International Journal of Petroleum and Petrochemical Engineering (IJPPE)
Volume 9, Issue 1, 2024, PP 1-8
ISSN 2454-7980 (Online)
DOI: http://dx.doi.org/10.20431/2454-7980.0901001
www.arcjournals.org

Corrosion and Corrosion Protection of Carbon Steel in Petroleum Industry

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Abstract: *Carbon steel is a very important metal for petroleum industries. Petroleum refineries are used bulk amount of carbon steel for purification of crude oil. Some amount of carbon dioxide and sulphur dioxide present in crude oil. Both gases are acidic in nature so they generate hostile medium for metal. These gases convert into carbonic and sulphuric acid and develop electrochemical cell on the surface of metal and aggravate corrosion reaction. Metal undergoes corrosion reaction and it exhibits various forms of corrosion like galvanic, pitting, stress and crevice corrosion. During processing of crude oil different temperatures can be applied due to temperature variation so metal shows crack and intergranular corrosion. Hetero-cyclic organic compound 6, 11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea was synthesized to mitigate corrosion of carbon steel. The corrosion rate of metal was calculated by gravimetric method and potentiostat technique. Poteintiostat used to determine electrode potential, corrosion current and corrosion current density. The immersion test of uncoated and coated metal can be done at different temperatures and concentrations of carbonic acid. The coating compound adsorption phenomenon studied by Langmuir, Freundlich and Temkin isotherms. Thermal parameters like activation energy, heat of adsorption, free energy, enthalpy and entropy confirmed bonding, thin film formation randomness and nature of reaction of coating compound. This compound enhanced durability, stability, surface coverage area and coating efficiency in carbon dioxide medium.*

Keywords: *Corrosion, carbon steel, thin film barrier, carbon dioxide, temperature, crude oil.*

1. INTRODUCTION

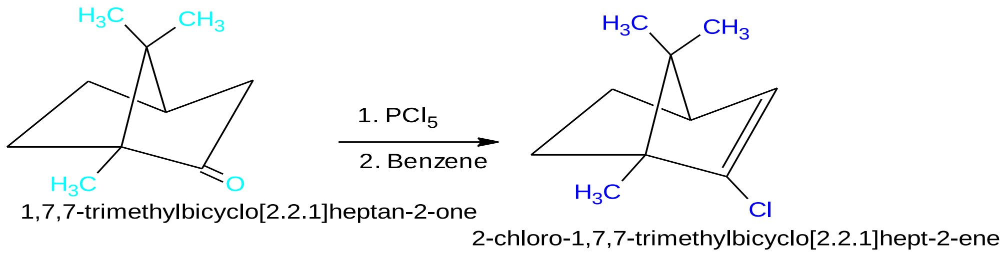
Corrosion is major problem in petroleum crude oil refinery industries [1] due to availability corrosive gases like carbon dioxide [2] and sulphur dioxide [3]. These industries expense huge money for repairing and replacement of corrode metal parts [4]. Corrosion chemists and researchers used several methods for corrosion control materials. Generally, metallic and nonmetallic coating [5] use to check corrosion of metal in hostile medium but these coating did not protect metal in longer time. Other protective coatings processes applied like electroplating [6], flame spraying [7], cladding [8] , hot dipping [9] and vapour deposition [10] but such coating cannot control corrosion. The outer face of metal laminated by polymers [11], rubbers [12], thermoplastic [13] and thermoset plastic [14] but such coating did not protective base metal. Inhibitors are organic and inorganic substances [15] which use in lesser quantity for corrosion protective. They used as anodic inhibitors [16], cathodic inhibitor [17] and mixed inhibitors [18] to minimize corrosion potential and corrosion current and enhance current density. Nano-coating techniques [19] used for corrosion protection of materials. This type of coating can be done by top layer coating [20], chemical conversion [21], thermal barrier coating [22] and insertion of nano-crystal into matrix of metal [23]. Nano-compounds low dose covered more surface area and they bonded with base metal by chemical bonding [24]. These coating compounds developed lots of porosities which did not stop osmosis process of corrosive substance so they corroded materials. The compound used for this research work occupied larger area and formed strong chemical bond with carbon steel. It reduced the attack of hostile substances and increased mechanical properties of metal.

