



World Scientific News

An International Scientific Journal

WSN 139(2) (2020) 155-172

EISSN 2392-2192

Composite Barrier to Control the Corrosion of Mild Steel in Oil Well

Rajesh Kumar Singh^{1,*}, Manjay Kumar Thakur², Parshun Kumar²

¹Department of Chemistry, Jagdam College, J P University, Chpara-84130, India

²Research Scholar, Department of Chemistry, Jagdam College, J P University, Chapra-841301, India

*E-mail address: rks_jpujc@yahoo.co.in

ABSTRACT

Mild steel is a very important engineering metal. Petrochemical industries are used bulk amount for their various purposes like recovery of crude oil, refinery units and transportation. Crude oil is a very highly viscous liquid for the opening of the month well strong HCl acid and saline water is used. They produce hostile environment of mild steel. Gaseous substances like CO₂ and SO₂ gases are found into the well of petroleum. Large amount of saline water are used during recovery of crude oil in this water CO₂ and SO₂ are dissolved to produce H₂CO₃ and H₂SO₄. These acids create an acidic medium of mild steel. Saline waters have possessed Cl⁻ ions. It produces ambient environment for mild steel. The solution of salty water contains dissolve oxygen which develop corrosive environment of mild steel. These major corrosive substances are available during recovery of crude oil and they form corrosion cell with base metal. Metal produces galvanic, pitting, stress, crevice, intergranular corrosion. Nanocoating and filler methods are used to protect metal in such un-friendly environment. The corrosion rate of metal was calculated by weight loss experiment in absence and presence of nanocoating and filler materials. The synthesized organic compound octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone is applied for nanocoating and MgS as filler. The coating and filling works were completed by chemical vapour deposition and nozzle spray method. Potentiostat used for determination corrosion potential and corrosion current density. The surface adsorption was studied by thermal parameters like activation energy, heat of adsorption, free energy, enthalpy and entropy. The thermal parameters results were shown that coating and filler compounds were adhered with base metal by chemical bonding. The thermal results were calculated by Arrhenius equation and Langmuir isotherm. The coating and the filler substance formed composite barrier with metal and developed a protective barrier for the corrosive substances.

Keywords: Mild steel, HCl, Saline water, filler, thermal parameters, composite barrier

1. INTRODUCTION

Mild steel is protected by polymeric coating. But this coating is not shaved mild steel in moist air, sulphur dioxide and chloride ions environment. It produces chemical and electrochemical reaction with polymeric-coated metal and accelerates corrosion reaction. Chloride ions are entered inside by osmosis or diffusion process and develop corrosion cell on metal surface. Oxygen deficiency occurs inside and outside of polymeric-coated mild steel thus corrosion cell is automatically formed. These pollutants corrode polymer and metal in this ways start interior and exterior corrosion of polymeric-coated-metal.

These pollutants rupture internal bond of polymer and produce disbonding between base metal and coating material. Petrochemical industries expense bulk amount of money for corrosion protection of materials. It is not fully control but its affect is controlled by the use of corrosion mitigation techniques. It is necessary for materials manufacturing industries to monitor carefully their internal morphology, shape and design. Materials can be synthesized (Bhadra S, 2011) as per need of surrounding environment (Szabo T, 2011) which does not change their physical, chemical and biological properties (Wen N T, 2008) and provide thermal stability, durability, capability, resistance power against corrosive medium (Boerio F J, 2005).

Materials corrosion protection (Deveci H, 2012) check with application of coatings, inhibitors, sacrificial anodic protection and impressed current process are in ambient environment (Genzer J, 2005). There are various types of coating available like metallic, nonmetallic, polymeric and paint. Such coatings do not protect materials longer times. Inhibitors (Leon-Silva U, 2010) are used to control corrosion of metal in petroleum industries. Inhibitors are utilized in several forms (Baier R E, 2006) like organic, inorganic and mixed types inhibitors which are related to anodic as well as cathodic.

Their application (Rao BVA, 2010) can be done in the form (Liu X Y, 2009) of solid, liquid and gas as requirement of corrosive medium. Electron rich compounds (Liao Q Q, 2009) alkane, alkene, alkyne, cyclic, aromatic and heterocyclic contain nitrogen, oxygen and sulphur are used as organic inhibitors in petroleum industries (Zhang D Q, 2009), sugar industries (Sahoo R R, 2009), phosphate industries (Raman R, 2007), pulp and paper industries (Li D G, 2006) to control the corrosion of mild steel (Cristiani P, 2008) and stainless steel (Cristiani P, 2005).

These inhibitors do not provide protection longer periods (Videla H, 2009). Metallic pipe corrosion (Bibber J W, 2009) is mitigated by anodic protection and impressed current but they do not give good results in aggressive medium (Ghareba G S, 2010; Ikpi, 2017; Abeng, 2017; Magu, 2017). Aloe Vera is used check corrosion metallic can (Singh R K, 2016) which contain beverages, orange juice, milk and vegetables. It works as natural inhibitor. In acidic soil the life of earthworms (Singh R K 2017) become miserable such environment their life can be protected by the application aloe vera juice.

Human skin is face corrosion problem in mega and metro cities environment such corrosion is control by the use of aloe vera and turmeric coating. Nanocoating and filler compounds (Singh R K, 2017) are used to control the corrosion of polymeric-coated metal in ambient of effluents.

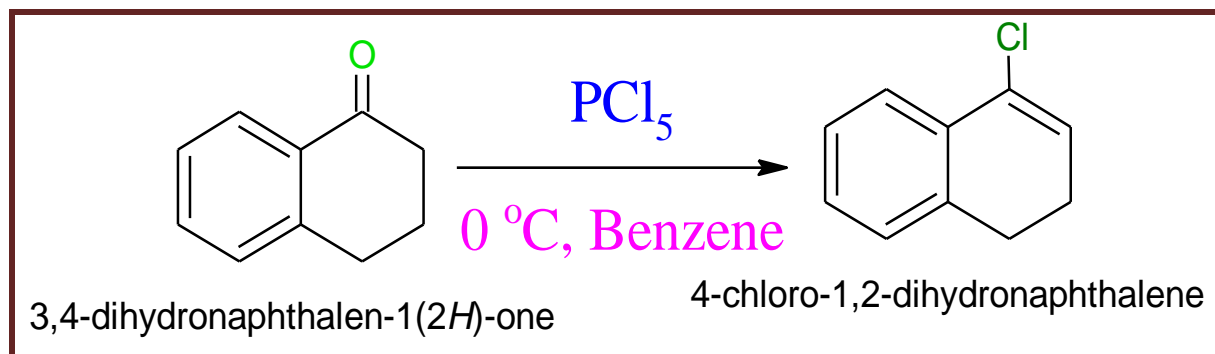
2. EXPERIMENTAL

Mild steel sample (3X9X0.1) cm² was taken for experimental work. The samples were kept in HCl and saline water medium. It was coated with polybutadiene and kept in SO₂ moist and Cl⁻ ions environment. The corrosion rate of samples were determined by gravimetric technique at 283, 293, 303, 312 and 323 K temperatures and that temperatures exposor times were 3, 5, 8, 11 and 14 days.

