

Corrosion Protection of Aluminium in Sulphur dioxide Environment by the use of Nanocoating and Electropray Techniques

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Abstract

Aluminium is a very useful metal. It is easily converted into suitable forms so it fits for in various appliances like households, industries, aerospace, electronic, transport and other processes. It is produced corroding affect in sulphur dioxide environment. Al interacts with sulphur dioxide in presence of humidity to produce corrosive medium for its. It creates acidic environment for Al metal and forms corrosion cell on its surface. The electrode potential difference occur between Al|Al³⁺ anode and cathode H⁺|H₂ thus corrosion reaction takes place on the surface of base metal and produces different forms corrosion like galvanic, pitting, stress, crevice, intergranular etc. The organic compound terahydro-dibenzo[a,d][7]annulene-5,11-dioxime and zinc oxide electropray were used for corrosion protection of Al in sulphur dioxide environment. The terahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO electropray formed composite barrier on aluminium metal that barrier produced a passive layer for sulphur dioxide. The corrosion rate of uncoated and coated aluminium studied in different temperatures, concentrations, humidity and duration of days. The corrosion rate of metal was determined by gravimetric and potentiostat techniques. The surface adsorption phenomenon of coating compound terahydro-dibenzo[a,d][7]annulene-5,11-dioxime and zinc oxide electropray was studied by Langmuir, Freundlich and Temkin isotherm and Arrhenius equation. The composite barrier formation on the surface of aluminium by terahydro-dibenzo[a,d][7]annulene-5,11-dioxime and electropray zinc oxide was studied by activation energy, heat of adsorption, free energy, enthalpy and entropy. The surface coverage area and percentage coating efficiency of coating and electropray compounds results found to be high in sulphur dioxide medium. Both compounds developed composited in sulphur dioxide to be stable and also enhanced durability of aluminium metal.

Keywords: Corrosion of aluminium; composite barrier; electropray; sulphur dioxide etc.

Introduction

Corrosion is a surface phenomenon [1]. Materials corrode in hostile medium [2] and change occur their internal [3] and external morphology [4]. There are several remedies applied [5] to control the corrosion of materials [6] as per their environmental conditions [7]. There are several methods applied for corrosion protection of metals like metallic [8] and nonmetallic coatings [9], polymeric coating [10], inhibitors [11] and nano-coating [12]. Metallic coating [13] is related to electroplating, hot dipping, flame sprayed; vapour deposition, chemical conversion and diffusion [14]. Surface treatment used to check the corrosion of materials [15]. Various types of inorganic and organic inhibitors

used to control the corrosion of metals in hostile medium [16]. The organic compounds acyclic, cyclic, aromatic, heterocyclic possessed primary, secondary, tertiary, quaternary amines, thiol, thioether, oxime, hydrazone, semicarbazone, phenylhydrazone functional groups [17] to decrease corrosion of metals in acidic medium. These functional groups formed thin barrier on metals surface and reduce the concentration of H⁺ ions [18]. The salts of inorganic compounds contain phosphorous applied for corrosion control. Polymeric coating provide protective barrier in corrosive medium [19]. Organic paint can be used to minimize corrosion in acidic medium [20]. Nano-coating methods applied for corrosion

protection of metals by the use of chemical vapour deposition, nozzle spray, plasma spray and laser spray [21]. The composite barrier developed by the application of organic compounds and oxide of active metals.

Experimental

Weight loss experiment: The test samples of Al cut into (3X5X0.1) cm² and rubbed with emery paper. The use of samples washed with acetone and dry with hot air gun. The samples were kept into 250 PPM sulphur dioxide environment. The corrosion rate of sample calculated without coating and with coating tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO electro-spray at 283, 293, 303, 313 and 323 K temperatures and that temperature recorded time 10, 20, 30, 40 and 50 days. The concentration of coating tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO electro-spray compounds used 30 mM and 10 mM by the used weight loss method.

