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Kinetic study for the hydroxymethylation of the rubeonic acid in alkaline medium and evaluation of Rubeonic and its derivatives as corrosion inhibitor for carbon steel by theoretical study.

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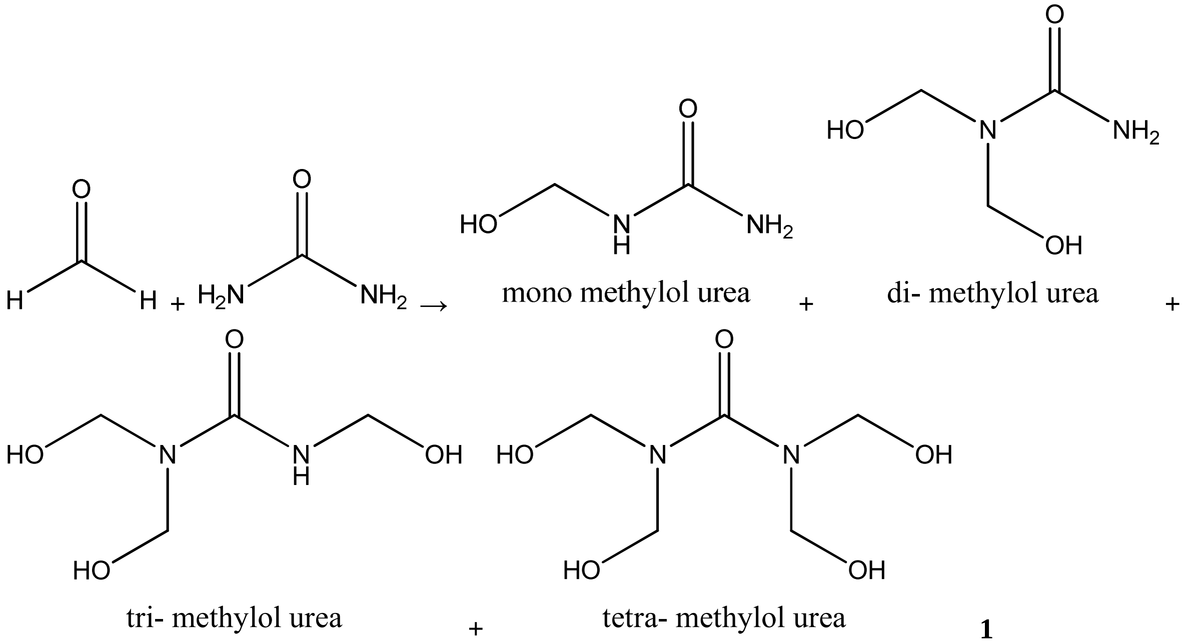
Abstract

Hydroxymethylation process for robeonic acid by the reaction of rubeonic acid with formalin solution 37% in alkaline medium of 10% NaOH has been studied at different temperature, i.e.,. 30,40,50, and 60ºC respectively at constant time 3hours. The reaction prefer the conditions include the temperature 60ºC and the time is 3hours. Thus, the energy of activation decreased as temperature increase , then the time of reaction was decreased. therefore; the consumption of formaldehyde molecules increased as the time of reaction increased at constant temperature. The efficiency of the rubeonic acid (RUA) and its derivatives that include MRU,DRU,N-DRU,TRU, and TERU as corrosion inhibitor for carbon steel was evaluated depending on theoretical calculations especially on the calculations of the E_{HOMO} , E_{LUMO}, and the energy gap ΔE, by using semi-empirical calculations. It was found that RUA has higher efficiency than their derivatives. Hence, the substitution of hydrogen atom by methylol group in RUA reduce the efficiency. Hence, the increasing of the methylol groups on RUA leads to decrease the efficiency, that corresponding to increase in the energy gap ΔE , and decrease the partial charge on N-atom on the products MRU to TREU compared with RUA, also the free energy of corrosion reaction ΔG was increasing as the substituted methylol groups increase on RUA, i.e., from MRU to TREU.

Keywords: Kinetic, Rubeonic acid, hydroxymethylation , corrosion , carbon steel.

Introduction:

Amino resins are often used to modify the properties of other materials[1-2]. Urea-formaldehyde resins are formed by the reaction of urea and formaldehyde. The overall reaction of urea with formaldehyde is quite complex and, although initially studied early in this century, is not completely understood at the present time[3]. The synthesis of a urea-formaldehyde resin takes place by hydroxymethylation of the urea by the addition of formaldehyde to the amino groups (Scheme 1). This reaction is in reality a series of reactions that lead to the formation of mono-,di-, trimethylolureas and tetramethylolurea. The reaction rate is dependent on the pH. The rate for the addition of formaldehyde to successively form one, two, and three methylol groups has been estimated to be in the ratio of 9:3:1, respectively. The exact ratio, of course, is dependent on the reaction conditions employed in the addition reaction [4].



