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Corrosion and Corrosion Protection of Cast iron due to Bio-organism

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Abstract

Cast iron is a high tensile strength metal. It is generally used for making tools, pipe fitting, electrical fitting equipment and rail track. It interacts with corrosive substances to develop electrochemical cell on their interface. Corrosive substances are acids, bases, salts, bio-wastes, particulates and pollutants. These substances produce hostile medium for materials. These harmful wastes discharge by industries, households, agricultural, urbanization, development of infrastructure, construction works, thermal power stations, hydropower, nuclear power station, transport vehicles, decomposition of leaving species etc. Acidic gases like CO_2, NO_2 and SO_2 create acidic environment for metals. Other factors like, humidity, acid rain, global warming and climate change responsible for corrosion of materials. Metals corrode in above mentioned corrosive medium and they exhibit galvanic, pitting, stress, crevice and other forms of corrosion. The corrosive substances change internal and external morphology of metals and alter their physical, chemical and mechanical properties. Cast iron undergoes in process graphitization corrosion. The corrosion rate of aforesaid metal is calculated by weight loss method whereas potentiostat uses for the determination of corrosion potential, corrosion current and current density. By the use of these techniques, corrosion rates of metals obtained uncoated and coated metal in different temperatures and concentrations in presence of bio-wastes The coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo [8] annulene-5,10-diylidenebishydrazine synthesized and it used for corrosion protection of cast iron. The coating efficiency and surface coverage were calculated by the use of weight loss method. The coating compound develops passive barrier on metal surface which suppress the attack of hydronium ions. The passive barrier formation studied by thermo-dynamical parameters like activation energy, heat of adsorption, free energy, enthalpy and entropy.

Keywords: Cast iron, climate change, acidic gases, moisture, micro & macro-organism, passive barrier, coating compound, thermal parameters

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INTRODUCTION

Cast iron is used for the construction of railway track. Disintegration occurs into cast iron when it interacts with bio-wastes [1]. Bio-wastes can develop aerobic [2] and anaerobic bacteria [3] by the aerobic [4] and anaerobic [5] reactions. Aerobic bacteria are a thiobaccillus [6] which oxidize sulphur into sulphuric acid [7] to produces extremely corrosive environment. Anaerobic bacteria are D. desulfuricans [8] and they reduce sulphate ion into sulphide ions to accelerate anodic dissolution [9]. On these process organisms create corrosive medium for metals [10]. Generally, metallic corrosion can be checked by metallic and nonmetals coatings whereas these coatings cannot provide long time protection of base materials.

Atmospheric pollutants like oxides of carbon [11], oxides of nitrogen [12], oxides of sulphur [13], oxides of halogen [14], hydride of nitrogen [15] and sulphur [16] and oxide of metal [17] also responsible for corrosion. Cast iron undergoes in selective leaching corrosion [18] in presence bio-wastes that process is called graphitization [19]. Graphitic corrosion occurs due to availability mild environment pollutants. The flue gases also develop graphitization reaction with cast iron. Hazardous wastes [20] produce graphitic corrosion in cast iron. During corrosion reaction iron works as anode and graphite as cathode thus dissolution occurs at iron surface and leaving a porous mass consisting of graphite looks like voids and rust [21]. The strength of cast iron reduces and decrease metallic properties. Rusting is observed on outer surface and decrease metallic strength [22]. The degree of loss depends upon attacking of corrosive substances [23]. The process of graphitization [24] is time taken. Cast iron corrodes in corrosive environment [25] to exhibit more or less uniform corrosion [24]. Soil provides hostile medium for the corrosion of cast iron [26]. Graphite network [27] is noticed only after removal iron in interaction corrosive materials [28]. Organic compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine used to mitigation of cast iron and improve metallic strength.