Potentiostat

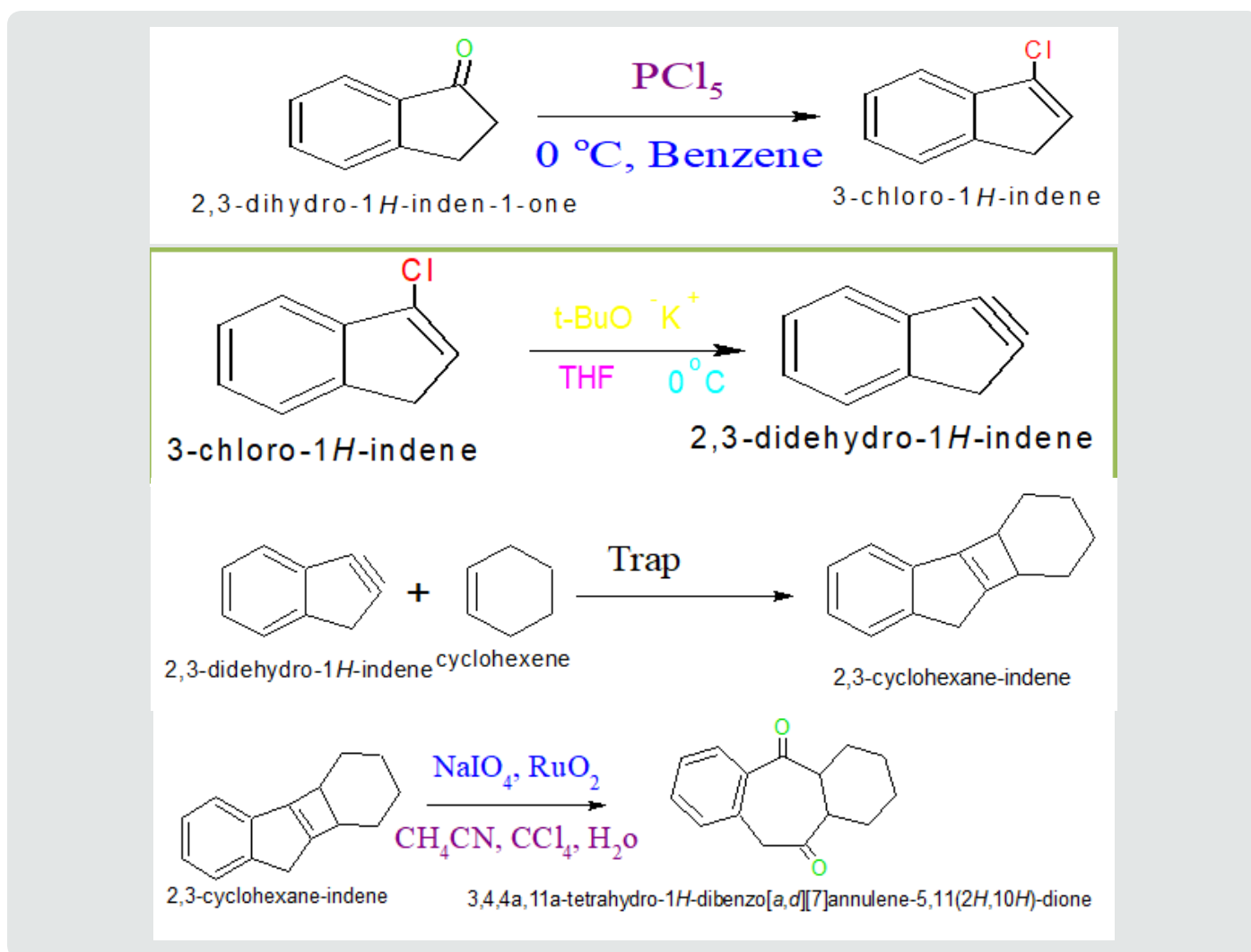
The 173 model EG & PG Princeton used to determine corrosion

Results and discussion

potential, corrosion current and corrosion current density. The electrochemical cell formed when Al sample kept between calomel auxiliary electrode and Pt electrode as reference electrode. The corrosion potential obtained absence and presence of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO electro-spray.

The used organic compound was synthesized in laboratory and its method expressed as:

Synthetic method of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime coating compound: Indanone poured into PCl₅ at 0°C temperature in benzene solvent and reaction mixture was stirred two hours to produce 3-chloro-1H-indene. It used with potassium t-butoxide in THF solvent to give 2, 3-didehydro-1H-indene. It trapped with cyclohexene to yield 2, 3-cyclohexane-indene. It oxidized with NaIO₄ and RuO₂ in solvent methylnitrile, carbon tetrachloride and water to obtain tetrahydro-dibenzo[a,d][7]annulene-5,11-dione. It heated with NH₂OH with HCl, C₂H₅OH and pyridine solvent. The reaction mixture refluxed two hours to yield tetrahydrodibenzo[a,d][7]annulene-5,11-dioxime. The chemical reactions were written as