2. METHODOLOGY

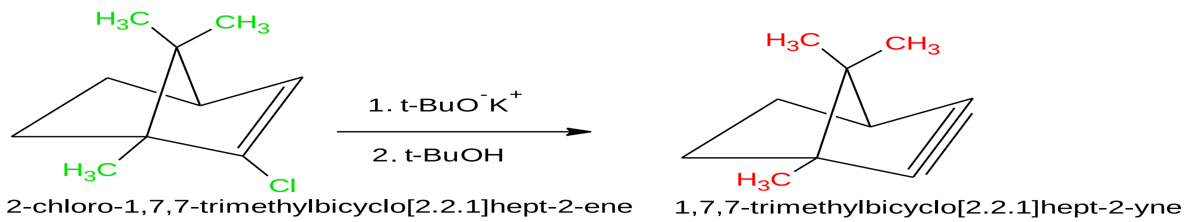
Carbon steel cut into size of (3X5) cm^2 and cleaned the surface of samples with empery paper and wash with acetone then after kept into desiccator for the protection of moisture. Organic compound 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea synthesized in laboratory and its process of synthesis was written as:

When the solution of phosphorus pentachloride and benzene added into 1,7,7-trimethylbicyclo [2.2.1]heptan-2-one at 0^oC temperature to yield of 2-chloro-1,7,7-trimethylbicyclo[2.2.1] hept-2-ene. It used with strong base $t^-BuO^-K^+$ in presence of t-butyl alcohol after completion of reaction to produce 1,7,7-trimethylbicyclo[2.2.1]hep-2-yne and mixed cyclohexene as a trapping agent to give 1,9,9-trimethyl-1,2,3,4,4b,5,6,7,8-decahydro-1,4-methanobiphenylene. It oxidized with $NaIO_4$ to form 6,11,11-trimethyldecahydro-6,9-methano-benzo[8]annulene-5,10-dione. It passed through solution of thiourea in presence of alkali base in ethanol solution to yield 6,11,11-trimethyldecahydo-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea.

