Table (3.6) and Fig. (6) demonstrate that the optimum shaking time was (60 min.) to reach the equlibria of complexation reaction and giving higher distribution ratio (D), the shaking time less than optimum shaking time not allow to reach for equilibria and giving low distribution ratio (D), but at shaking time more than optimum time effect to favor the dissociation step on the complexation and minimize the distribution ratio (D) depend on the kinetic energy of reaction.

Table 3.6 : Effect of shaking time on extraction of Uo (II)ion

Shaking Time	UO^{+2}		
	Log D	D	E%
10	0.037	1.088	52.11
20	0.197	1.573	61.14
30	0.417	2.613	72.32
40	0.712	5.15	84.64
50	0.878	7.547	88.29
60	1.318	20.79	95.41
70	0.999	9.99	90.90
80	0.777	5.99	85.69
90	0.535	3.429	77.42
100	0.343	2.205	68.92
110	0.085	1.217	54.89
120	0.029	1.070	51.69

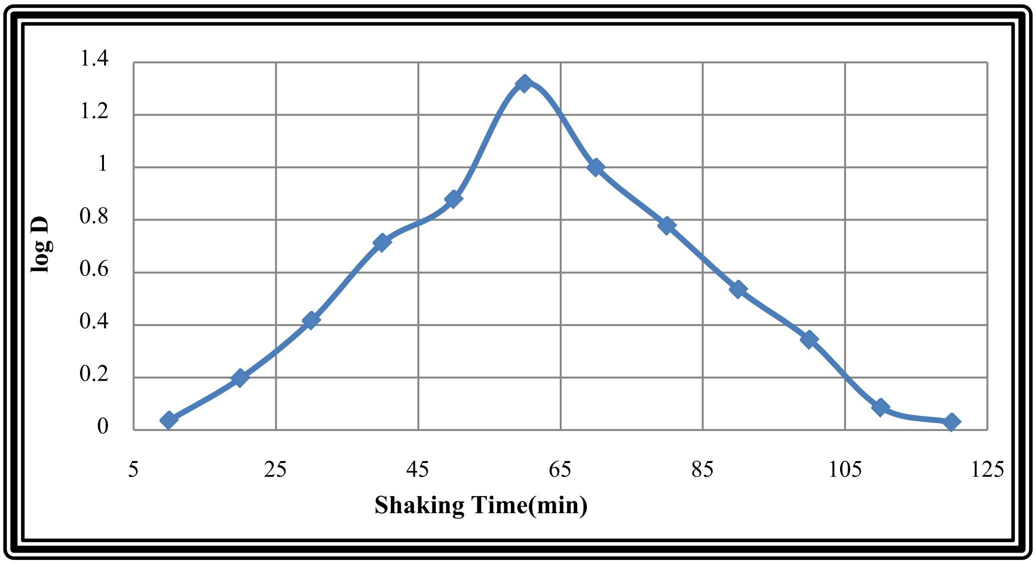


Figure 6 : Effect of shaking time on the extraction of Uo (II) ion

c) *Stoichiometry by Slope Analysis Method*

To knowing the more probable structure of Uo (II) ion pair complex produced, extracted (1×10^{-4} M) Uo (II) ion from (10 ml) aqueous phase at (pH= 5.2) by using (10 ml) of ligand solution dissolved in chloroform at different concentration (2 x10^{-5}M -3×10^{-4} M), after shaking the two layer for (60 min.), separate these layers and determine the remainder quantity of Uo (II) ion in aqueous phase and transfer quantity of Uo (II) ion to organic phase as complex, after that determine distribution ratio (D) and percentage of extraction (E_{ex}%) by previous method (spectrophotometric method). Afterward plot log D against log [Ligand]. The results in Table (3.7) and Fig. (7) shows from the slope of straight line that the more probable structure of ion pair complex extracted was 1: 1(metal : ligand).