Experimental

Cast iron cut into (0.04 x 0.02) m^2 size and their surface cleaned with empery paper. The samples rinsed with acetone and kept into desiccator to save humidity. The uncoated cast iron corrosion rates were calculated by weight loss method at 2mM of H_2CO_3, 4mM of HNO_3 and 6mM of H_2SO_4 and 298, 303, 308 and 313K temperatures. Cast iron coated with 60mM of 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine and its corrosion rate determined at above mentioned concentrations of acids temperatures. The corrosion rate also measured during climate change. The weight loss formula used for the corrosion rate determination is written as:

$$K = 13.56\ (W_o - W)/A \times d \times t \quad (1)$$

Where K = corrosion rate (mmpy), W_o = mass of metal before dipping, W = mass of metal after dipping, A = Area of sample (m^2), d = density(kg/m^3) and t = immersion time (hrs).

Potentiostat 173 model used for determination corrosion potential, corrosion current and corrosion current density. Electrode of cast iron kept between calomel electrode and hydrogen electrode with help of this technique calculated corrosion potential and corrosion current uncoated and coated cast iron. The anodic and cathodic process occurred during electrochemical corrosion. The imposing current or voltage on metal produced cathodic and anodic polarization. Electrode potential shifted in active direction thus other side behaved like passive to decrease corrosion rate. There are three techniques to use calculate the corrosion currents. The specimen was polarized anodic by potential of 50mV more positive direction thus corrosion potential and current develop and plotted Tafel graph. The specimen polarized in cathodic and anodic direction to produce corrosion potential in both directions whereas corrosion current density obtained by the intersection of the extrapolated cathodic and anodic Tafel lines.

The corrosion current (I_o) obtained with the help of Stern-Geary equation:

$$E/I_o = \beta_a \beta_c / 2.303\ I_J (\beta_a + \beta_c) \quad (2)$$

The meaning of symbols of equation (3.2)
$E/\Delta I_o$= polarization resistance (R),
β_a = Anodic Tafel
β_c = cathodic Tafel
I = corrosion current density in $\mu A/cm^2$.

The corrosion rate was calculated by the use of equation (3.3) which mentioned as:

$$K_R = 0.1288 \times I \times (E_m / d) \quad (3)$$

The meaning of symbol is written as;

I = corrosion current density
d = density of specimen
E_m = specimen equivalent weight.

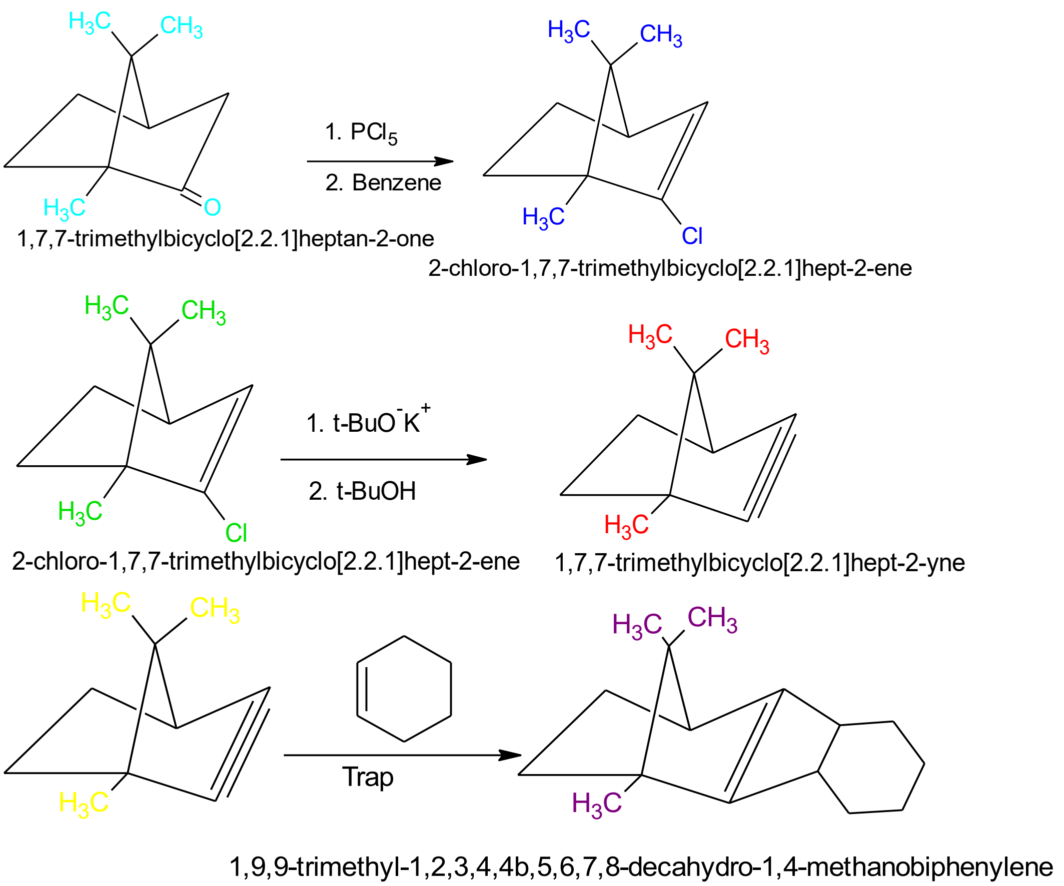
The equivalent weight of specimen was determined by equation (3) which expressed as:

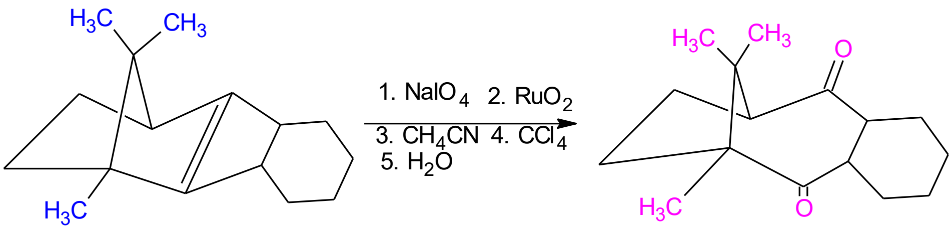
$$E_m = \sum Fi\ W_m / n_i \qquad (4)$$

The meaning of symbol is,

E_m = Equivalent weight of specimen
Fi = Atomic fraction
Wm = Atomic weight of specimen
n_i = component element

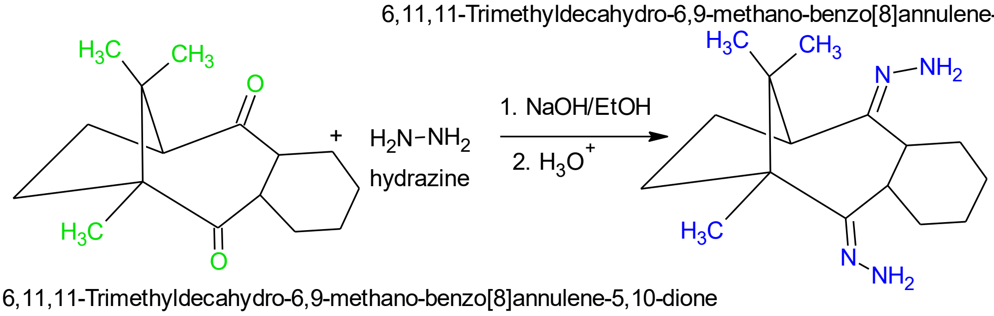
The process of synthesis of 6,11,11-trimethyldecahydo-6,8-methanobenzo[8]annulene-5,10-diylidenebishydrazine: Phosphorous pentachloride dissolved in benzene and its solution added in 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one to form 2-chloro-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene. This compound mixed with solution potassium t-butoxide in t-butylalcohol solvent to yield 1,7,7-trimethylbicyclo[2.2.1]hep-2-yne. When cyclohexene added into 1,7,7-trimethylbicyclo[2.2.1]hep-2-yne to form 1,9,9-trimethyl-1,2,3,4,4b,5,6,7,8-decahydro-1,4-methanobiphenylene. This compound oxidized with $NaIO_4$ in presence RuO_2 methyl cyanide, carbon tetrachloride and water to produce 6,11,11-trimethyldecahydro-6,9-methano-benzo[8]annulene-5,10-dione. Hydrazine treated with 6,11,11-trimethyldecahydro-6,9-methano-benzo[8]annulene-5,10-dione to yield 6,11,11-trimethyldecahydo-6,8-methanobenzo[8]annulene-5,10-diylidenebishydrazine. The reactions processes were written as:





1,9,9-Trimethyl-1,2,3,4,4b,5,6,7,8,8a-decahydro-1,4-methanobiphenylene

6,11,11-Trimethyldecahydro-6,9-methano-benzo[8]annulene-5,10-dione



6,11,11-Trimethyldecahydro-6,9-methano-benzo[8]annulene-5,10-dione

6,11,11-Trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidene)bis(hydrazine)

RESULTS AND DISCUSSION

Table1 consists of corrosion rate of uncoated and coated cast iron at 298, 303, 308 and 313 K temperatures in acidic medium. The corrosion rates calculated by 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). The 60mM of 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine used for coating and its corrosion rates were taken at 298, 303, 308 and 313 K temperatures. It observed that corrosion rate of uncoated cast iron increased but coated cast iron corrosion reduced as shown in Figure1 plotted between logK versus 1/T.

Cast iron coated with 6,11,11-Trimethyldecahydro-6,9-methanobenzo [8] annulene-5,10-diylidenebishydrazine and its values of log(ɵ/1-ɵ) recorded in Table1 at 298, 303, 308 and 313 K temperatures. The plot of log(ɵ/1-ɵ) versus 1/T found straight line as shown in Figure2. The results of Table1 and Figure2 indicated that coating compound reduced corrosion of cast iron.

Table1. Corrosion rate of uncoated and coated cast iron with 6,11,11-Trimethyldecahydro-6,9-methanobenzo [8] annulene-5,10-diylidenebishydrazine

O C	T	298 K	303 K	308 K	313 K	C(mM)
M(0)	Ko	1783	2101	2589	2982	0
	logKo	3.251	3.322	3.413	3.4745	
M(2)	K	212	346	354	518	60
	logK	2.326	2.539	2.549	2.714	
	Θ	0.88	0.83	0.86	0.82	
	(1-θ)	0.118	0.164	0.136	0.173	
	(θ/1-θ)	7.410	5.071	6.309	4.753	
	log(θ/1-θ)	0.869	0.705	0.801	0.677	
	K/T	63.283	104.848	109.259	162.382	
	log(K/T)	1.801	2.021	2.038	2.211	
	% CE	88.11	83.53	86.32	82.62	

[Meaning of abbreviations, OC= Organic compound, M(o)= uncoated, M(2)= coated with 6,11,11-Trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine]