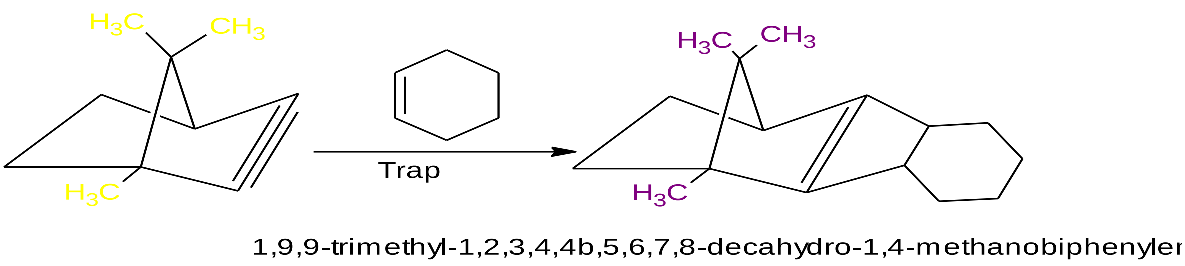
Scheme I



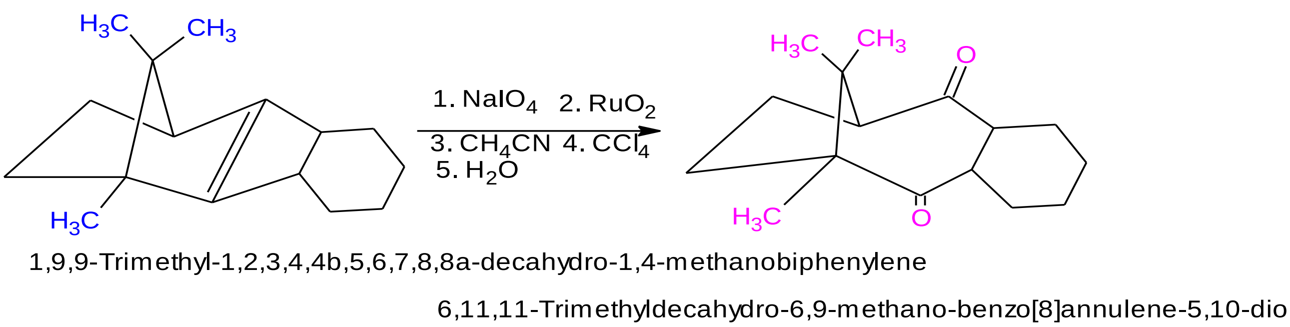
Scheme II



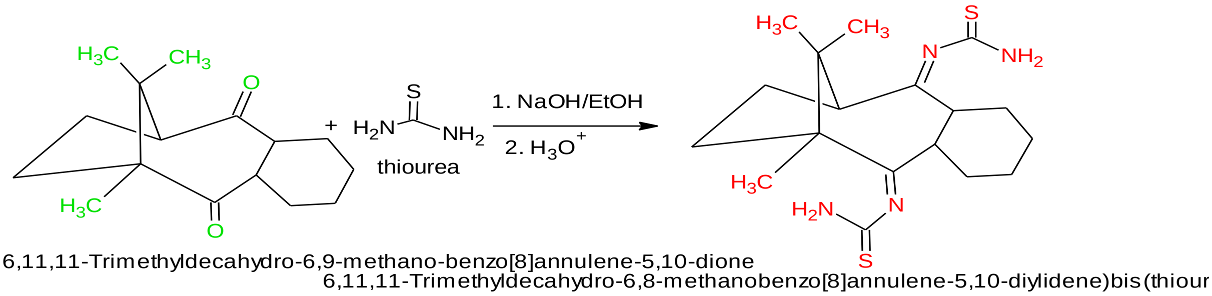
Scheme III



Scheme IV



Scheme V



The corrosion rate of uncoated and coated carbon steel determined by gravimetric method at different temperatures (298 K, 303 K, 308 K and 313 K) and mentioned time duration (3, 6, 9 and 12) months by the use of weight loss formula, K = 13.56 M / d A t (where K = corrosion rate, M = loss in mass, d = density, A = area and t = immersion time). Surface coverage area and percentage coating efficiency of uncoated and coated carbon steel were calculated by the formula $\theta = (1 - K / K_o)$ and % IE = $(1- K / K_o)$ (where θ= surface coverage area, K_o = corrosion rate of uncoated carbon steel, K= corrosion rate of coated carbon steel, %E= percentage coating efficiency). Thermal parameters like activation energy (Arrhenius equation $K= A\ e^{-Ea/RT}$), heat of adsorption ($\log (\theta/ 1-\theta) = \log A - (Q_{ads} / 2.303\ R\ T) + \log C$), free energy ($K_r = (KT/h)\ e^{-\Delta G\#/ R\ T}$), enthalpy and entropy by transition state equation ($K^{\#} = e^{\Delta S\# / R}\ e^{(-\Delta H\#/ R\ T)}$). The adsorption phenomenon of 6,11,11-trimethyldecahydo-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea confirmed by Langmuir ($\theta/ 1-\theta = A .C .e^{- qa /R T}$), Freundlich (C/ θ = KC) and Temkin (C/ θ = K logC) isotherms. Potentiostat 173 model used to obtain the values of electrode potential, corrosion current and corrosion current density.