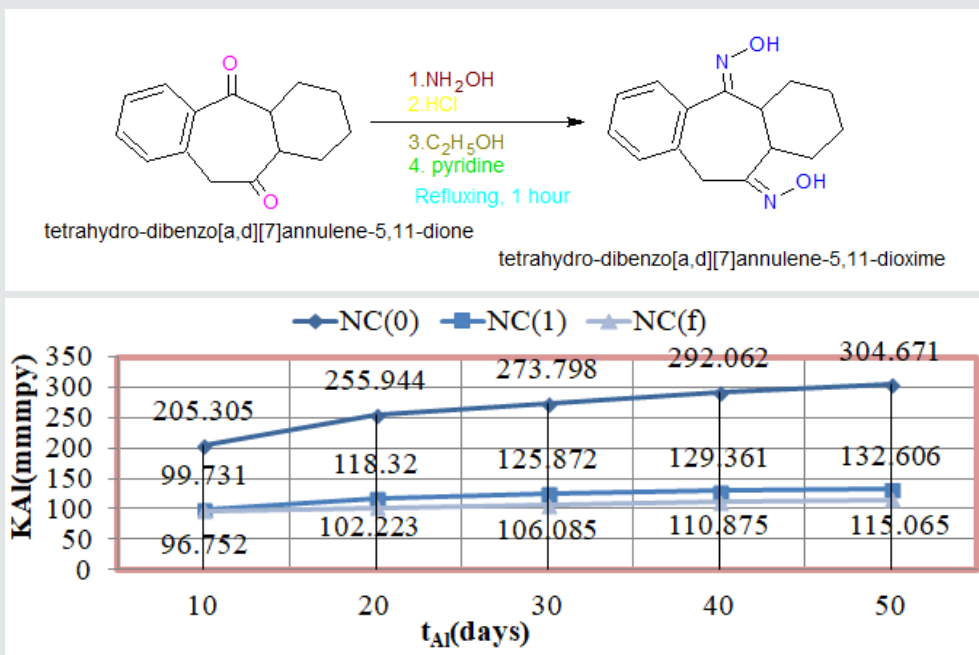


Figure 1: K_{Al} Vs t_{Al} for Al with nanocoating Ct and ZnO

The corrosion rate of Al with time in SO₂ environment: Its corrosion rate was calculated by weight loss equation $K_{Al}(mmpy) = 13.56 W_{Al} / D_{Al} A_{Al} t_{Al}$ (where W_{Al} = weight loss of test coupon expressed in kg, A_{Al} = Area of test coupon in square meter, D_{Al} = Density of the material in kg. m⁻³, t_{Al} = exposure time in hours) in absence and presence of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO electro-spray and plot between K versus t in (Figure 1). The corrosion rate of Al obtained at 10, 20, 30, 40 and 50 days with nanocoating of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO electro-spray and their values were written

in Table 1. The corrosion rates indicated that corrosion rate of Al reduced with coating and electro-spray metals such trends clearly noticed in (Figure 1).

Corrosion rate of Al with temperature in SO₂ environment: The corrosion rates Al obtained without coating of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and electro-spray ZnO and their values were given in (Table 1). (Figure 2) plotted between logK versus 1/T depicted that corrosion rate increased without coating but its values decreased after coating of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and electro-spray ZnO.

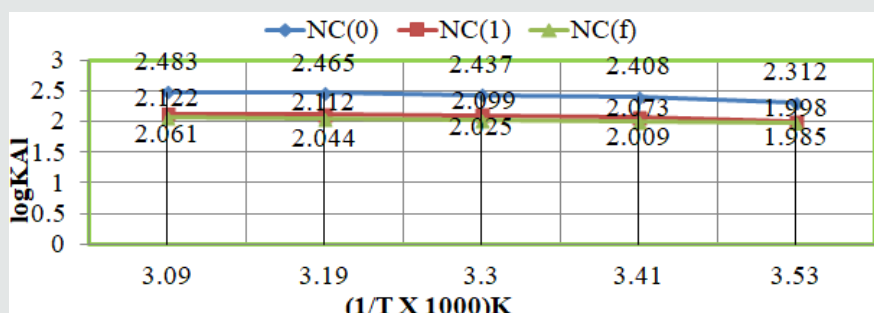


Figure 2: log K_{Al} Vs 1/T for Al with nanocoating of Ct and ZnO

Corrosion rate of Al with log(θAl/1-θAl): The values of log(θAl/1-θAl) for tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO versus 1/T plotted in Figure 3 and their values were written in (Table 1). The results of (Table 1) and (Figure 3) were shown that the values of log(θAl/1-θAl) versus 1/T decreased after coating.