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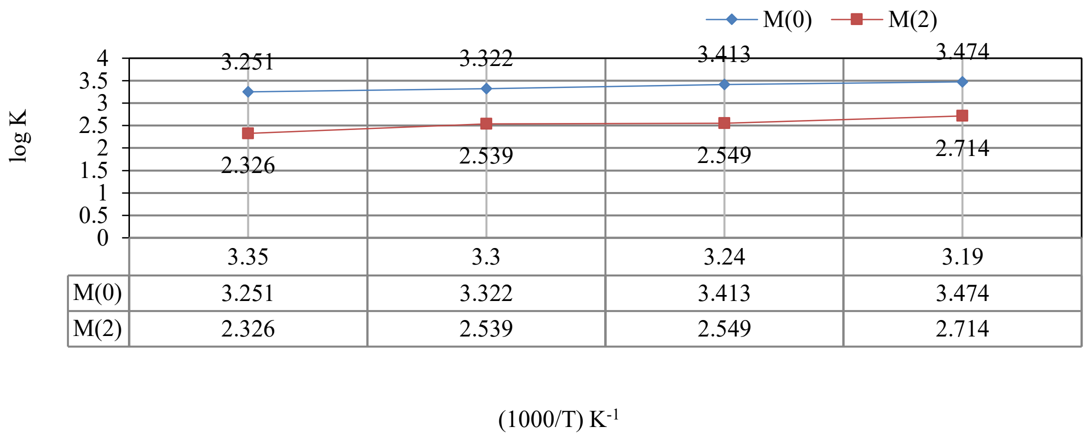


Figure 1. logK Vs 1/T for uncoated and coated cast iron

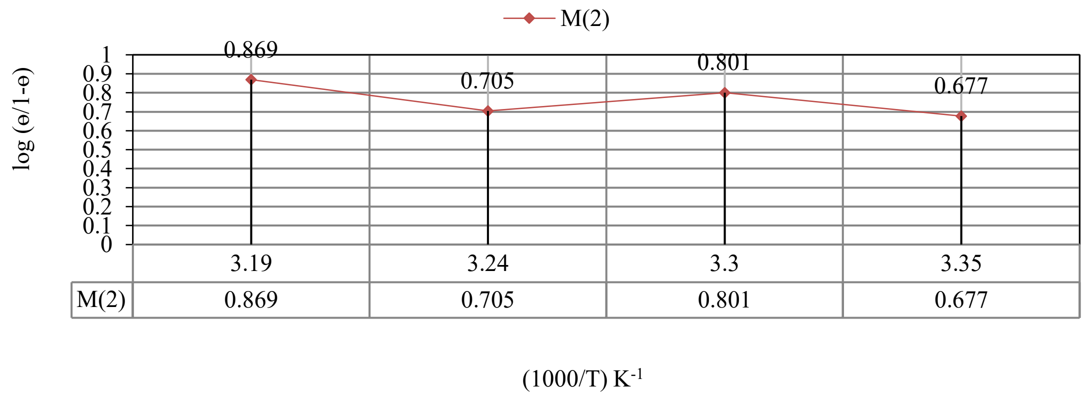


Figure 2. log (ɵ/1-ɵ) Vs 1/T for cast iron coated

The surface coverage of coated compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine calculated by formula $\theta = (1 - K / K_o)$ (where θ= surface coverage area, K_o= rate of corrosion of uncoated cast iron, K= corrosion rate of coated cast iron) and their values were mentioned in Table1. Figure3 plotted between θ (surface coverage) versus T (temperature) that Figure showed coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo [8] annulene-5,10-diylidenebishydrazine covered surface area.