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Scheme 1:Formation of mono, di ,tri-, and tetra methylolurea by the addition of formaldehyde to urea.

Kinetics is the study of the dependence of the extent or rate of a chemical reaction on time and temperature. The chief benefit of kinetics is its ability to predict performance at temperatures and times that are not easily tested. The first of these, known as the rate equation, describes the relationship between the rate of reaction, time, and amount of material. The second, called the Arrhenius equation, describes the relationship between reaction rate and temperature. These equations are usually combined into a single equation of the following form:

$$kf(\alpha) = A \times \exp(\frac{-E_a}{\mathrm{RT}}) \tag{1}$$

where is the reaction fraction, *A* is the preexponential factor, *f*(α) is the kinetic expression, *E* is the activation energy, *R* is the gas constant, and is the absolute temperature. The reaction is thought to be described when activation energy, preexponential factor, and the kinetic expression are known. The scientific study of kinetics centers on the determination of these values. Activation energy (*E*) is considered to be the most important of the kinetic parameters because it describes how the reaction changes as a function of temperature [5]. Thioureas can be synthesized as in urea formaldehyde reaction. They are commercially used in photographic films, plastics and textiles. Thioureas have shown antibacterial, fungicidal [6], hypnotic and antipyretic[7] activities. Some of the thioureas are screened for anticancer activity [8-10]. The use of thiozoles as a vulcanizing accelerators and dye intermediates has been reported [11]. The kinetics of the reaction of thiourea with formaldehyde was studied [12].

Organic compounds containing nitrogen atom are commonly used to reduce the corrosion attack on steel in acidic media. These compounds can adsorb on the metal surface, block active sites on the surfaces and thereby reduce the corrosion attack. The efficiency of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pair present [13-15]. The molecular structure and the electronic parameters that can be obtained through theoretical calculations, as HOMO, and LUMO, the energy gap (ΔE=ELUMO-

EHOMO) are involved in the activity of the inhibitors [16]. The effect of molecular structure on the chemical reactivity has been object of great interest in several disciplines of chemistry [17]. The development of semi-empirical quantum chemical calculations emphasizes the scientific approaches involved in the selection of inhibitors by correlating the experimental data with quantum-chemical properties. HOMO (the highest occupied molecular orbital) energy, and LUMO (the lowest unoccupied molecular orbital) energy, charges on reactive center and on formations of molecules have been used to achieve the appropriate correlations [18].

In this study, condensation polymerization between formaldehyde and Rubeonic acid (dithioxamide) were studied kinetically , the kinetic factors were calculated by using the appropriate relationships. On the other hand, the efficiency of the Rubeonic acid and its derivatives, i.e.,. mono-, di-, tri, and tetra methylol substitution as corrosion inhibitors for CS-alloy type N-80 was evaluated by using semi empirical hyperchem program depending on the E_{HOMO}, and E_{LUMO}, then the partial charge on N-atoms δ on the Rubeonic acid and its derivatives were calculated depending on the inhibition efficiency of each one of the all mentioned compounds, also the free energy ΔG of the inhibition were calculated , all these data were calculated by using the appropriate equations[19].

Experimental

Resin synthesis (general procedure)[20]:

10g of roubeonic acid was charged in three necks round flask, 50mL of 1N sodium hydroxide solution was added to the round, the constituents were mixed then with 50mL of formalin solution (37%) and 1.4g sodium bicarbonate were added to reaction vissile, the mixing continue for 3 hours at 60ºC and pH(10-10.5). After the time was finished, temperature slow down by cooling the mixture then neutralize by 10% v/v phosphoric acid solution. The water was evaporated by rotary evaporator at 40ºC, then the resin dissolved in alcohol. Hence, the salt was filtered, then the evaporated alcohol removed by the rotary evaporator and the product dry at 0.1mm Hg and 40 ºC for 24 hours.