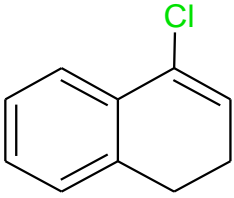
These samples were nanocoated with octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and corrosion rate calculated at above mentioned temperatures and days. Nanocoated samples were again coated with MgS and measured corrosion rates. Potentiostat technique used to calculate corrosion potential, corrosion current, corrosion current densities of sample without and with nanocoating above mentioned materials. Potentiostat 324 model consists pt electrode used as reference electrode, calomel as auxiliary electrode and polybutadine-coated mild steel sample electrode and this electrode can be with octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and coating with MgS. Nanocoated compound octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone was synthesized as:

Scheme 1. Synthesis of 4-chloro-1,2-dihydronaphthalene

Phosphorous pentachloride (30g) was added into benzene solution and mixed 3,4-dihydronaphthalen-1(2H)-one (25gm). The reaction mixture temperature maintained 0 °C and then after benzene (50gm) added, the reaction mixture was stirred for one hour. The reaction mixture was quenched with NaHCO₃ and did workup with diethyl ether. The solvent evaporated with rotator vapour. The product was purified by silica gel column chromatography and produced 89% 4-chloro-1,2-dihydronaphthalene.



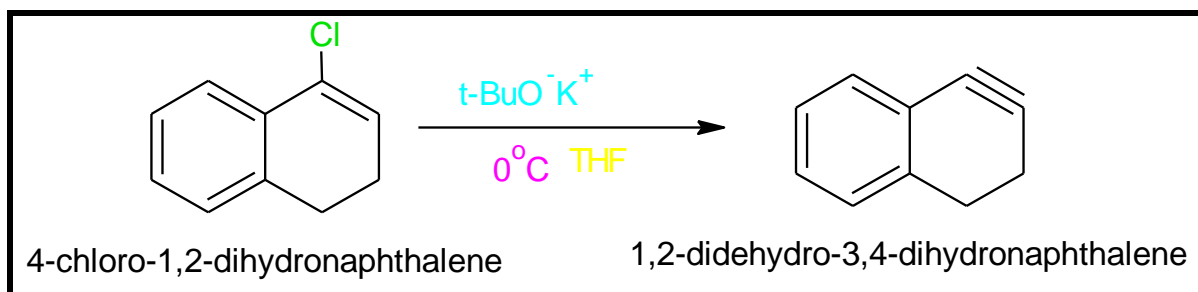
Physical properties of 4-chloro-1,2-dihydronaphthalene

	Molecular Formula	= C ₁₀ H ₉ Cl
	Formula Weight	= 164.63146
	Composition	= C(72.96%) H(5.51%) Cl(21.53%)
	Molar Refractivity	= 47.73 ± 0.4 cm ³
	Molar Volume	= 141.2 ± 5.0 cm ³
	Parachor	= 355.3 ± 6.0 cm ³
	Index of Refraction	= 1.590 ± 0.03
	Surface Tension	= 40.0 ± 5.0 dyne/cm
	Density	= 1.16 ± 0.1 g/cm ³
	Dielectric Constant	= Not available
	Polarizability	= 18.92 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 164.039278 Da
	Nominal Mass	= 164 Da
	Average Mass	= 164.6315 Da

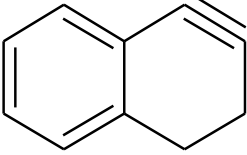
M+	= 164.038729 Da
M-	= 164.039827 Da
[M+H] ⁺	= 165.046554 Da
[M+H] ⁻	= 165.047652 Da
[M-H] ⁺	= 163.030904 Da
[M-H] ⁻	= 163.032002 Da

Scheme 2. Synthesis of 1,2-didehydro-3,4-dihydronaphthalene

4-Chloro-1,2-dihydronaphthalene (10gm) kept in two necks round bottle flask and potassium t-butoxide (25gm) dissolved in THF solution. This solution poured into 4-Chloro-1,2-dihydronaphthalene and reaction temperature 0 °C. The reaction was mixture stirring four hours after completion reaction added cyclohexene as trapping agent and again stirring reaction more two hours. After work up got adduct 90% of 1,2-didehydro-3,4-dihydronaphthalene.

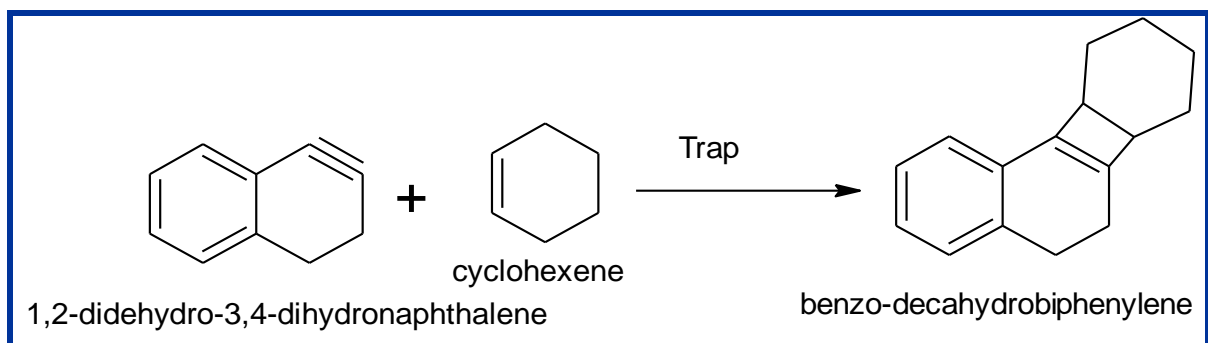


Physical properties of 1,2-didehydronaphthalene

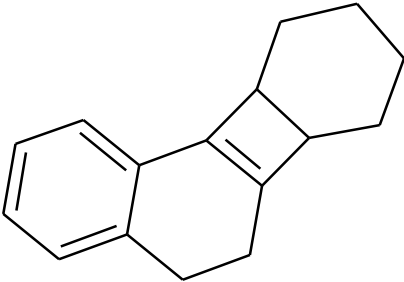
	Molecular Formula	= C ₁₀ H ₈
	Formula Weight	= 128.17052
	Composition	= C(93.71%) H(6.29%)
	Molar Refractivity	= 41.23 ± 0.4 cm ³
	Molar Volume	= 119.7 ± 5.0 cm ³
	Parachor	= 309.8 ± 6.0 cm ³
	Index of Refraction	= 1.604 ± 0.03
	Surface Tension	= 44.8 ± 5.0 dyne/cm
	Density	= 1.07 ± 0.1 g/cm ³
	Dielectric Constant	= Not available
	Polarizability	= 16.34 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 128.0626 Da
	Nominal Mass	= 128 Da
	Average Mass	= 128.1705 Da
	M+	= 128.062052 Da
M-	= 128.063149 Da	
[M+H] ⁺	= 129.069877 Da	
[M+H] ⁻	= 129.070974 Da	
[M-H] ⁺	= 127.054227 Da	
[M-H] ⁻	= 127.055324 Da	

Scheme 3. Synthesis of benzo-decahydrobiphenylene

When 1,2-didehydro-3,4-dihydronaphthalene was used with cyclohexene, it was trapped by 1,2-didehydro-3,4-dihydronaphthalene to yield benzo-decahydrobiphenylene.