Table 3.7 : Slope analysis method for extraction of Uo (II) ion

Log [L]	Uo(II)		
	D	E%	slope
-4.698	0.639	38.98	1.352
-4.522	1.387	58.11	
-4.397	1.932	65.89	
-4.301	2.911	74.43	
-4.097	6.109	85.93	
-4	18.58	94.89	
-3.698	18.03	94.75	
-3.522	17.87	94.70	

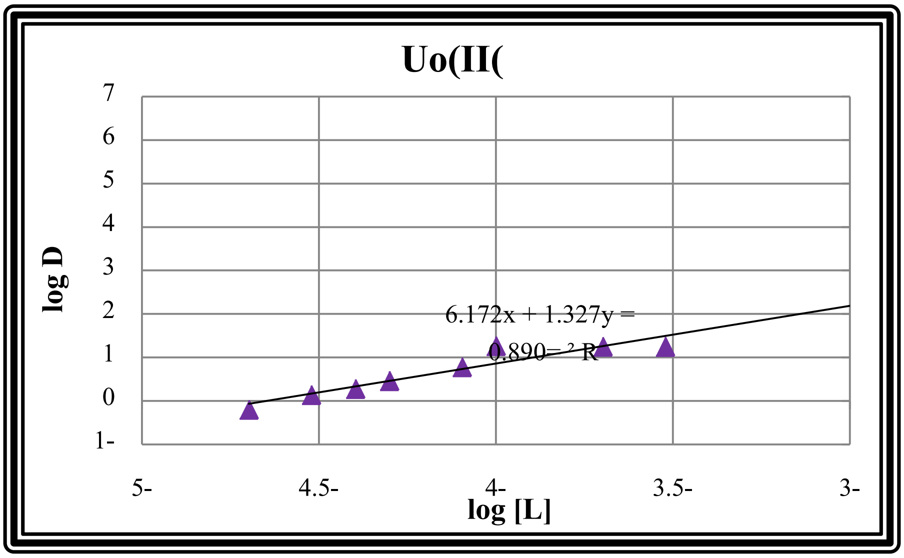


Figure 7 : Slope analysis method for extraction of Uo (II) ion

d) Organic Solvent Effect

Solvent extraction method take care of orgain extraction method; according to this concept extracted (1×10^{-4} M) Uo (II) ion in (10 ml) aqueous phase at (pH= 5.2) by (10 ml) organic phase contain ligand dissolved in different organic solvents at concentration of (1×10^{-4}M), after shaking for (60 min) separate the two layers and determine the remainder Uo (II)ion in aqueous phase and Uo (II) ion transfer to organic phase as Uo (II) complex, according to previous method, afterward calculate the distribution ratio (D) and percentage of extraction (E_{ex}%). The results in Table (3.8) shows there is not any linear relation between distribution ratio (D) and dielectric for organic solvents used in extraction method of Uo (II) ion, Fig(8) as well as this results reflect the effect of organic solvent structure on the extraction method and without any effect for polarity of organic solvent, and reflect the effect on ion pair complex extracted to be contact ion pair (tight ion pair) or solvennic solvent used t separated ion pair (loose ion pair).

Table 3.8 : Organic solvents effect on the extraction of Uo (II) ion

Solvents	ε	Uo(II)	
		D	E %
Dichloro methane	9.08	5.211	83.9
Chloroform	5.708	22.81	95.8
Benzene	2.804	1.770	63.9

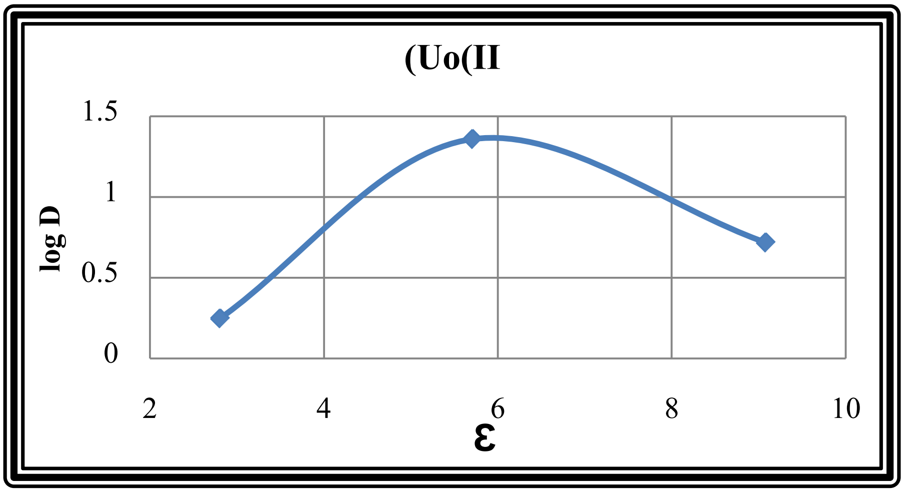


Figure 8 : Effect of solvents organic on the extraction of Uo (II) ion

e) *Effect of Temperature*

Extraction of Uo(II) ion in (10 ml) aqueous phase at (pH = 5.2) by using (10 ml) of (1×10^{-4} M) ligand dissolved in chloroform at different temperature (10 – 40°C), after shaking the two layers for optimum time and separate the two layers, determine distribution ratio (D) according to the general procedure. The results in Table (3.9) and Fig. (9) illustrate the complexation reaction between ligand and Uo(II) ion was Endothermic reaction, that is mean the coordination association between ligand and Uo (II) ion increase with temperature increasing.