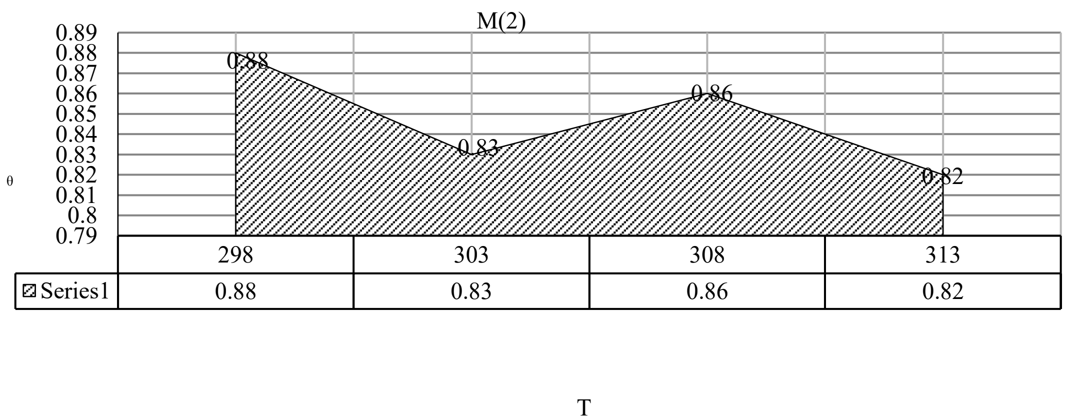


Figure 3. $^{\theta}$ Vs T for cast iron coated

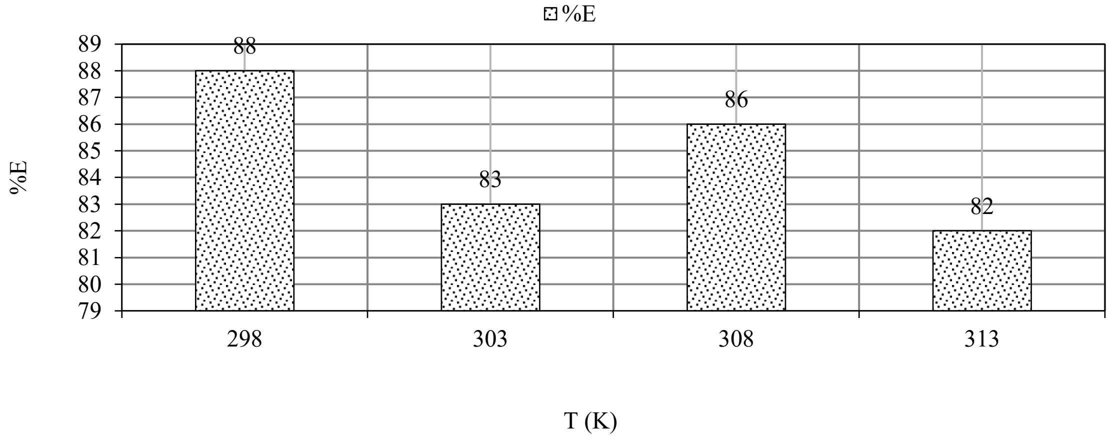


Figure 4 % E Vs T cast iron coated M(2)

The percentage efficiencies of coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine was determined by formula % IE = (1- K / K_o) (where, %E= percentage coating efficiency, K_o = corrosion rate of uncoated cast iron, K= corrosion rate of coated cast iron,) and their results mentioned in Table1. The coating of 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine decreased as temperature increased from 298 to 313K. Figure 4 plotted between %E (percentage coating efficiency) versus T (Temperature) described coating compound have higher efficiency at lower temperature.

Activation energy of uncoated and coated cast iron calculated with help of Arrhenius equation, $K= A\ e^{-Ea/RT}$ and its values were written in Table2. The results of Table2 observed that without coating activation energy increased but after coating their values were reduced. It stated that coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine boned with cast iron by chemical bonding.

Heat of adsorption of coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine determined by Langmuir Isotherm equation (log (θ/ 1-θ) = log A - (Q_{ads} / 2.303 R T) + log C) and Figure2. The values of heat of adsorption were mentioned in Table2. The heat of adsorption found to be negative which confirmed coating accommodated on base metal by chemical bonding. Heat of adsorption decreased at 298, 303, 308 and 313K whereas surface coverage increased on these temperatures.

Free energy of coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine calculated by formula ($K_r = (KT/h)\ e^{-\Delta G\#/RT}$) and Figure1 and its values were given in Table2. Free energy results depicted that chemisorptions occurred during coating of cast iron with 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine. Figure5 was shown that free energy reduced at different temperatures but surface coverage increased.

Enthalpy of coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine determined by transition state equation, ($K^{\#} = e^{\Delta S\#/R}\ e^{(-\Delta H\#/RT)}$) and its values were given in Table2. Enthalpy produced by coating found to be negative which indicated that coating compound adhered on the surface of cast iron by chemical bonding. Figure5 exhibited enthalpy energy decreased as temperature rising from 298 to 313 K whereas surface coverage area enhanced.