Results and discussion:

Kinetic study

1. Measuring the active protons in rubeonic acid:

Active protons can be calculated at the same conditions of blank that has all constituent reaction except rubeonic acid, by calculating the number of moles for reacting formaldehyde with rubeonic acid by using hydroxylamine hydrochloride[21-22]. Thus, hydroxylamine hydrochloride reacts with the un reacted formaldehyde at pH=4.12 that liberating hydrochloric acid, when its titrate with standard sodium hydroxide, the liberating acid equals the number of moles for the un reacted formaldehyde. Table 1 explain the reaction mixture constituents for sample and blank. The 10mL of 10%w/v hydroxylamine hydrochloride was added, solution should be mixing for 5min then titrate with 0.5N standard solution for sodium hydroxide to get pH=4.12, the mixture should be left for 25min before pH=4.12, blank solution should be treated at the same conditions and the value of addition , the results can be obtained according to below relationship[23].

$$\text{No.of active protons} = \left(\frac{\text{Blank titrate(mL)} - \text{Sample titrate(mL)}}{\text{Rubeonic weight(g)}}\right) \times \text{VNaOH(mL)} \times 0.120$$
$$= \frac{\text{Moles of formaline solution}}{\text{Moles of Rubeonic}} \qquad (2)$$

Where 0.120 refers to the molecular weight by Kg/mole , Blank titrate refers to sodium hydroxide volume that ready to turn back pH=4.12 after acid liberation in blank and sample solution respectively [24].

Table 1 The mixture reaction constituents which using for calculating active protons in rubeonic acid.

Reaction mixture	RUA(g)	NaOH(g)	$NaHCO_3$(g)	Form. Solution (37g/mL)	H_2O(mL)
Sample	2	0.3	0.2	22	20
Blank	0	0.3	0.2	22	20

Where, RUA is rubeonic acid, and Form is Formalin, the blank is hydroxyl amine hydrochloride respectively.

2. Rate of reaction and activation energy calculating method

Rubeonic acid formaldehyde reaction was achieved at different temperature, i.e., 30,40,50, and 60 ºC respectively for 3hours. Thus, zero time reaction was recorded in initially addition of the formalin solution. Formaldehyde concentration can be calculated through the reaction time at different regulating periods by using hydroxylamine hydrochloride, where 5mL of the reaction mixture solution was added after 30min then cooled to 4ºC, the mixture is diluted by adding 50mL of the distilled water at regulating pH=4.12 by using 0.1N hydrochloric acid , then 5mL of 10% hydroxylamine hydrochloride solution added with continuous mixing where pH value down according to the following equation:

$$nCH_2O + H_2NOH.HCl \rightarrow H_2CNOH + n\ HCl + H_2 \qquad (3)$$

Then the reaction mixture titrated with standard solution of 0.5N sodium hydroxide after 5min to get pH=4.12, formaldehyde concentration was calculated according to the following relationship.
meq of HCl= meq of NaOH = meq of CH_2O 3
then second order reaction equation was used [25].

$$\frac{1}{[A]0-[B]0}\ln\frac{[A]t[B]0}{[A]0[B]t}=k(T)t \qquad (4)$$

Where $[A]_\circ$, $[A]_t$, the initial and concentration at t time for A reactant and $[B]_\circ$, $[B]_t$ the initial concentration and the concentration at t time for reactant B in mole/l respectively, k(T) represent the rate of reaction constant at absolute temperature T. Especially, kinetic factors can be calculated depending on the above equation for this reaction, by plotting equation 4. The rate constant should be obtained from the slope, then activation energy (Ea) can be calculated by plotting the values of rate constant against inverse values of absolute temperature (1/T) according to equation 1.

Table 2 Indicate to weight percentage for starting materials in kinetic study

Comp.	Weight (g)	mol	NaOH (g)	$NaHCO_3$ (g)	Formald.(g)	pH	Reactive site
RUA	5	0.042	2	1.4	18.5	10.5	4

Where a, b represent active sites in 5g RUA .

In this study reactivity of rubeonic acid was studied kinetically by lowering of formaldehyde concentrations that react with rubeonic acid in alkaline medium as catalyst at different temperatures i.e.,30,40,50 and 60ºC respectively. Thus, methylol groups were substituted by protons in amino group for rubeonic acid. Hence, RUA depends on the reactive protons that substituted by formaldehyde , where either increasing or decreasing of active hydrogen refers to increasing or decreasing the activity of RUA in this reactions, this factor estimate in Rubeonic acid as shown in Figure 1 and Table 2 that equal to 4 protons per mol respectively. Different values can be obtained from this value in number of protons, where RUA contain four protons like urea active towards formaldehyde. Thus, number of active protons in RUA were calculated by number of formaldehyde moles that react with RUA at standard conditions assumingthat no undesirable reactions happened like cannizaro reaction or deficient of formaldehyde due to evaporation to prevent this factors at 60 ºC as good and maximum temperature for completing the reaction for 3hours with less evaporation of formaldehyde[20]. The consuming of formaldehyde relative to the time can be calculated according to equation 2 at different temperatures this can be shown in Figure 1.