3. Results and Dissuasion

3.1. Corrosion Rate of Uncoated and Coated Carbon Steel in Carbon Dioxide Medium

The corrosion rate of uncoated and coated carbon steel mentioned in Table1 at 298, 303, 308 and 313 K temperatures and these temperatures dipping time 3, 6, 9 and 12 months by the use of organic compound 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea. It observed that carbon steel corrosion rate increased without coating but after coating with 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea its values reduced. Such trends clearly noticed in Figure1 which plotted between log K versus 1/T.

Table1. *Corrosion rate of Carbon steel uncoated and Coated with 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea in* CO_2

O C	T	298 K	303 K	308 K	313 K	C(PPM)
	Months	3	6	9	12	
M(o)	Ko	1783	2101	2589	2982	0
	logKo	3.251	3.322	3.413	3.474	
M(1)	K	238	372	431	693	200
	logK	2.376	2.570	2.634	2.840	
	Ɵ	0.86	0.82	0.84	0.76	
	(1-θ)	0.133	0.177	0.166	0.232	
	(θ/1-θ)	6.490	4.646	5.006	3.302	
	log(θ/1-θ)	0.81	0.67	0.69	0.51	
	K/T	71.044	112.727	133.024	217.241	
	log(K/T)	1.851	2.052	2.123	2.336	
	% E	86	82	83	76	

[Where M(1): 6,11,11-trimethyldecahydro-6,8-methanobenzo[8] annulene-5,10-diylidenebisthiourea]

3.2. Activation Energy

The Figure1 graph plotted between logK versus 1/T found to straight line which satisfied Arrhenius plot. This graph exhibited that without coating corrosion rate of carbon steel enhanced but its values decreased coating with 6,11,11-trimethyldecahydro-6,8-methanobenzo [8]annulene-5,10-diylidenebisthiourea. With help of Figure 1 calculated the values of activation energy and its results were recorded in Table2. Uncoated carbon steel produced high activation energies but its values reduced after coating.

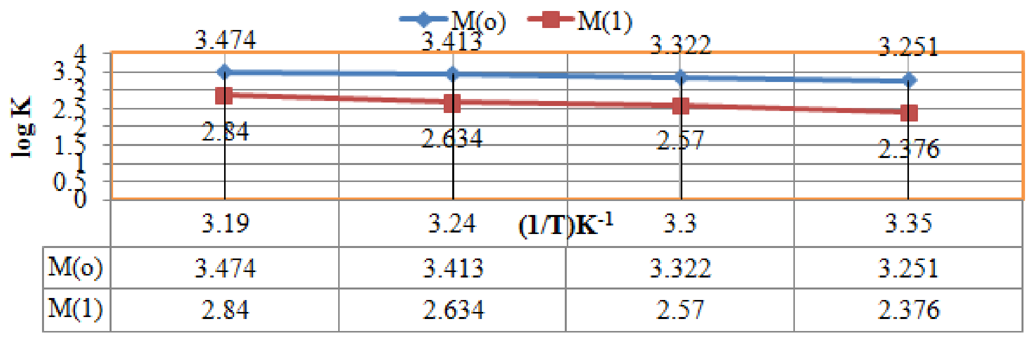


Figure1 log K Vs 1/T for carbon steel

3.3. Heat of Adsorption

The coating compound 6,11,11-trimethyldecahydro-6,8-methanobenzo[8] annulene-5,10-diylidenebisthiourea produced adsorption energy which indicated that coating compound bonded with base metal by chemical bonding as results of Table2. Figure2 log(ɵ/1-ɵ) versus 1/T obey Langmuir adsorption isotherm.