Table 3.9 : Temperature effect on the extraction of Uo (II) ion

T.C^0	T.K^0	1/Tx10^{-3} K^0	Uo(II)		
			Log D	D	E %
10	283	283	0.389	2.45	71.02
20	293	293	0.905	8.04	88.93
30	303	303	1.391	24.6	96.09
40	313	313	2.093	124	99.2

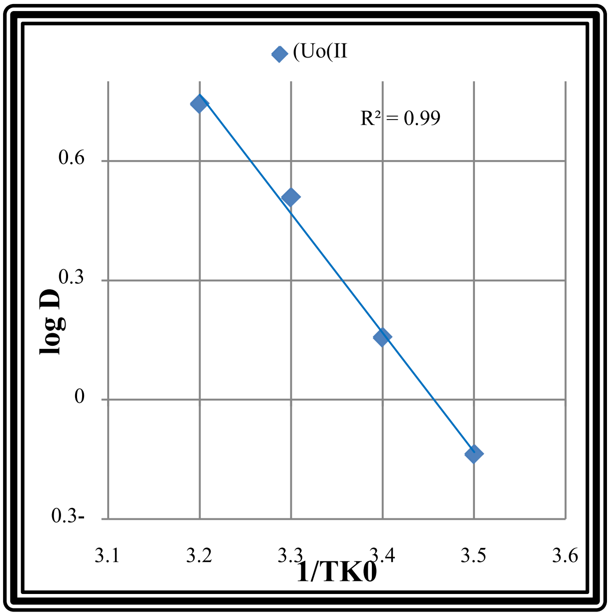


Figure 9 : Temperature effect on the extraction of Uo (II) ion

After calculated the thermodynamic data for extraction method to Uo (II) ion by using the below relation:
Using the below relation:

$$\mathbf{K_{ex}} = \frac{\mathbf{D}}{[\mathbf{M^{n+}}]_{\mathbf{aq}}[\mathbf{L}]_{\mathbf{org}}} \qquad (\mathbf{4.1})$$

Plot log K_{ex} against 1/T °K and determine the slope of the straight line relation, calculate ΔH_{ex} as in the relation:

$$\frac{\Delta \log K_{ex}}{\Delta \frac{1}{T}} = \frac{-\Delta H}{2.303\ R} \quad (4.2)$$

$$\text{Slope} = \frac{-\Delta H}{2.303\ R} \qquad (4.3)$$

$$\Delta G_{ext} = \text{-RT InK}_{ext} \qquad (4.4)$$

$$(4.5)\Delta G_{ext} = \Delta H_{ext} \text{ -T}\Delta S_{ext}$$

After application of these relation, found the value of enthalpy for extraction of Uo(II) ion was (ΔH_{ex} = 108.76 kJmol^{-1}) and Gibbs free energy was (ΔG_{ex} = -61.06kJmol^{-1}), as well as the entropy was (ΔS_{ex} = 542.56J mol-1) these results shows from the value of ΔH_{ex} the ion pair complex structure was 1 : 1 which is giving low value for ΔH_{ex}, but the high value for ΔS_{ex} reflect that complexation reaction was entropic in region [39]from other hand the endothermic reaction shows good association between Uo (II) ion and ligand and may be produce contact ion pair (Tight ion pair).

Table 3.10 : Thermodynamic parameters of Ligand from extraction of Uo (II)ion

Cation	K$_{ext}$	ΔS_{ext} jK^{-1}mol^{-1}	ΔG_{ext} kjmol^{-1}	ΔH_{ext} kjmol^{-1}
Uo(II)	15.5 x 10^9	542.56	-61.06	108.76

V. BIOLOGICAL ACTIVITY

During the last two or three decades, attention has been increasingly paid to the synthesis of Schiff bases which exhibits various biological activities including antibacterial, fungicidal, tuberculostatic and plant growth regulative properties **[41]**. It was judicious to investigate the synthesis of various new types of Schiff base and studied their antibacterial activity against four strains of bacteria (Bacillus subtilis, Escherichia coli, Staphylococcus aureus, Salmonella typhi). The concentrations used for the screened compounds are 50, 100, and 200 µg/ml. Ciprofloxacin was used as reference standard while DMSO as control and inhibition zones are measured in mm. The new compounds were tested against one strain each of a gram positive and two gram negative. The test results presence in Table (3.11), a new compound was active against tested and another compounds are no active.