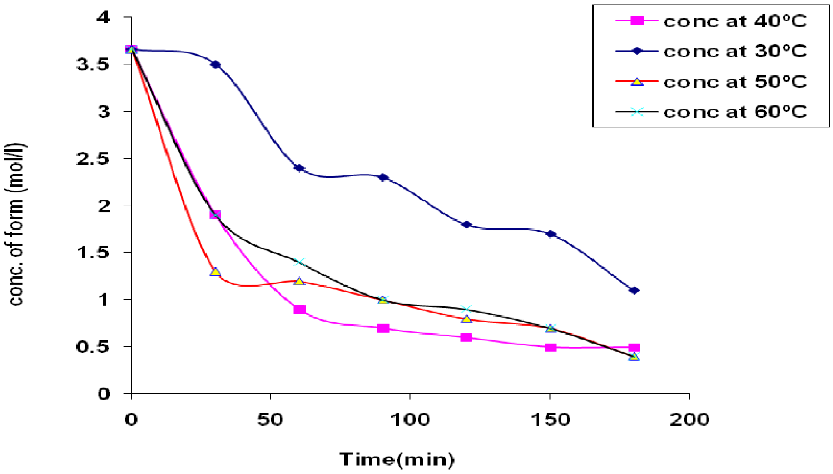


Figure 1 Consuming of formaldehyde with the time at different temperatures.

Figure 1 explain that the concentration of formaldehyde decrease by the reaction with RUA as time increase at each one of the temperatures, i.e., the active protons in RUA were substituted by formaldehyde to form methylol groups[23], hence, as temperature increase, the consuming of formaldehyde increase, i.e., the rate of reaction increase, it is cleared at 60ºC, due to increasing in the kinetic energy for the reactant molecules (RUA and formaldehyde).Thus, the rate constant of the reaction between the RUA and formaldehyde can be calculate according to equation3. Hence, the slope is equal to the rate constant k. Figure 2 explain the calculation of the rate constant at different temperatures, where the R Values in the mentioned figures are referred to the value $\frac{1}{[A]0-[B]0}\ln\frac{[A]t[B]0}{[A]0[B]t}$.

From the figure below, it concluded that the rate constant increase as temperature increase, then the rate of the reaction also increase as temperature increase. Tables 3 explain the values of the rate constant k at the above temperatures.

Table 3. The rate constant for the reaction between rubeonic acid and formaldehyde at different temperature.

k(L/mol.min)	Temperature(ºC)
0.7747	30
1.4422	40
1.7538	50
1.9629	60

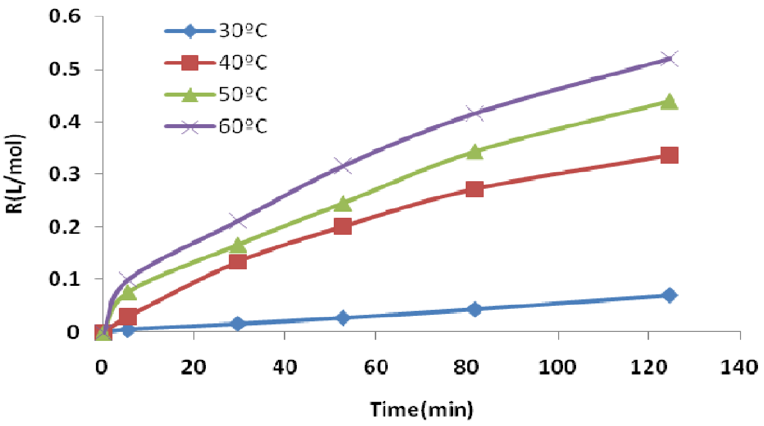


Figure 2 the variation of the concentration of the reactants with the time at different temperature.

The activation energy of the above reaction can be calculated according the Arrhenius equation by plotting the natural algorithm of the rate constant with respect to the reverse of the absolute temperature. Table 4 explains the data that used to the above calculations.

Table 4 the data that used to calculate the activation energy for the above reaction.

k(L/mol.min)	-lnk	T(k)	1/T× 10^{-3} (k^{-1})
0.7747	2.17	303	3.30
1.4422	4.23	313	3.19
1.7538	5.78	323	3.09
1.9629	7.12	333	3.00

Figure 3 explain the Arrhenius plotting. Thus, the activation energy for the reaction (the slope) is equal to 16.44 kJ/mole and the frequency factor (intercept) A is equal to 56.51 min^{-1}.