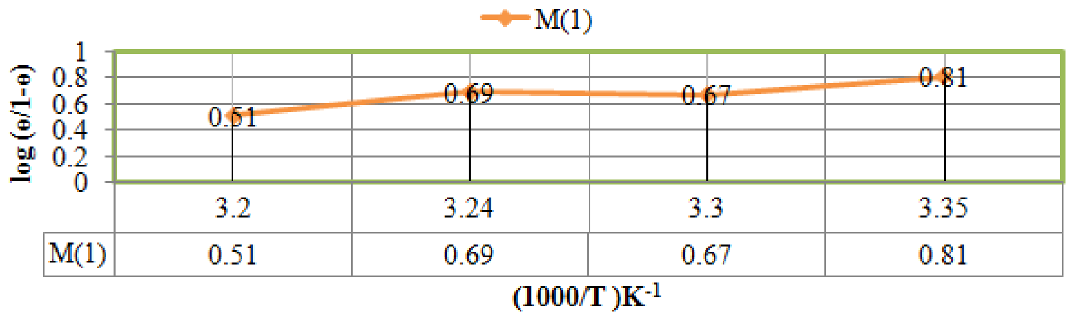


Figure 2 log (ɵ/1-ɵ) Vs 1/T carbon steel

3.4. Surface Coverage Area

Organic compound 6,11,11-trimethyldecahydro-6,8-methanobenzo[8] annulene-5,10-diylidenebis thiourea covered more surface area at lower temperature and its values decreased at higher temperature as shown in Table1 and Figure2 plotted log(ɵ/1-ɵ) versus 1/T.

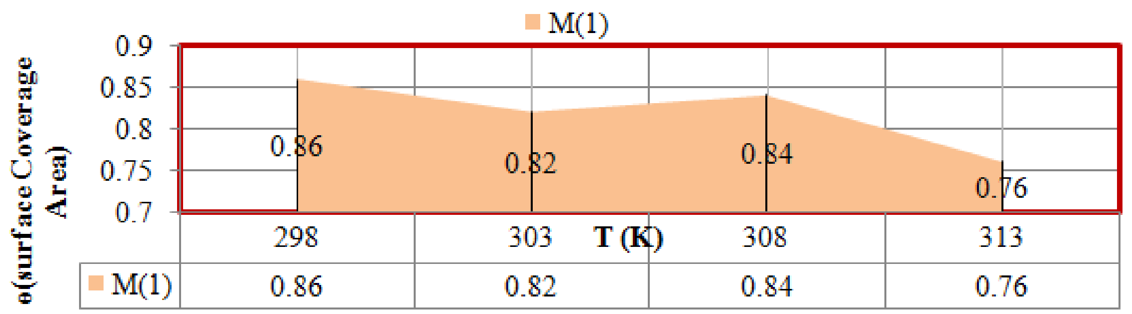


Figure 3 ɵ Vs T carbon steel

3.5. Coating Efficiency

Figure4 graph plotted between %E (Percentage efficiency) versus T (temperature) of coating 6,11,11-Trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea and their values were written in Table1 at 298, 303, 308 and 313 K. It observed that percentage efficiency increased at lower temperature but its values decreased at higher temperature.

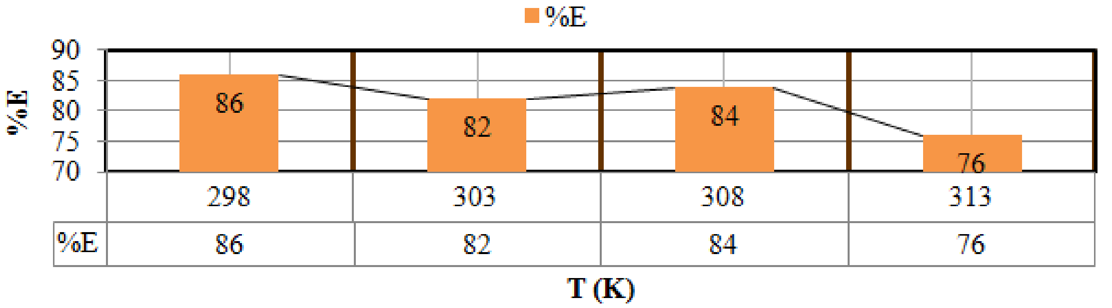


Figure 4 %E Vs T for carbon steel coating with M(1)

3.6. Free Energy

Free energy of coating compound 6,11,11-trimethyldecahydro-6,8-methanobenzo[8] annulene-5,10-diylidenebisthiourea mentioned in Table2. The results of free energy indicated that coating compound produced exothermic reaction. It boned with carbon steel by chemical bonding. It observed that free energy decreased and surface coverage area increased.