All compounds are no active where used 50, 100 µg/ml but active in the concentrations 200 µg/ml see table (3.4).

Table 3.11 : Effect of new azo Schiff bases on the growth of tested bacteria (conc.200 µg/ml)

Shiff base	Bacteria			
	Gram negative		Gram positive	
	B. subtilis	S. aureus	E.coli	S. typhi
I	20 mm	18 mm	17 mm	19 mm
Control	00 mm	00 mm	00 mm	00 mm
Ciprofloxacin	20 mm	20 mm	20 mm	20 mm

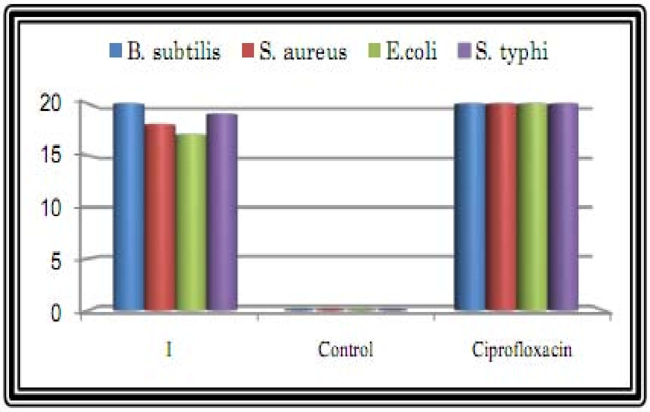


Figure 9 : Antibacterial activity (Gram positive, negative) of synthesized compounds

VI. Conclusion

1. The (I) compound is new and was prepared for the first time.
2. The new compound was identified by 1HNMR, IR, LC-MS spectral methods.
3. The compound showed a high draw ratio of copper ion at pH = 5.2 and the best organic stores is chloroform and that there is no linear relationship between the polarity of the shops and the distribution ratio (D).
4. That shaking a time more than a time best, which represents the time required to complete the process complexity and give a complex stable lead to lower values ratios distribution D and this would lead to the possibility of a reflection of interaction and increase the speed of interaction back and eventually dismantle the complex and perhaps a few Side reactions that may lead to the occurrence of the phenomenon of the three layers (Three layers) for the analysis of solutions and this is what requires us to comply with a time of shaking out the best.
5. That the rate of ion correlation between copper and composite studied by Molar (cation: connected (1:1) between the ligand and the cation.
6. Calculated some parameters associated with extraction, such as constant extraction as well as parameters thermodynamic namely, enthalpy change(ΔH^*),entropy change (ΔS^*), and Gibbs free energy change (ΔG^*).
7. proven data study the effect of different temperatures on the recovery operations that the formation of complexes between ligand and cation studied endothermic (Endothermic) , as indicated negative values of energy free to spontaneous reactions, as also indicated positive values of entropy system that many random.
8. The prepared compound has been biologically screened i.e. studying their effects against two gram-positive, two gram-negative bacteria. The results show that their activities were found to vary from moderate to very strong.