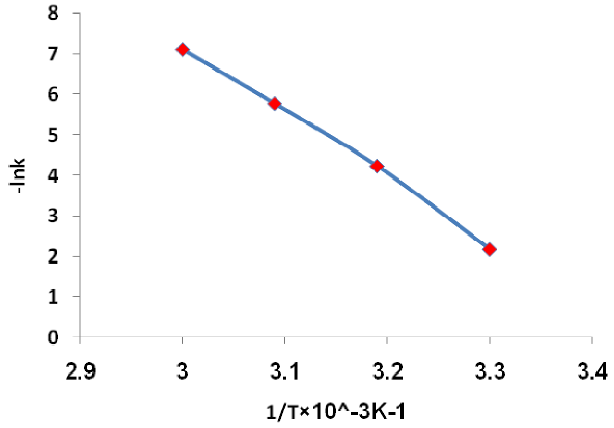


Figure 3. Depending the rate constant on the temperature for the reaction between formaldehyde and rubeonic acid.

Theoretical study

In this study the structural and electronic properties of rubeonic acid and its derivatives were investigated by performing semi-empirical molecular orbital theory at the level of PM3.The semi-empirical method are done on Hyperchem program version 6.0 [24] running on a Windows 7 workstation with a Pentium IV PC. Geometry optimization of the rubeonic acid and its derivatives were done by performing the semi-empirical molecular orbital theory at the level PM3 [25] using the restricted Hartree–Fock (RHF) procedure [26]. The Polak–Ribier algorithm was used for the optimization [27]. The convergence is set to 0.001 kcal.mol.

The optimized structures of rubeonic acid and its derivatives are shown in Figures(4-9). The PM3 geometry optimizations yield Some of molecular information about the molecules studied are given in Table 5,the E_{HOMO} and E_{LUMO} used to calculate the inhibition efficiency. The efficiency used to calculate corrosion rate(CR), corrosion current density(I_{corr}) depending on the calculation of the corrosion rate then the corrosion current density for the Carbon steel alloy in absence of the inhibitors that equal to 14.47 mpy in near neutral medium , the partial charge on N-atoms in the rubeonic and its derivatives δ and the free energy ΔG according the following equations[19].

$$\mathrm{ELUMO} = [\mathrm{eff\%} + 31.1831 + 8.602 \times \mathrm{EHOMO}] \times (0.115) \tag{5}$$

$$\delta = (74.13157 - \mathrm{eff\%}) \times (0.119) \tag{6}$$

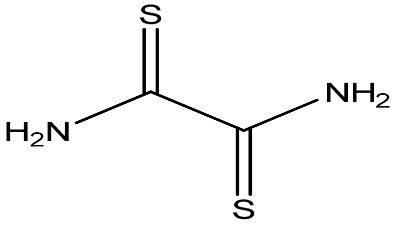
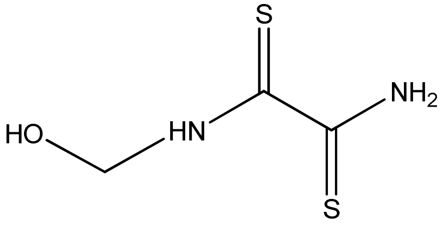
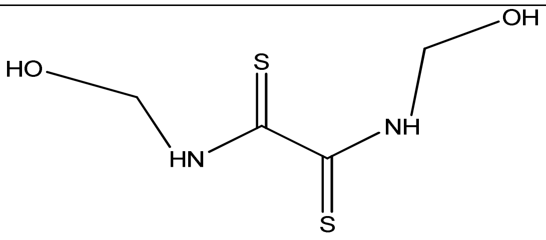
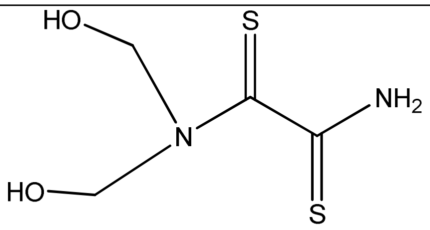
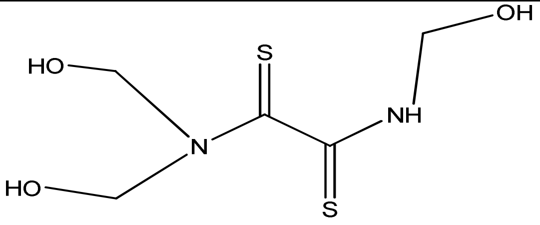
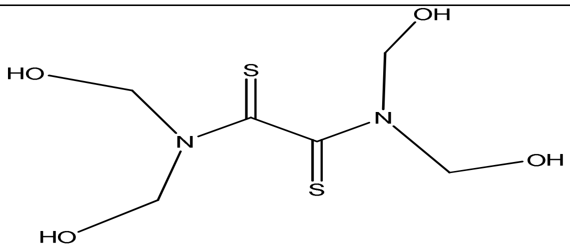
$$\Delta G = (\mathrm{eff\%} - 84.38198) \times (16.45) \tag{7}$$

Table 5 Calculated quantum chemical properties for RUA and its derivatives.