3.7. Enthalpy

Enthalpy of 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebist hiourea was written in Table2. Its values decreased as temperatures increased from 298 to 313 K. Enthalpy energy results were shown during coating exothermic reaction occurred. The negative sign of free energy depicted that coating substance attached with base metal by chemical bonding. It also observed that enthalpy decreasing and surface coverage increasing.

3.8. Entropy

Entropy energies developed by 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea were given Table2. Entropy values depicted that coating compound accommodated on carbon steel in order matrix by chemical bonding. Figure5 plotted ΔG (Free energy), ΔH (Enthalpy), ΔS (Entropy) versus ɵ (Surface coverage) at 298, 303, 308 and 313 K temperatures noticed that these thermal parameters values reduced and surface coverage area enhanced.

Table2. *Thermal values of 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidene bisthiourea*

Temp	**298 K**	**303 K**	**308 K**	**313K**	**C(PPM)**
E_a(o)	233	235	237	238	
$E_{a(S1)}$	170	181	183	194	200
q(S1)	-58	-70	-48	-35	
ΔG(S1)	-295	-305	-304	-313	
ΔH(S1)	-132	-145	-147	-159	
ΔS(S1)	-127	-136	-139	-147	
ɵ (S1)	0.86	0.82	0.84	0.76	

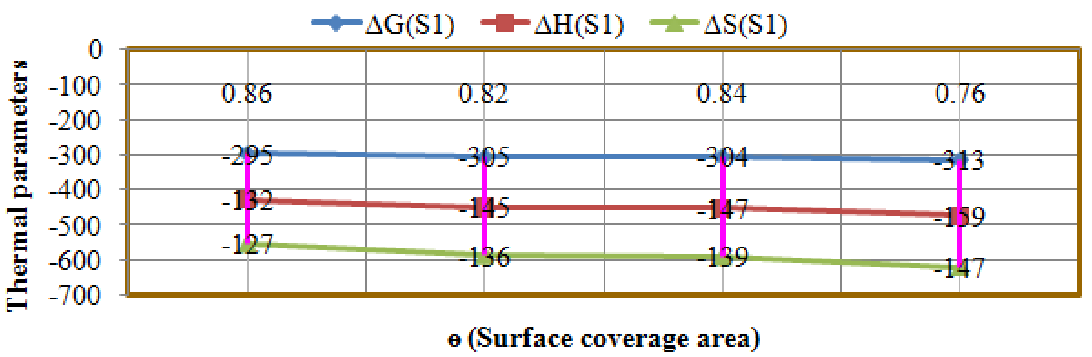


Figure5 Thermal parameters Vs ɵ (Surface coverage area)

Potentiostatic polarization results of uncoated and coated copper with 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea were recorded in Table3. Uncoated carbon steel developed higher electrode potential, corrosion current and anodic polarization but these values became lower with coating compound. The coating material increased cathodic polarization and current density. It reduced corrosion rate and enhanced surface coverage as well as coating efficiency. It formed thin film passive barrier with base which checked the attack of H^+ on metal. Figure6 plotted between E(Electrode potential) versus I_c(Current density) which depicted electrode potential and current density of uncoated carbon steel increased but these values decreased with coating substance.