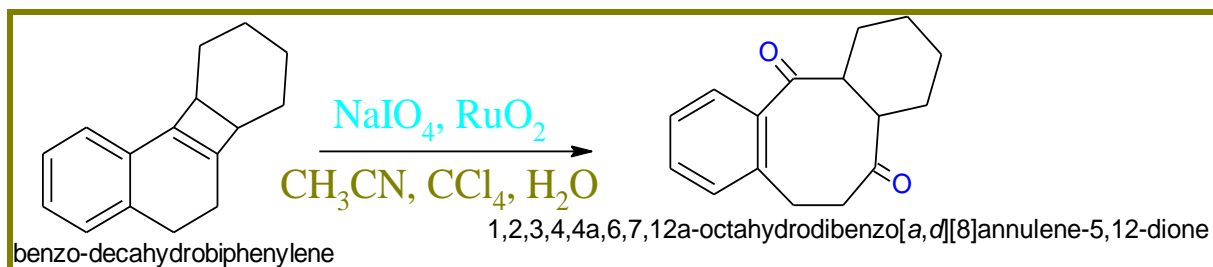


Physical properties of benzo-decahydrobiphenylene

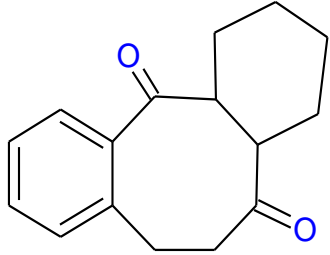
	Molecular Formula	= C ₁₆ H ₁₈
	Formula Weight	= 210.31412
	Composition	= C(91.37%) H(8.63%)
	Molar Refractivity	= 66.33 ± 0.4 cm ³
	Molar Volume	= 191.6 ± 5.0 cm ³
	Parachor	= 490.1 ± 6.0 cm ³
	Index of Refraction	= 1.608 ± 0.03
	Surface Tension	= 42.7 ± 5.0 dyne/cm
	Density	= 1.09 ± 0.1 g/cm ³
	Dielectric Constant	= 3.09 ± 0.2
	Polarizability	= 26.29 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 210.140851 Da
	Nominal Mass	= 210 Da
	Average Mass	= 210.3141 Da
	M+	= 210.140302 Da
M-	= 210.141399 Da	
[M+H] ⁺	= 211.148127 Da	
[M+H] ⁻	= 211.149224 Da	
[M-H] ⁺	= 209.132477 Da	
[M-H] ⁻	= 209.133574 Da	

Scheme 4. Synthesis of octahydrodibenzo[a,d][8]annulene-5,12-dione

Adduct (20gm) oxidized into benzo-decahydrobiphenylene with addition of NaIO₄ (10gm) and RuO₂ (15g) in the presence of solvent CH₃CN and CCl₄. The reaction was quenched with H₂O and after workup 87% yield of octahydrodibenzo[a,d][8]annulene-5,12-dione was obtained.



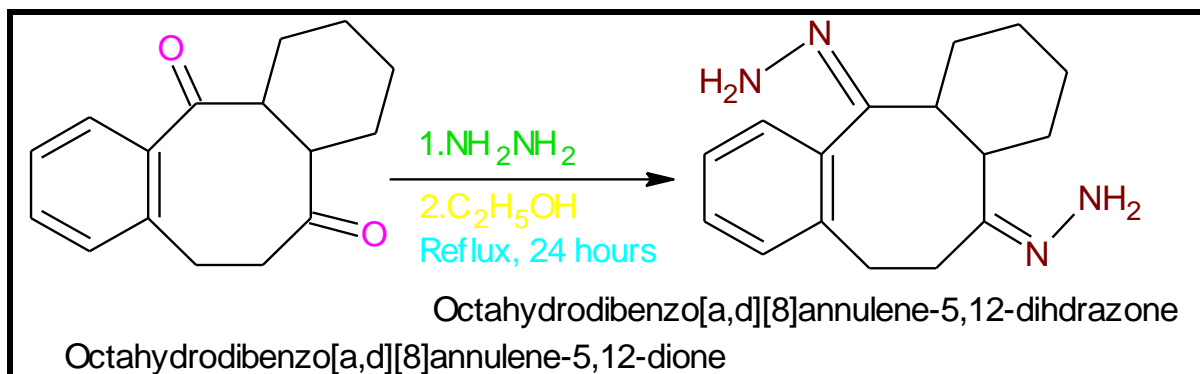
Physical properties of octahydrodibenzo[a,d][8]annulene-5,12-dione

	Molecular Formula	= C ₁₆ H ₁₈ O ₂
	Formula Weight	= 242.31292
	Composition	= C(79.31%) H(7.49%) O(13.21%)
	Molar Refractivity	= 69.02 ± 0.3 cm ³
	Molar Volume	= 216.7 ± 3.0 cm ³
	Parachor	= 549.8 ± 6.0 cm ³
	Index of Refraction	= 1.549 ± 0.02
	Surface Tension	= 41.4 ± 3.0 dyne/cm
	Density	= 1.118 ± 0.06 g/cm ³
	Dielectric Constant	= Not available
	Polarizability	= 27.36 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 242.13068 Da
	Nominal Mass	= 242 Da
	Average Mass	= 242.3129 Da

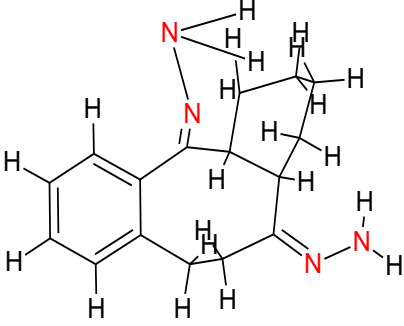
M+	= 242.130131 Da
M-	= 242.131228 Da
[M+H] ⁺	= 243.137956 Da
[M+H] ⁻	= 243.139053 Da
[M-H] ⁺	= 241.122306 Da
[M-H] ⁻	= 241.123403 Da

Scheme 5. Synthesis of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone

Octahydrodibenzo[a,d][8]annulene-5,12-dione (35g) was taken in a round bottomed flask and 75g of hydrazine hydrate was added and the mixture was heated under reflux for 24 hours. The solution was cooled in an ice bath and the octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone was separated by suction filtration. The crystals were washed with 150ml of cold ethanol and dried on the suction filter for 1 hour. The yield of octahydrodibenzo[a,d][8]annulene-5,12-dioxime 90% was obtained.



Physical properties of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone

	Molecular Formula	= C ₁₆ H ₂₂ N ₄
	Formula Weight	= 270.37268
	Composition	= C(71.08%) H(8.20%) N(20.72%)
	Molar Refractivity	= 78.57 ± 0.5 cm ³
	Molar Volume	= 207.6 ± 7.0 cm ³
	Parachor	= 561.5 ± 8.0 cm ³
	Index of Refraction	= 1.681 ± 0.05
	Surface Tension	= 53.5 ± 7.0 dyne/cm
	Density	= 1.30 ± 0.1 g/cm ³
	Dielectric Constant	= Not available
	Polarizability	= 31.14 ± 0.5 10 ⁻²⁴ cm ³
	Monoisotopic Mass	= 270.184447 Da
	Nominal Mass	= 270 Da
	Average Mass	= 270.3727 Da
	M+	= 270.183898 Da
	M-	= 270.184995 Da
[M+H] ⁺	= 271.191723 Da	
[M+H] ⁻	= 271.19282 Da	
[M-H] ⁺	= 269.176073 Da	
[M-H] ⁻	= 269.17717 Da	