Entropy of coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine calculated by transition state equation, ($K^{\#} = e^{\Delta S\#/R}\ e^{(-\Delta H\#/RT)}$) and its values were written in Table2. Enthalpy results noticed that coating compound attached with cast iron order matrix. Figure5 exhibited that entropy values decreased and surface coverage area increased.

Table 2. Thermal parameters of coated cast iron with 6,11,11-trimethyldecahydro-6,9-methanobenzo [8] annulene-5,10diylidenebishydrazine

Temp	298 K	303 K	308 K	313K	C(mM)
E_a^o(kJ/mol)	233	235	237	238	60
E_a(kJ/mol)	167	179	177	175	
q_a(kJ/mol)	-62	-50	-55	-46	
ΔG(S2)(kJ/mol)	-292	-303	-298	-304	
ΔH(S2)kJ/mol)	-129	-142	-141	-151	
ΔS(S2)(J/K)	-123	-130	-133	-142	
ɵ	0.88	0.83	0.86	0.82	

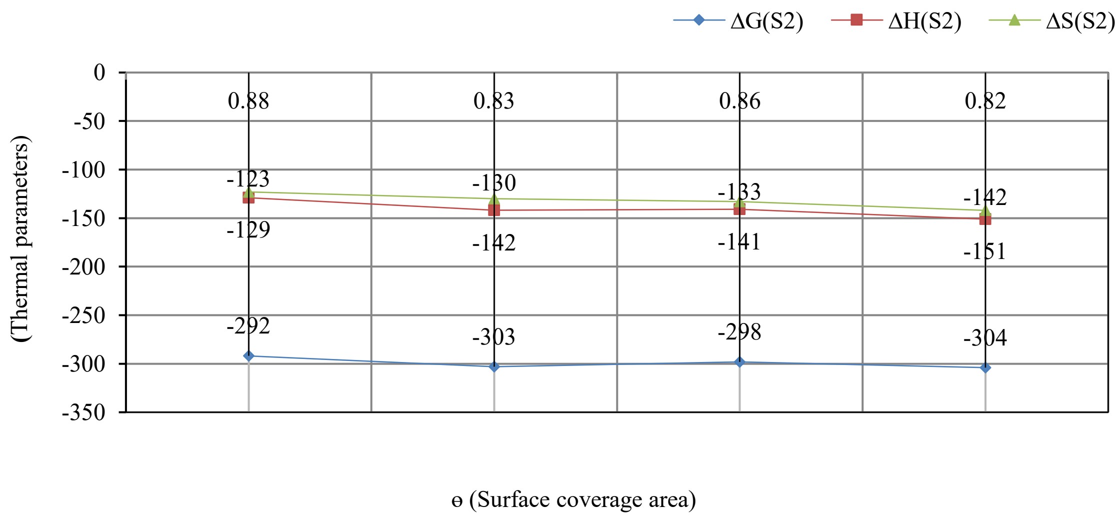


Figure 5 Thermal parameters Vs ɵ (Surface coverage area).

Potentiostat results obtained by the use of equation I = βa βc/2.3 (βa+βc) I_c and corrosion rate K=0.128 X Ic X (E/d) (I_c is corrosion current, E_{eq} is equivalent weight and d is density) and Figure6 and their values were recorded Table3. It observed that uncoated cast iron produced higher electrode potential, corrosion current and anodic current but these values become less after coating of 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine as shown in Table3 and Figure6. The coating compound increased corrosion current density and cathodic polarization. Table3 results were shown that coating compound reduced corrosion rate and enhance surface coverage area.

Table 3. Potentiost results of coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo [8] annulene-5,10-diylidenebishydrazine.