Comp.	Eff%.	I_{corr} (µA/cm^2)	CR (mpy)	Total energy Kcal/mol	ΔE (eV)	E_{HOMO} eV	E_{LUMO} eV	δ	ΔG Kcal/mol
RUA	62.95	11.65	5.36	-22917.57	7.008	-9.069	-2.061	1.33	-352.556
MRU	62.37	11.87	5.46	-33135.03	7.029	-8.990	-1.961	1.40	-362.097
DRU	60.16	12.52	5.76	-43352.05	7.402	-9.425	-2.023	1.66	-398.452
NDRU	60.78	12.35	5.68	-43349.71	7.254	-9.199	-1.945	1.59	-388.253
TRU	59.63	12.70	5.84	-53565.28	7.383	-9.258	-1.875	1.73	-407.170
TERU	59.41	12.76	5.87	-63778.46	7.365	-9.165	-1.800	1.75	-410.789

Where:
RUA=Rubeonic acid.
MRU=Monomethylolrubeonic acid.
DRU=Dimethylolrubeonic acid.
NDRU=N- Dimethylolrubeonic acid.
TRU=Trimethylolrubeonic acid.
TERU=Tetramethylolrubeonic acid.

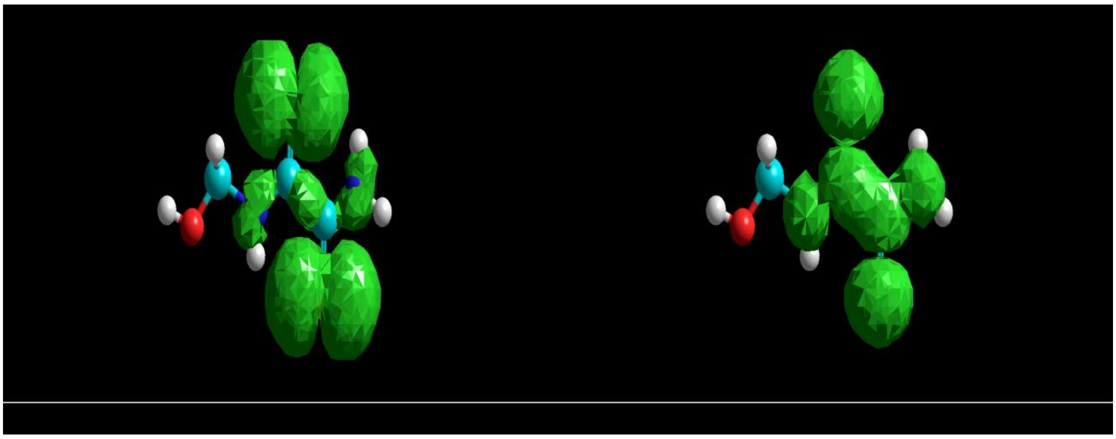
The structures for the Rubeonic acid and its derivatives can be shown in Table 6.

 **RUA**	 **MRU**
 **DRU**	 **NDRU**
 **TRU**	 **TERU**

Figures 4-9 explained the energies levels for RUA and its derivatives:

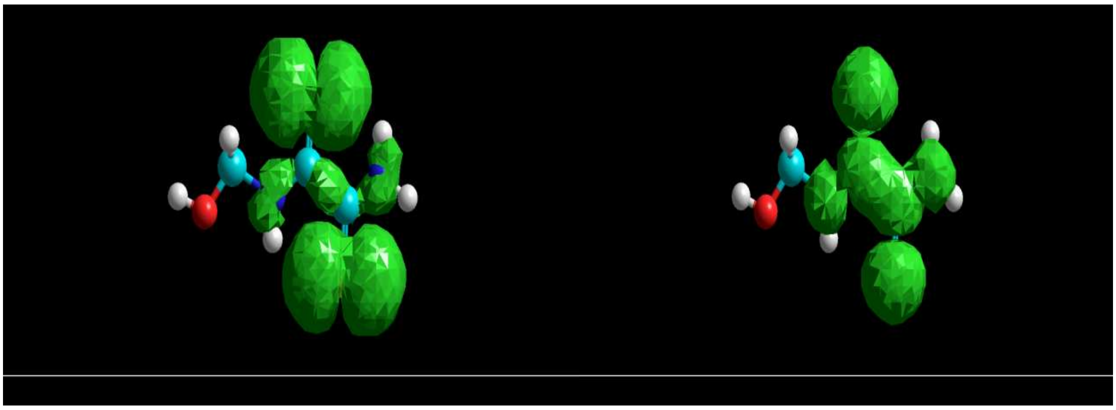
(b)HOMO interaction. (b)LUMO interaction.