3. RESULTS AND DISCUSSION

Octahydrobenzo[a,d][8]annulene-5,12-dihydrazone was nanocoated on the surface of polybutadiene-coated mild steel and their porosities were blocked by MgS filler. The corrosion of metal was determined in marine water in three stages, one polybutadiene-coated mild steel, second nanocoated octahydrobenzo[a,d][8]annulene5,12-dihydrazone and third was coated with MgS. The corrosion rate of each material was calculated by weight loss formula K (mmpy) = $13.56 W / D A t$ (where W = weight loss of test coupon expressed in kg, A = area of test coupon in square meter, D = Density of the material in $\text{kg}\cdot\text{m}^{-3}$) at 283, 293, 303, 312 and 323 K temperatures and time mentioned 3, 5, 8, 11 and 14 days. Their corrosion rate recorded in table1 and the results of table1 indicated that in marine water corrosion rate of polybutadiene-coated mild steel increased but its values decreased with the nanocoating of nanocoated and filler compounds. The plot between K (mmpy) versus t (days) in Figure1 confirmed the above mentioned trends. The corrosion rate of polybutadiene increased with nanocoated octahydrobenzo[a,d][8]dihydrazone but this decreased with MgS filler, it observed different interval of times. Polybutadiene-coated mild steel face sever crevice corrosion problem due to depletion of O_2 inside and outside of polybutadiene. The use of nanocoating of octahydrobenzo [a,d][8]dihydrazone and MgS filler create composite thin film barrier which is more stable in marine water. This barrier is thermally stable and suppresses the attack of corrosive ions. MgS is active compounds which are entered into porosities of octahydrobenzo[a,d][8]annulene5,12-dihydrazone and forms complex this nitrogen containing compound. This surface film attaches with base materials by chemical bonding and forms a passive layer.

Table 1. Corrosion rate of mild steel nanocoated with octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone [NC(1)]and MgS filler in acidic medium

N C & F	Temp (K)	283 K	293 K	303 K	313 K	323 K	C (mM)
	Time (days)	2	5	8	11	14	
NC(0)	K	94.641	115.187	143.308	160.366	172.684	00
	logK	1.976	2.061	2.156	2.205	2.237	
NC(1)	K	21.842	26.086	36.49	42.546	47.049	50
	logK	1.339	1.416	1.562	1.628	1.672	
	log(K/T)	0.791	0.883	1.043	1.125	1.182	
	θ	0.7692	0.7735	0.7453	0.7338	0.7225	
	(1- θ)	0.2308	0.2265	0.2562	0.2662	0.2725	
	($\theta/1-\theta$)	3.332	3.415	2.909	2.756	2.651	
	log($\theta/1-\theta$)	0.522	0.533	0.463	0.440	0.423	
F(MgS)	%CE	76.92	77.35	74.53	73.38	72.75	10
	K	17.671	19.847	24.385	26.471	28.129	
	logK	1.247	1.297	1.387	1.422	1.449	
	log(K/T)	0.699	0.764	0.868	0.918	0.959	
	θ	0.8132	0.8276	0.8298	0.8349	0.8371	
	(1- θ)	0.1863	0.1724	0.1702	0.1651	0.1629	
	($\theta/1-\theta$)	4.353	4.801	4.862	5.056	5.138	
	log($\theta/1-\theta$)	0.638	0.681	0.686	0.703	0.711	
	%CE	81.32	82.76	82.98	83.49	83.71	

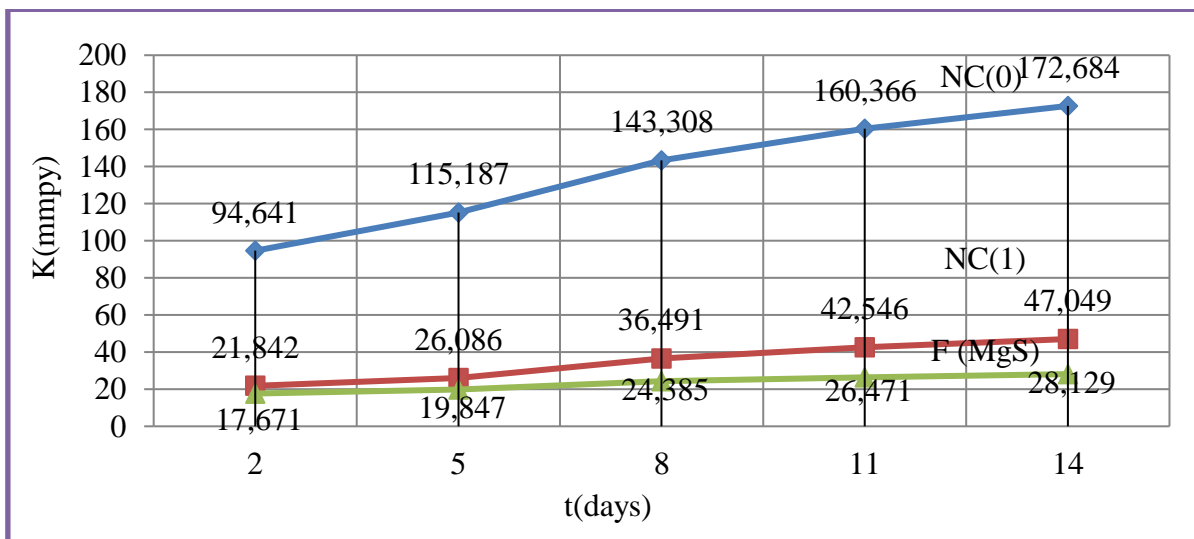


Figure 1. K(mmpy) Vs t(days) for nanocoating of NC(1) & MgS filler on mild steel

There was Studied the effect of temperatures at 283, 293, 303, 313 and 323 K on mild steel and after nanocoated with octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler, it was observed that with the rise of temperatures corrosion enhanced but nanocoating and filler compounds reduced their values. This effect clearly depicted in Table1 and Figure 2 which plotted between logK verse 1/T.

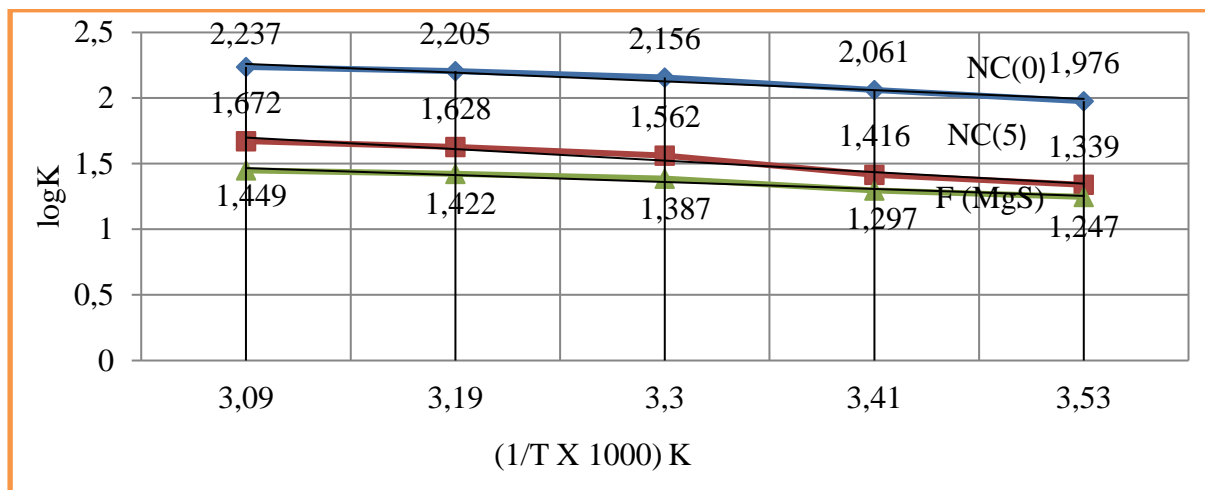


Figure 2. logK Vs 1/T for nanocoating of NC(1) & MgS filler on mild steel

The values of $\log(\theta/1-\theta)$ for octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler mentioned in table1 at different temperatures, it was found that $\log(\theta/1-\theta)$ decreased with nanocoating material as increasing temperatures but its values increased with filler as shown in Table 1 and Figure 3 which plotted between $\log(\theta/1-\theta)$ versus 1/T . The nanocoating and filler compounds developed a non osmosis barrier that neutralized the attack of Cl⁻ ions and H₂CO₃.