Table3. *Potentiostat results of 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea*

Coating	ΔE	ΔI	βa	βc	βaβc/βa+βc	Ic	Kcr	θ
M(o)	-1150	815	572	421	242	74	316	
	-1200	845	601	491	270	82	350	
	-1300	900	657	543	297	89	379	
	-1400	1050	734	602	330	103	441	
M(1)	-750	379	350	445	195	42	134	0.42
	-800	400	400	455	212	46	154	0.44
	-900	450	425	460	220	47	175	0.46
	-910	480	440	470	232	53	215	0.48

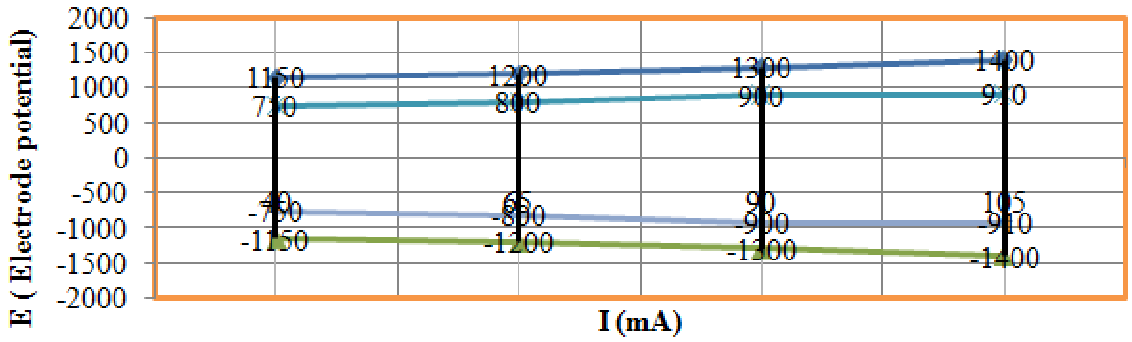


Figure 6 E Vs I uncoated and coated carbon steel with M(1)

3.9. Mechanism of coating Compound

The organic compound 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea is a highly electron rich containing functional groups as shown in Figure7 so it forms a thin film barrier with carbon steel. This compound forms strong chemical bonding in corrosive medium and reduce the mobility of H^+ ions. The film barrier is stable in high temperature. It covered more surface area even low quantity and exhibited high coating efficiency in acidic environment.

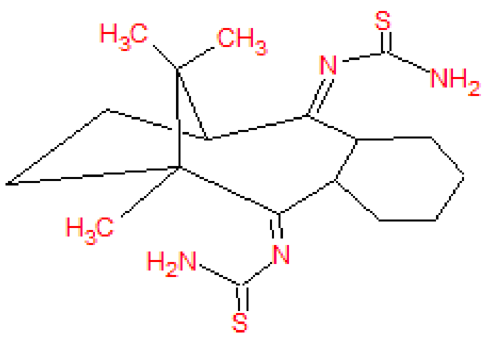


Figure7. Electron rich Functional groups

4. CONCLUSION

The experimental results indicated that coating compound 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea decreased the corrosion rate of carbon steel in carbon dioxide . The results of surface coverage noticed that this compound covered more surface areas in different temperatures and concentrations. The various isothermals plots exhibited coating material adsorbed on the surface carbon steel. This compound bonded with base metal by chemical bonding to conform by thermal parameters results. The protective barrier produced by coating substance not only suppressed the corrosion rate but also enhanced durability and strength. The compound 6,11,11-trimethyldecahydro-6,8-methanobenzo[8]annulene-5,10-diylidenebisthiourea had capability to minimize physical, chemical and mechanical to produce by carbon dioxide medium.

ACKNOWLEDGEMENT

The UGC-New Delhi provided finical support for the research work. I appreciate suggestions of Professor G Udaybhanu, Applied Chemistry, IITD(ISM), Jharkhand, India, Professor INN Namboothari, Department of Chemistry, IITB, Mumbai and Professor Sanjoy Misra, Ranchi University, Ranchi, Jarkhand, India. I am thankful Professor Kuldeep Singh, Deparment of Applied Chemistry, Amity University, Gwalior, M P, India for analysis data and graphs.

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Citation: *Dr. Rajesh Kumar Singh (DSc) et al. (2024). "Corrosion and Corrosion Protection of Carbon Steel in Petroleum Industry", International Journal of Petroleum and Petrochemical Engineering (IJPPE), 9(1), pp.1-8, DOI: http://dx.doi.org/10.20431/2454-7980.0901001*