Figure 4. E_{HOMO} and E_{LUMO} for RUA.



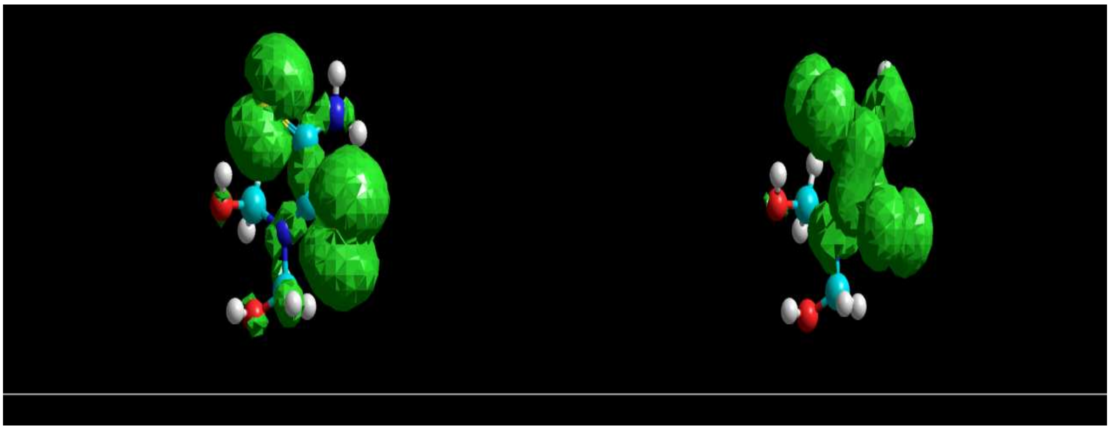
(b)HOMO interaction. (b)LUMO interaction.

Figure 5. E_{HOMO} and E_{LUMO} for MRU.



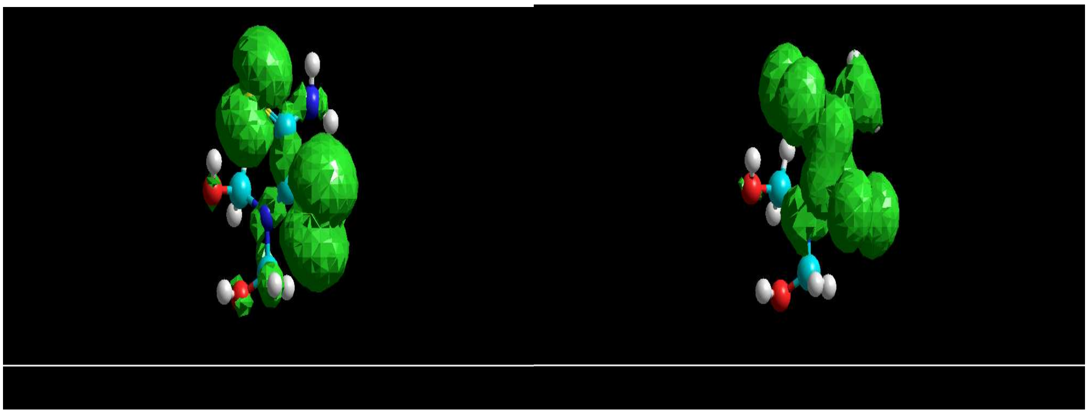
(b)HOMO interaction. (b)LUMO interaction.

Figure 6. E_{HOMO} and E_{LUMO} for DRU.