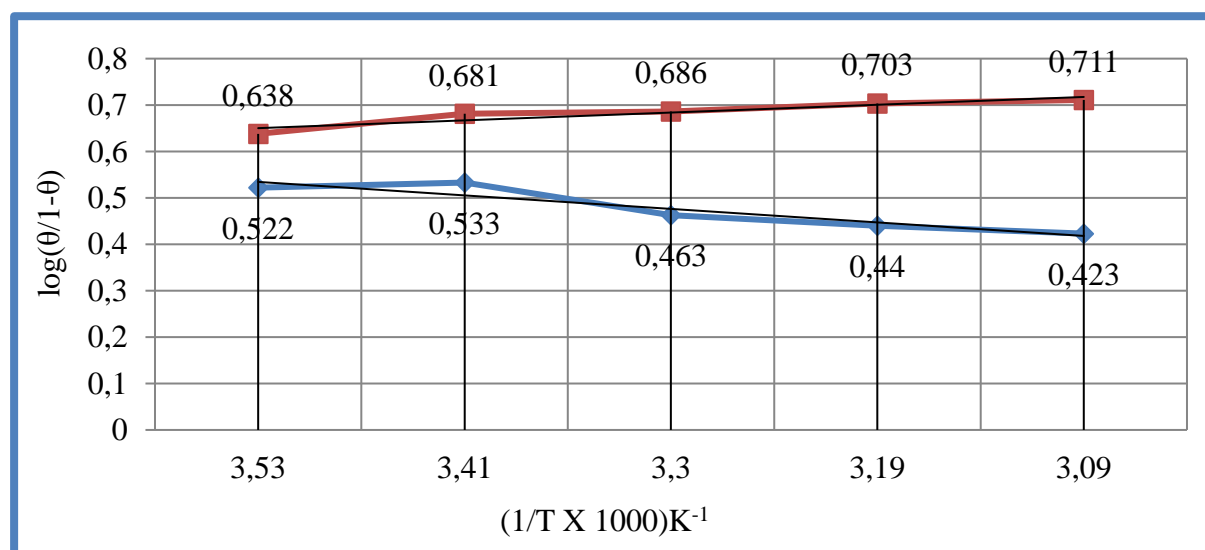


Figure 3. log(θ/1-θ) Vs 1/T for nanocoating of NC (1) & MgS filler on mild steel

The surface coverage areas were covered by octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler at various temperatures and calculated by formula $\theta = (1 - K / K_o)$ (where K is the corrosion rate before coating and K_o is the corrosion rate after coating) and their values were written in Table1. It was observed that nanocoating compound increased surface coverage area but filler improved the mitigation character of surface coverage area. Such types of trends noticed in Figure 4 which plotted between θ (surface coverage area) versus T (temperature).

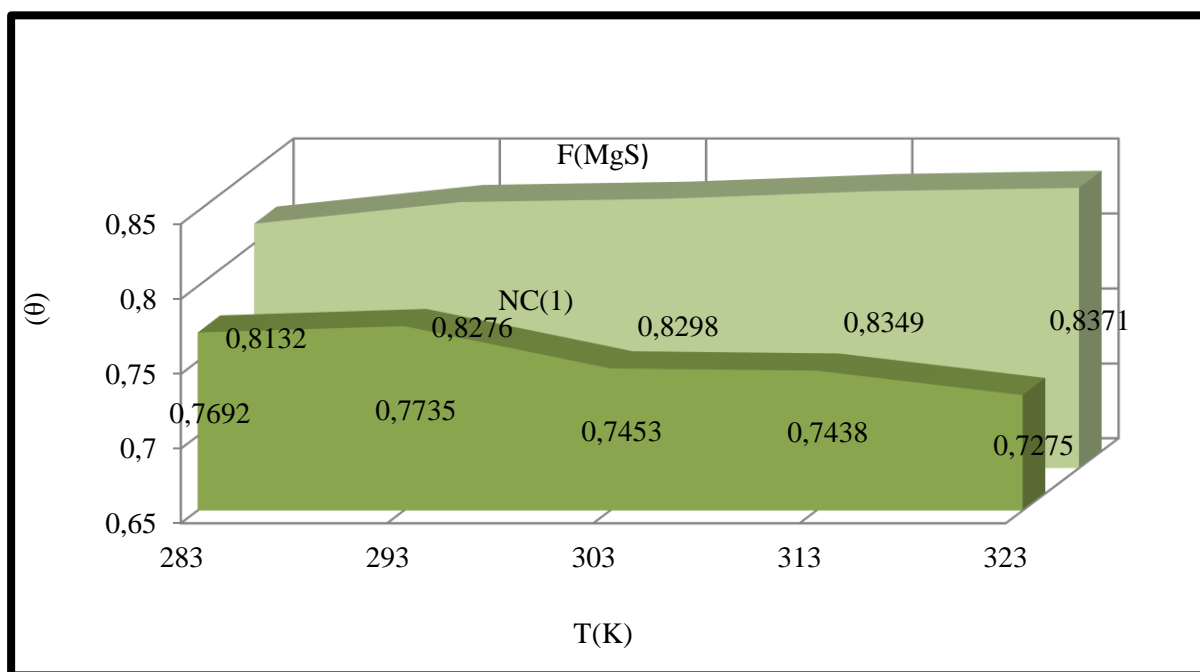


Figure. 4 θ Vs T for nanocoating of NC(1) & MgS filler on mild steel

The percentage coating efficiency of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler were calculated by formula:

$$\% CE = (1 - K / K_o) \times 100$$

where: CE = coating efficiency, K = Corrosion rate with coating, K_o = corrosion rate without coating) and its values were mentioned in Table1. These results show that nanocoating and filler compounds increased coating efficiency but filler enhanced more efficiency. Figure 5 plotted between % CE (percentage coating efficiency) versus T (temperature), it was observed that MgS filler increased coating efficiency of nanocoating compound in marine water.

Activation energy of mild steel, octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler were calculated by Figure 2 and Arrhenius equation, $d / dt (\log K) = E_a / R T^2$ (where T is temperature in Kelvin, R is universal gas constant and E_a is the activation energy of the reaction). The values of activation energies were expressed in Table 2 and plot between $\log K$ versus $1/T$ found to be straight lines in Figure 2. The positive values of activation energy indicated that nanocoated and filler compounds developed a thin film by chemical bonding. At

higher temperature, activation energy reduced so both compounds formed stable barrier on the surface of base material.