VII. Acknowledgment

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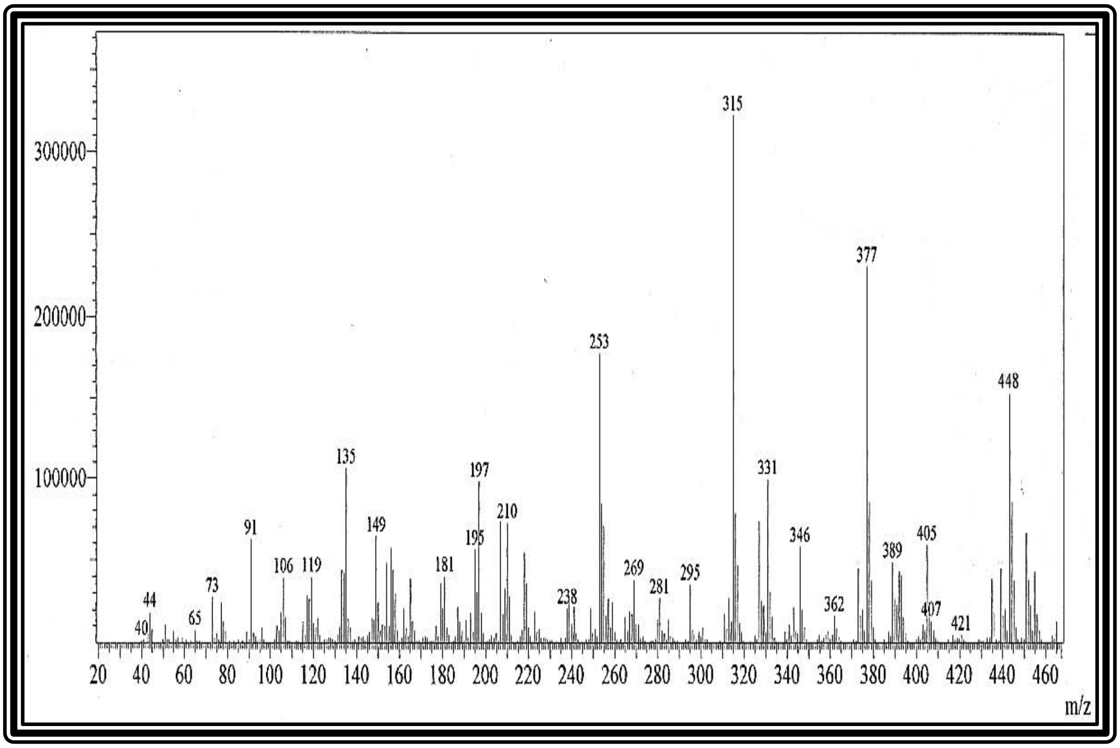

Figure 1 : MS spectra of ligand (I)

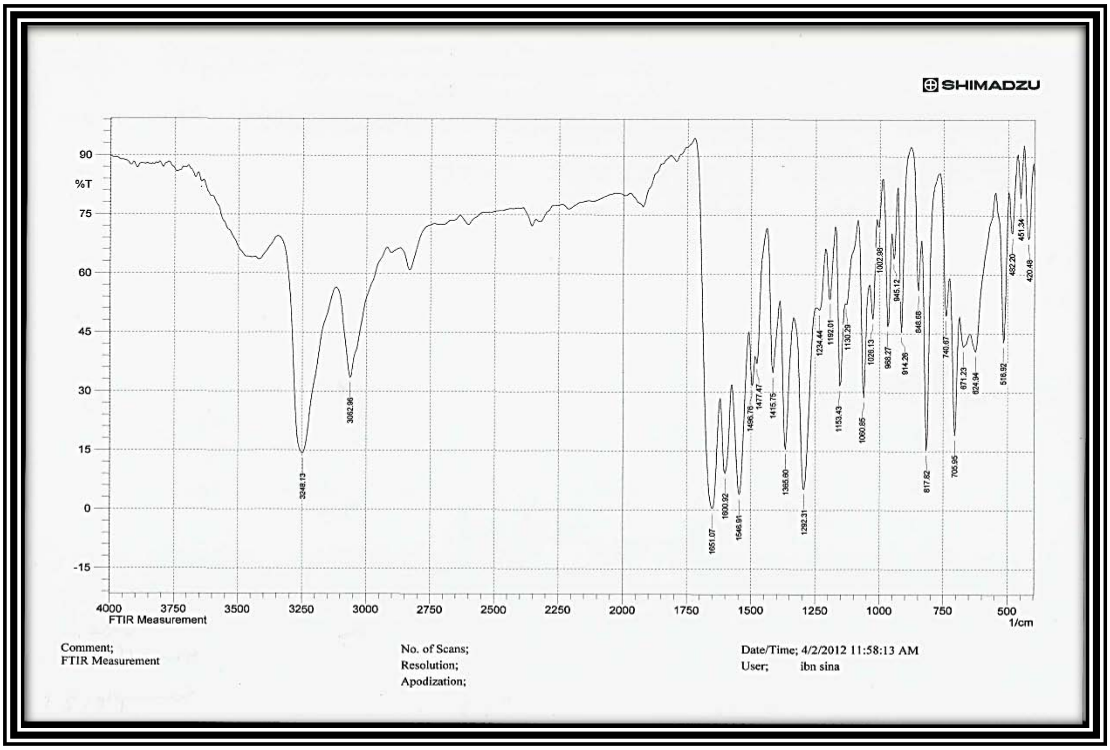

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Figure 2 : IR spectra of ligand (I)