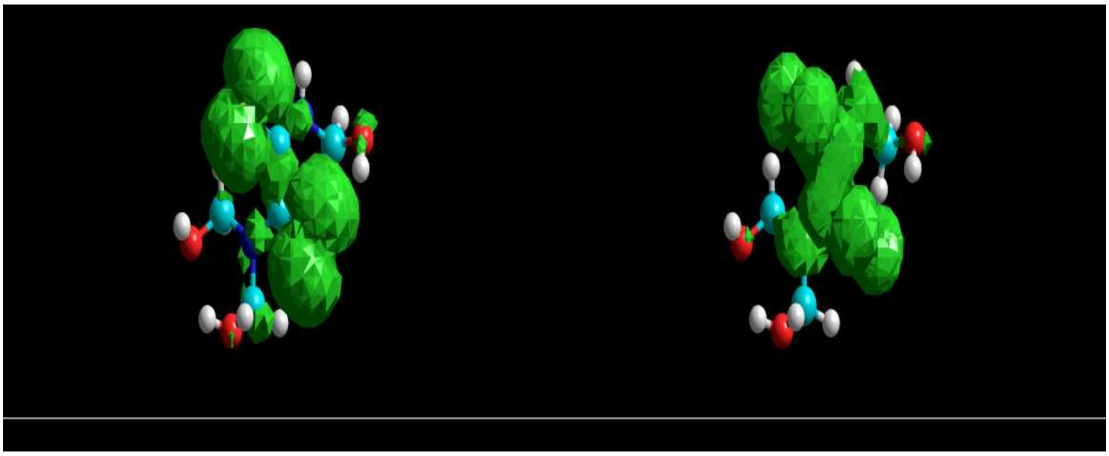
(b)HOMO interaction. (b)LUMO interaction.

Figure 7. E_{HOMO} and E_{LUMO} for N-DRU.



(b)HOMO interaction. (b)LUMO interaction.

Figure 8. E_{HOMO} and E_{LUMO} for TRU.



(b)HOMO interaction. (b)LUMO interaction.

Figure 9. E_{HOMO} and E_{LUMO} for TERU.

As E_{HOMO} is often associated with the electron donating ability of the molecule, high values of E_{HOMO} are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. In Table 5 explained that RUA has higher efficiency than other inhibitors. It is clear that as E_{HOMO} increases for the RUA compared with E_{HOMO} for the derivatives, the inhibition efficiency decrease, the reverse case happened for the E_{LUMO}, i.e., increasing the energy gap ΔE for the derivatives compared with this value for RUA reduce the efficiency because the activation energy of the inhibition increase as the substituted methylol increase, the comparison between NDRU and DRU explained the efficiency for NDRU is higher than DRU due to the presence the two methylol groups on the same N-atom make the adsorption of the O-atoms for the two methylol groups easily compared with DRU that the two methylol groups are present in two different N-atoms. The negative sign of E_{HOMO} indicates that the ability of inhibitor to adsorbed on the alloy increased, and the type adsorption is refers to physisorption mode[19,28].On the other hand, the relationship between the charge on the nitrogen atom for the RUA and its derivatives group and the inhibition efficiency is explained in Table 5. It is clear that the charge values are positive each one of the inhibitors has efficiency less than 75% , but as general form decrease the value of charge in N-atom toward the negative corresponding to increase the efficiency of the inhibitor as in Table 5 ,where as increasing the substituted methylol groups on N-atom, the δ value decrease, it is obvious when the comparison between NDRU and DRU, where the first is less δ than the second because in NDRU the two methylol groups are substituted on the same N-atom , then δ value is less than in DUR that the two methylol groups are substituted on two N-atoms, taking into account the little positive value of δ referees higher efficiency for the compound containing hetero atoms compared with the higher positive value of δ , because the δ value should negative, and the little positive value of δ is considered near to the negative value compared with the higher positive value of the δ[19]. Thus, the inhibition efficiency increased as δ increased because it takes part to adsorption of the inhibitor on the metal surface , therefore; RDU has higher efficiency than its derivatives. On the other hand the lower ΔG value of the corrosion reaction in presence of RDU is less negative than the ΔG values of the derivatives, means that the corrosion reaction in presence should be less spontaneous than its derivatives, therefore RDU has higher efficiency than its derivatives. Hence, NDUR has higher efficiency than RDU corresponding to the less spontaneous corrosion reaction in presence of NDRU compared in case of RDU when the ΔG value of the corrosion reaction in presence of RDU compared with ΔG value of the corrosion reaction in presence of NRDU as in the Table.

Conclusions:

There are many conclusions can be summarized as bellow.

1. The substitution of methylol group depends on the presence of active hydrogen.
2. As temperature increase, the rate of reaction, the time of reaction decrease due to the reducing the activation energy.
3. 60ºC and 3 hours, are the better temperature and time to synthesis the substituted methylol groups on the RUA.
4. Due to presence of hetero atoms in RUA and its derivatives, they can be evaluated as corrosion inhibitors for metals and alloys.
5. The theoretical studies can give imagining on the inhibition efficiency for each compound , and the role of the effect of structure on inhibition efficiency.
6. The substitution of methylol groups on RUA leads to reduce the inhibition efficiency due to the steric effect and isist that N-atoms is the essential atoms that take part to the adsorption on the metal surface, this can be explained from ΔG, ΔE(the energy gap between E_{HOMO} and E_{LUMO}), the partial charge on N-atoms(δ).

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