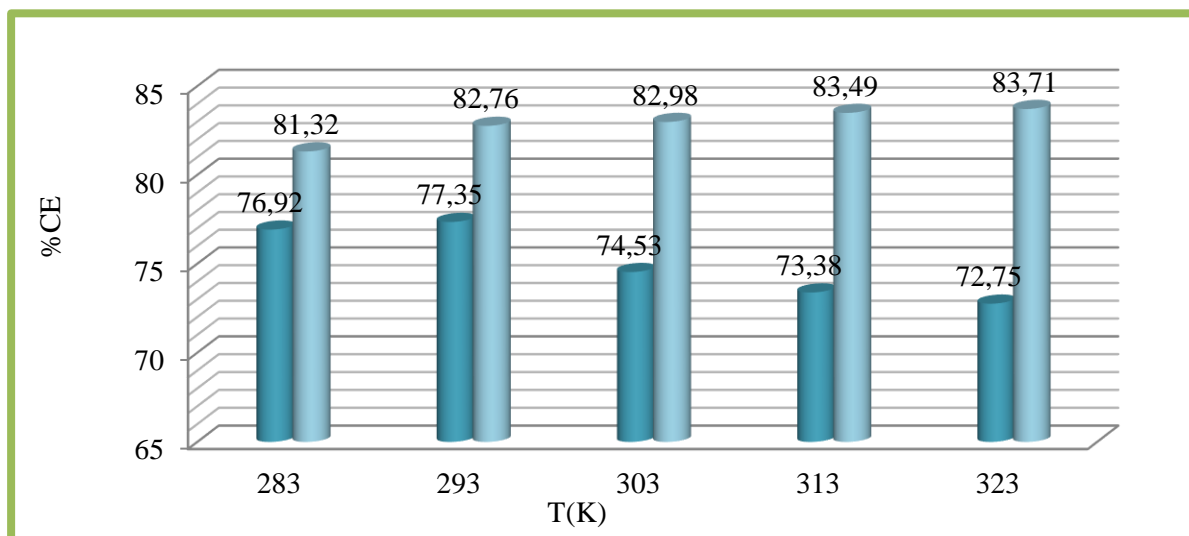


Figure 5. %CE Vs T for nanocoating of NC(1) & NC(F) on mild steel

Heat of adsorption of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler were obtained by Langmuir equation, $\log(\theta / 1-\theta) = \log(A.C) - (q / 2.303R T)$ (where T is temperature in Kelvin and q heat of adsorption) and Figure 3 a linear graph between $\log(\theta / 1-\theta)$ versus $1/T$. Their values mentioned in Table 2 confirmed that nanocoating and filler compounds attached with base material by chemical bonding.

Free energy of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler were determined by formula, $\Delta G = -2.303RT \log(33.3K)$ (where R is universal gas constant, T be temperature and K corrosion rate) and their recorded values in Table 2 gave information during coating exothermic reaction occurred. The results of Table 2 noticed that nanocoating and filler compounds were adhered with base material by chemical bonding.

Enthalpy and entropy of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler were calculated by transition state equation, $K = R T / N h \log(\Delta S^\# / R) X \log(-\Delta H^\# / R T)$ (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) and figure6 a linear graph between $\log(K/)$ versus $1/T$ and their values were written in Table 2. Nanocoating and filler compounds exhibited negative values of enthalpy and entropy. This sign indicated that coating is an exothermic process. Nanocoating and filler compounds were accommodated on the surface of base material by chemical bonding. Entropy values determined that filler compound arranged into matrix of nanocoating compound in ordered manner. Enthalpy and entropy of nanocoating of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and ZnS filler indicate that the coating of both compounds is exothermic process.

The results of all thermal parameters like activation energy, heat of adsorption, free energy, enthalpy and entropy at different temperatures were written in Table 2 and their graph plotted in Figure 7. After analysis of the results of all thermal parameters, it was found that surface coverage area increased as temperatures enhanced. The nanocoating and filler

compounds formed thin surface film barrier on polybutadiene by chemical bonding that barrier stopped osmosis or diffusion process of marine water.

Table 2. Thermal parameter of octahydrodibenzo[a,d][8]annulene-5,12-dihyrazone and MgS filler mild steel in acidic medium

Thermal Parameters	283 K	293 K	303 K	313 K	323 K
$E_a(0)$	133.43	134.44	136.10	139.19	132.23
$E_a, NC(1)$	90.42	90.32	98.61	99.34	98.83
$q, NC(1)$	-35.25	-34.76	-29.23	-26.85	-25.01
$\Delta G, NC(1)$	-193.24	-191.71	-194.72	-192.30	-188.86
$\Delta H, NC(1)$	-53.45	-57.64	-65.88	-68.65	-69.90
$\Delta S, NC(1)$	-69.88	-73.12	-78.96	-81.80	-83.74
$\theta, NC(1)$	0.7692	0.7735	0.7453	0.7338	0.7275
$E_a, F(MgS)$	84.21	84.61	87.55	86.77	85.65
$q, F(MgS)$	-43.08	-44.42	-43.31	-42.90	-42.02
$\Delta G, F(MgS)$	-187.03	-183.96	-183.67	-179.73	-175.65
$\Delta H, F(MgS)$	-47.23	-49.89	-54.83	-56.08	-56.69
$\Delta S, F(MgS)$	-66.36	-68.57	-72.27	-73.92	-75.19
$\theta, F(MgS)$	0.8132	0.8276	0.8298	0.8349	0.8371

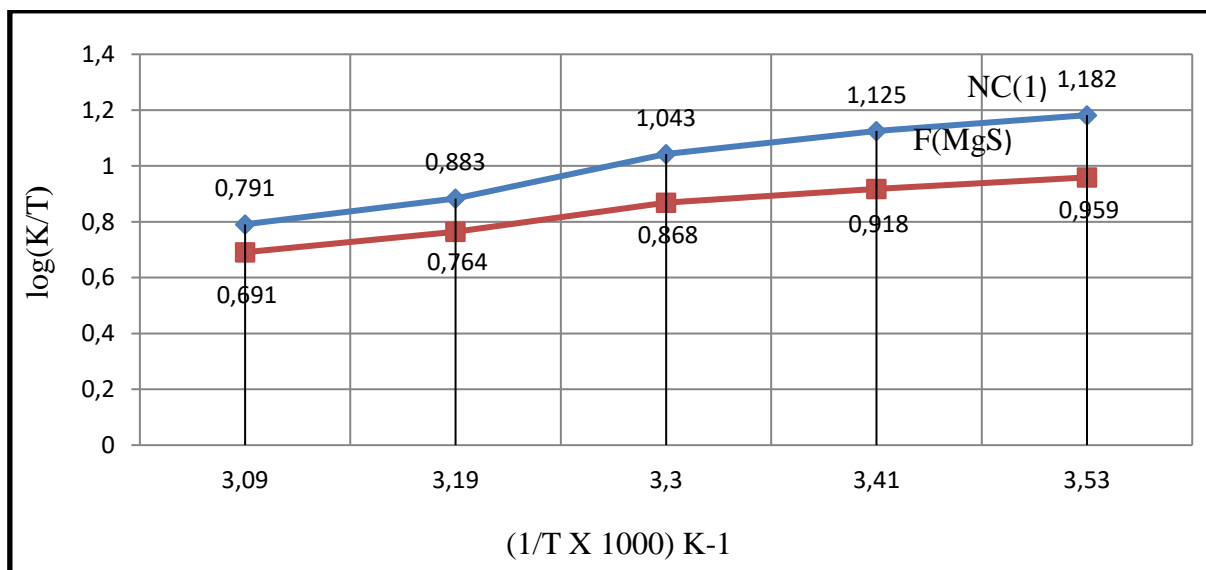


Figure 6. $\log(K/T)$ Vs $1/T$ for nanocoating of NC(1) & MgS filler on mild steel