	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(2)	650	315	260	480	168	35	166	0.52
	670	340	275	490	176	38	185	0.53
	700	360	285	503	181	40	206	0.54
	721	380	302	509	189	43	257	0.58

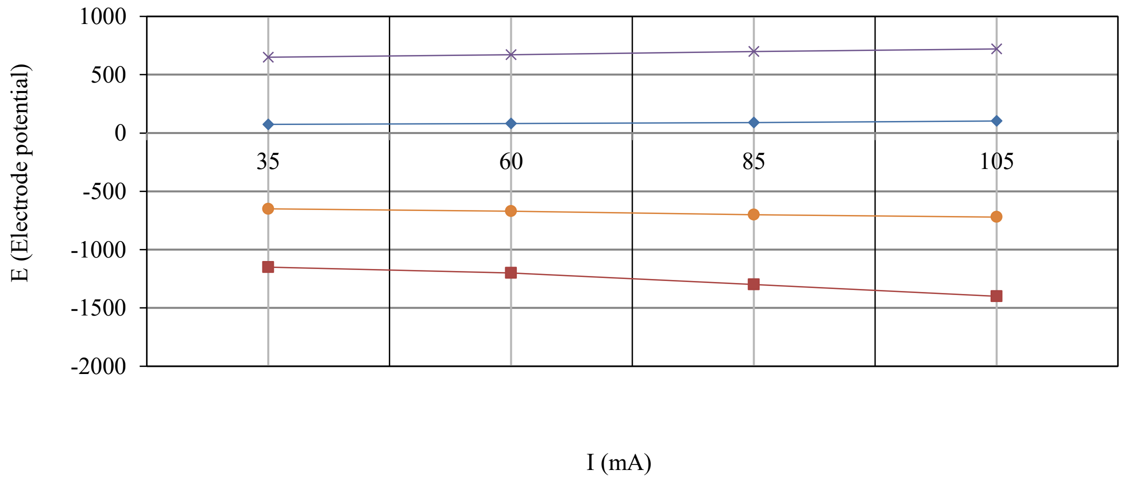
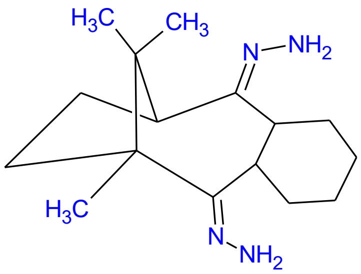


Figure 6. E (Electrode potential Vs I (current density).



Mechanism of coating compound: The coating compound 6,11,11-trimethyldecahydro-6,9-methanobenzo [8] annulene-5,10-diylidenebishydrazine contained electron releasing functional groups. It forms thin film barrier on the surface of cast iron and minimize the attack of acids. The protective barrier formation can be confirmed by thermal results of activation energy, heat of adsorption, free energy, enthalpy and entropy. This compound adhered with metal by chemical bonding. It covered more surface area even uses low dose. The results of surface coverage area and coating efficiency indicated that coating compound formed a strong bonding with cast iron at high temperatures in acidic medium. The coating compound produced stable composite barrier indicates donor position in compound 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine.

CONCLUSION

Cast iron corrosion controlled by the use of 6,11,11-trimethyldecahydro-6,9-methanobenzo[8]annulene-5,10-diylidenebishydrazine in acidic environment. This compound protective barrier produced passive behavior during climate change. The coating compound possessed electrode donating functional groups so it checked mobility of H^+ ions. It formed a passive thin film barrier on the surface cast iron to stop electrochemical cell formation and corrosion reaction. It reduced corrosion rate and enhanced surface coverage area as well as coating efficiency in presence of corrosive substances, different temperatures and climate change. Langmuir isotherm exhibited that coating compound adsorbed on base metal. Thermal results were shown that coating compound attached with cast iron by chemical bonding so the compound was strongly bonded with base metal and nullify the attack of corrosive materials. It provided metal mechanical strength and thermal stability in hostile environment.

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