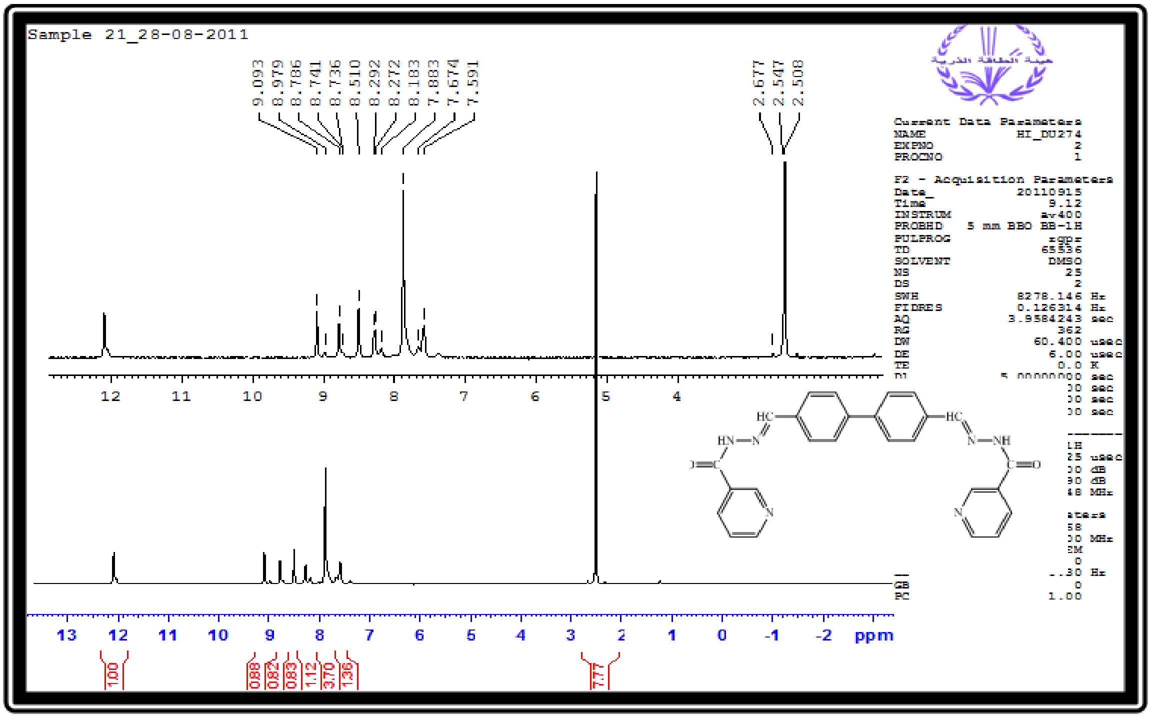

Figure 3 : $^{1-}$H-NMR spectra of ligand (I)

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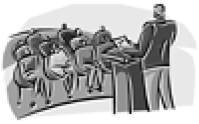

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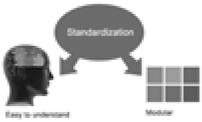

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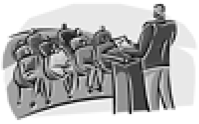

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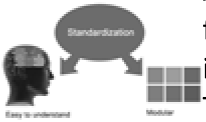

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- Manuscript should complement any figures or tables, not duplicate the identical information.
- Never confuse figures with tables - there is a difference.

Approach

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

Figures and tables

- If you put figures and tables at the end of the details, make certain that they are visibly distinguished from any attach appendix materials, such as raw facts
- Despite of position, each figure must be numbered one after the other and complete with subtitle
- In spite of position, each table must be titled, numbered one after the other and complete with heading
- All figure and table must be adequately complete that it could situate on its own, divide from text

Discussion:

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

- Make a decision if each premise is supported, discarded, or if you cannot make a conclusion with assurance. Do not just dismiss a study or part of a study as "uncertain."
- Research papers are not acknowledged if the work is imperfect. Draw what conclusions you can based upon the results that you have, and take care of the study as a finished work
- You may propose future guidelines, such as how the experiment might be personalized to accomplish a new idea.
- Give details all of your remarks as much as possible, focus on mechanisms.
- Make a decision if the tentative design sufficiently addressed the theory, and whether or not it was correctly restricted.
- Try to present substitute explanations if sensible alternatives be present.
- One research will not counter an overall question, so maintain the large picture in mind, where do you go next? The best studies unlock new avenues of study. What questions remain?
- Recommendations for detailed papers will offer supplementary suggestions.

Approach:

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

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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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