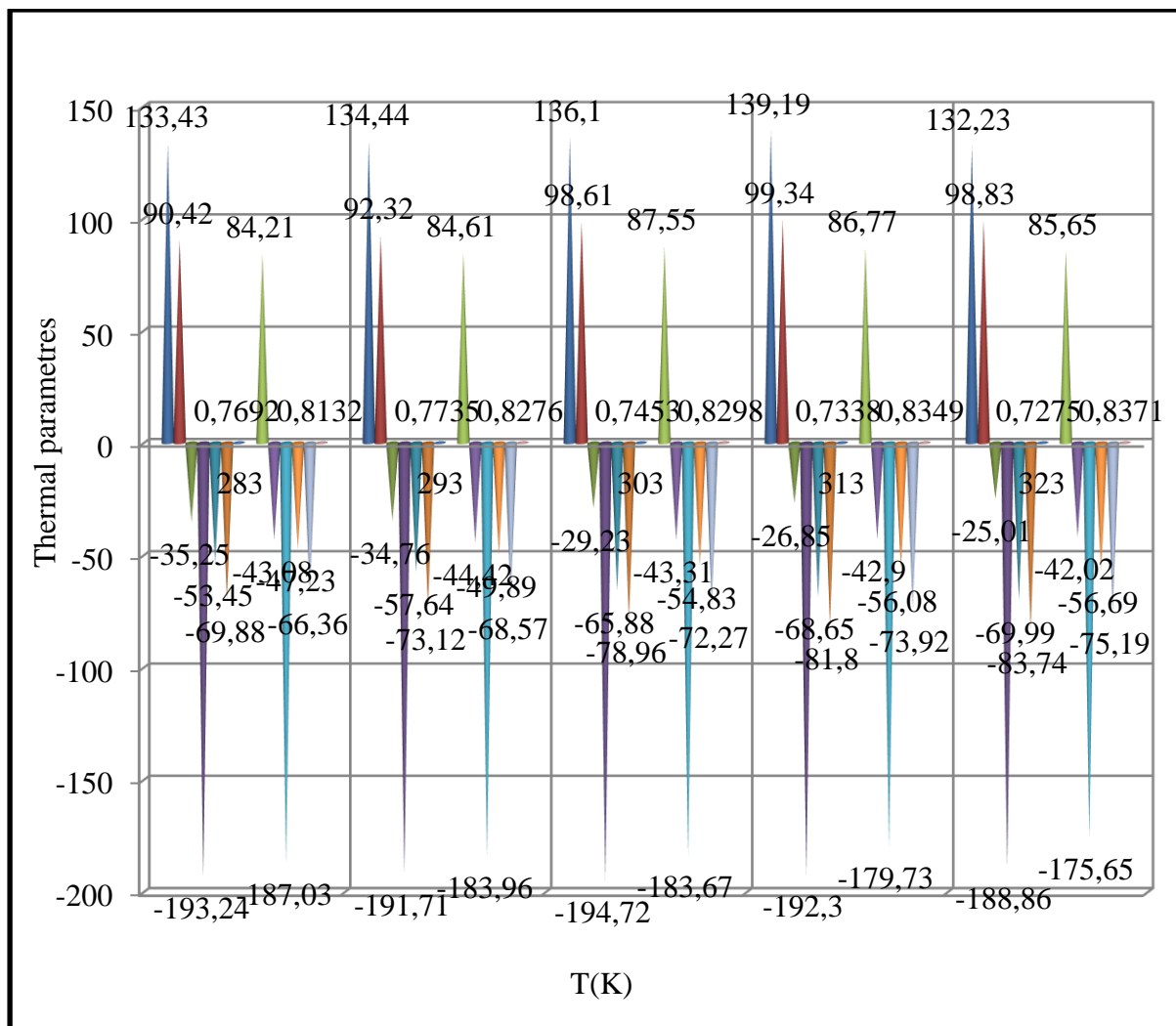


Figure 7. Thermal parameters Vs T for nanocoating of NC(1) & MgS on mild steel

Potentiostat polarization results of mild steel, octahydrodibenzo[a,d][8]annulene-5,12-dihydrazine and MgS filler were calculated by formula, $\Delta E/\Delta I = \beta_a \beta_c / 2.303 I_{corr} (\beta_a + \beta_c)$ (where $\Delta E/\Delta I$ is the slope which linear polarization resistance (R_p), β_a and β_c are anodic and cathodic Tafel slope respectively and I is the corrosion current density in mA/cm^2) and Tafel plot between $\Delta E(\text{mV}$, electrode potential) versus $I(\text{mA}/\text{cm}^2$, corrosion current density) in figure 8 and their values were recorded in Table 3. It was observed that electrode potential and anodic current density was high with polybutadiene-coated mild steel but these values decreased with nanocoating and filler compounds. Both compounds enhanced cathodic current density and reduced electrode potential. Corrosion current of polybutadiene-coated mild, octahydrodibenzo[a,d][8]annulene-5,12-dihydrazine and MgS filler were obtained by above equation and their values were put in equation, $C. R (\text{mmpy}) = 0.1288 I_{corr} (\text{mA}/\text{cm}^2) \times Eq. Wt (g) / \rho (\text{g}/\text{cm}^3)$ (where I_{corr} is the corrosion current density ρ is specimen density and Eq.Wt is specimen equivalent weight) produced corrosion rate.

The corrosion rate of all three materials were given in Table 3, it was observed that corrosion rate of polybutadiene-coated mild steel were high but these values were decreased with nanocoating and filler compounds. MgS filler enhanced cathodic current density and percentage coating efficiency with respect of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone. Filler compound reduced more corrosion rate with octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone. Nanocoating and filler form a composite thin film on the surface of polybutadiene-coated mild steel during coating and its stability is good in hostile marine water. The results were obtained by weight loss experiment for polybutadiene-coated mild steel in marine water by nanocoating of octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS were tally with the results of potentiostat.

Table 3. Potentiostatic polarization of nanocoating octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler on mild steel.

NC	ΔE (mV)	ΔI	β_a	β_c	I_{corr} (mA/cm ²)	K (mmpy)	θ	% CE	C (mM)
NC(0)	-451	112	172	151	8.69	264.69	0	0	
NC(1)	-311	65	75	180	4.81	146.51	0.71	71	0.0
F(MgS)	-251	55	65	195	4.65	141.63	0.88	88	

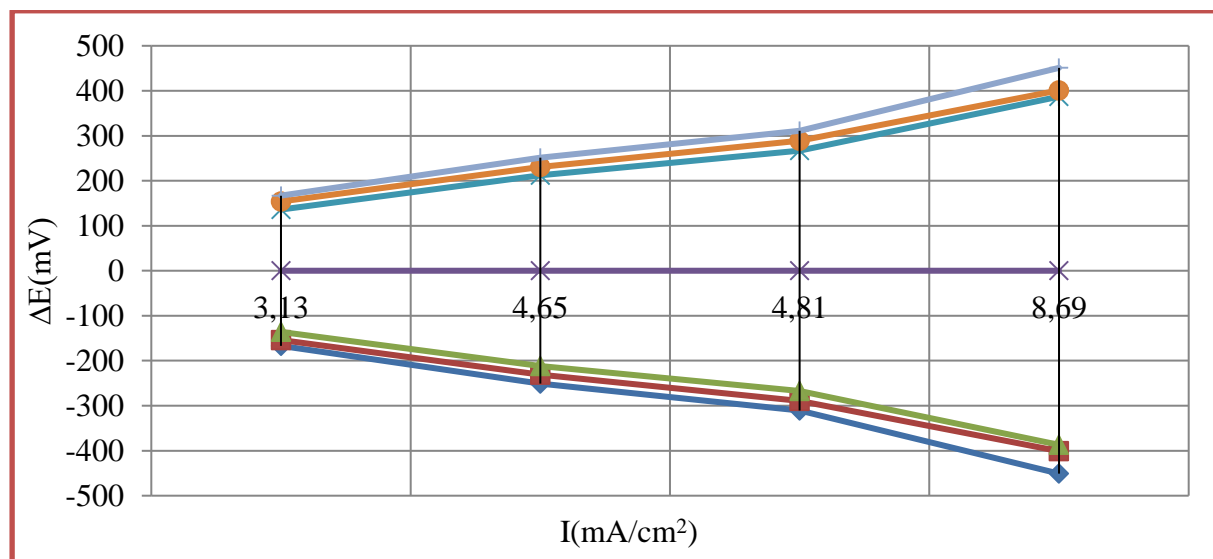


Figure 8. ΔE (mV) Vs I (mA/cm²) for nanocoating of NC(1) & MgS filler on mild steel

4. CONCLUSION

Octahydrodibenzo[a,d][8]annulene-5,12-dihydrazone and MgS filler used for the corrosion protection of polybutadiene-coated mild steel. These materials formed coating composite coating barrier on the surface of base polybutadiene-coated mild steel. Nanocoating compounds and filler compounds thermals parameters were indicated that composite surface barrier creation was exothermic process. The corrosive environment did not produce corrosion cell. The coating efficiencies and surface coverage area of nanocoating and filler compounds enhanced in different temperatures, atmosphere and weather changes.

Acknowledgement

Authors is thankful for UGC-New Delhi to provide financial support for this work. I give my thanks to laboratory staffs for their supports during experimental work.

References

- [1] Bhadra S, Singh N K and Khastgir D (2011). Polyaniline based anticorrosive and anti-molding coating. *Journal of Chemical Engineering and Materials Science* Vol. 2(1) 1-11.
- [2] Szabo T, Molnar-Nagy L, and Telegdi J (2011). Self-healing microcapsules and slow release microspheres in paints. *Progress in Organic Coatings*, 72, 52-57.
- [3] Wen N T, Lin C S, Bai C Y, and Ger M D (2008). Structures and characteristics of Cr (III) based conversion coatings on electrogalvanized steels. *Surf. Coat. Technol* 203, 317.
- [4] Boerio F J, Shah P (2005). Adhesion of injection molded PVC to steel substrates. *J of Adhesion* 81(6), 645-675.
- [5] Deveci H, Ahmetti G and Ersoz M, (2012). Modified styrenes: Corrosion physico-mechanical and thermal properties evaluation. *Prog. Org. Coat.* 73, 1-7.
- [6] Genzer J (2005). Templating Surfaces with Gradient Assemblies. *J of Adhesion* 81, 417-435.
- [7] Leon-Silva U, Nicho M E (2010). Poly(3-octylthiophene) and polystyrene blends thermally treated as coating for corrosion protection of stainless steel 304. *J. Solid State Electrochem*, 14, 1487-1497.
- [8] Baier R E (2006). Surface behaviour of biomaterials: Surface for biocompatibility. *J. Mater. Sci. Mater. Med.* 17, 1057-1062.
- [9] Rao BVA, Iqbal M Y and Sreehar B (2010). Electrochemical and surface analytical studies of the self assembled monolayer of 5-methoxy-2-(octadecylthiol) benzimidazole in corrosion protection of copper. *Electrochim, Acta*, 55, 620-631.
- [10] Liu X Y, Ma H Y and Hou M Z (2009), Self-assembled monolayers of stearic imidazoline on copper electrodes detected using electro chemical measurement, XPS, molecular simulation and FTIR, *Chinese Sci. Bull.* 54, 374-381.

- [11] Liao Q Q, Yue Z W and Zhou Q (2009). Corrosion inhibition effect of self-assembled monolayers of ammonium pyrrolidine dithiocarbamate on copper. *Acta Phys. Chin. Sin.* 25, 1655-1661.
- [12] Zhang D Q, He X M and Kim G S (2009). Arginine self-assembled monolayers against copper corrosion and synergetic effect of iodide ion. *J. Appl. Electrochem* 39, 1193-1198.
- [13] Sahoo R R and Biswas S K (2009). Frictional response of fatty acids on steel. *J. Colloid Interf. Sci.* 333, 707-718.
- [14] Raman R and Gawalt E S (2007). Selfassembled monolayers of alkanolic acid on the native oxide surface of SS316L by solution deposition. *Langmuir*, 23, 2284-2288.
- [15] Li D G, Chen S H and Zhao S Y (2006). The corrosion Inhibition of the self-assembled Au and Ag nanoparticles films on the surface of copper. *Colloid. Surface A* 273, 16-23.
- [16] Cristiani P, Perboni G and Debenedetti A (2008). Effect of chlorination on the corrosion of Cu|Ni 70|30 condenser tubing. *Electrochim. Acta* 54, 100-107.
- [17] Cristiani P (2005). Solutions fouling in power station condensers. *Appl. Therm. Eng.* 25, 2630-2640.
- [18] Videla H and L K Herrera (2009). Understanding microbial inhibition of corrosion. *Electrochem Acta*, 39, 229-234.
- [19] Bibber J W (2009). Chromium free conversion coating for zinc and its alloys. *Journal of Applied Surface Finishing*, Vol. 2(4), 273-275.
- [20] Ghareba G S and Omanovic S (2010). Interaction of 12-aminododecanoic acid with a carbon steel surface: Towards the development of 'green' corrosion inhibitors. *Corrosion Sci.* 52, 2104-2113.
- [21] M. E. Ikpi, F. E. Abeng, O. E. Obono, (2017). Adsorption and Thermodynamic Studies for Corrosion Inhibition of API 5L X-52 Steel in 2 M HCl Solution by Moxifloxacin. *World News of Natural Sciences* 9, 52-61
- [22] M. E. Ikpi, F. E. Abeng, B. O. Okonkwo, (2017). Experimental and computational study of levofloxacin as corrosion inhibitor for carbon steel in acidic media. *World News of Natural Sciences* 9, 79-90
- [23] F. E. Abeng, V. D. Idim, P. J. Nna, (2017). Kinetics and Thermodynamic Studies of Corrosion Inhibition of Mild Steel Using Methanolic Extract of *Erigeron floribundus* (Kunth) in 2 M HCl Solution. *World News of Natural Sciences* 10, 26-38
- [24] T. O. Magu, V. M. Basse, B. E. Nyong, O. E. Obono, N. A. Nzeata-Ibe, O. U. Akakuru, (2017). Inhibition studies of *Spondias mombin* L. in 0.1 HCl solution on mild steel and verification of a new temperature coefficient of inhibition efficiency equation for adsorption mechanism elucidation. *World News of Natural Sciences* 8, 15-26
- [25] Singh R K (2016). Corrosion protection of transport vehicles by nanocoating of decahydrobenzo[8]annulene-5,10-dihydrazone and SiC filler in H₂O(moist), CO₂, SO₂ environments and weather change. *Journal of Metallurgy and Materials Science*, 58, 167-179.

- [26] Singh R K (2017). Corrosion protection of transport vehicles by nanocoating of decahydrobenzo[8]annulene-5,10-dihydrazone in corrosive environments and weather change. *Journal of Powder Metallurgy & Mining*, 1, 2-8.
- [27] Singh R K (2017). Atmospheric corrosion protection of epoxy-coated stainless steel by nanocoating of decahydrobenzo[8]annulene-5,10-disemecarbazone and TiN filler. *International Journal of Nanotechnology in Medicine & Engineering* 2(4), 17-32.