Surface coverage area developed by tetrahydro-dibenzo[a,d][7]

annulene-5,11-dioxime and ZnO: The covered area was calculated by equation, $\theta_{Al} = (K_{Al0} - K_{Al}) / K_{Al}$ and their values were given in (Table 1). The graph of Figure 4 plotted between θAl (surface coverage area) versus T (temperature) for tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO. It observed that nanocoating and electro-spray compounds increased surface coverage areas in SO₂ environment. Nanocoating and electro-spray developed a passive composite barrier that is suppressed the attack of SO₂.

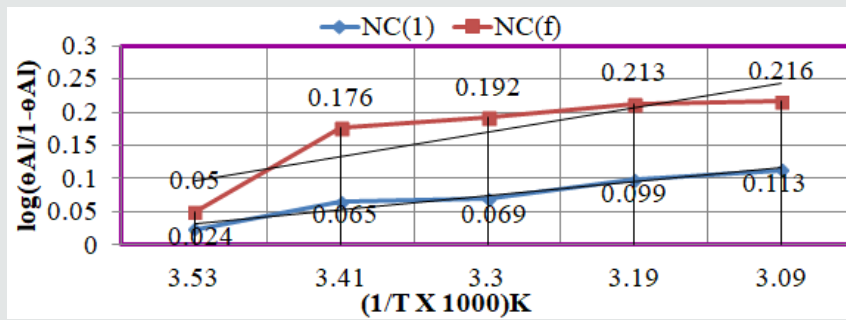


Figure 3: $\log(\theta_{Al}/1-\theta_{Al})$ Vs $1/T$ for Al with nanocoating Ct & ZnO

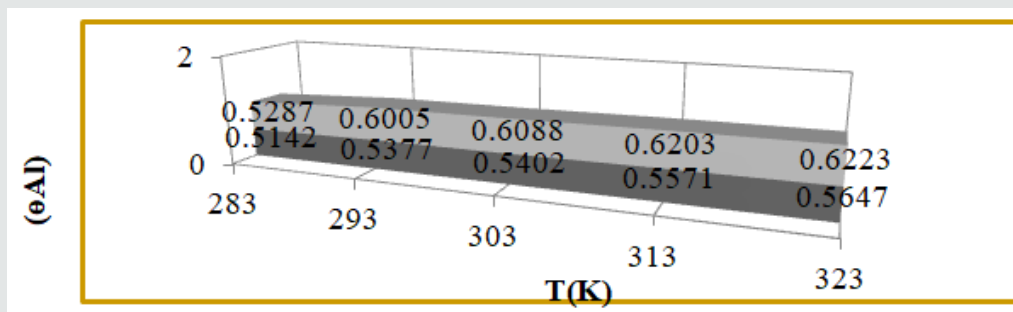


Figure 4: θ_{Al} Vs T for Al with nanocoating of Ct & ZnO

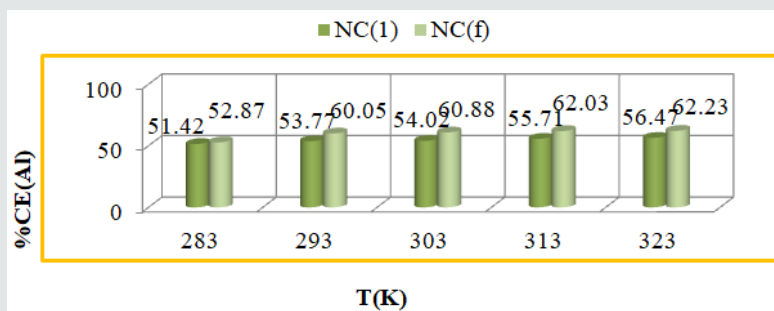


Figure 5: % CE(Al) Vs T for Al with nanocoating of Ct & ZnO

Table 1: Corrosion rate of Al with nanocoating of tetrahydro-dibenzo [a,d] [7]annulene-5,11-dioxime [Ct] and ZnO in SO₂ environment.

coating & E Spray	T(K)	2830K	2930K	3030K	3130K
	Time (days)	10	20	30	40
C _o	K0	205	255	273	292
	logK0	2.312	2.408	2.437	2.465
C _t	KAl	99.731	118.32	125.87	129.36
	logKAl	1.998	2.073	2.099	2.112
	log(KAl/T)	1.451	1.54	1.581	1.608
	θAl	0.5142	0.5377	0.5402	0.5571
	(1-θAl)	0.4858	0.4628	0.4598	0.4429
	log(θAl/1-θAl)	0.024	0.065	0.069	0.099

(C_o = Uncoated, C_t = tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime)

Percentage coating efficiency of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO: The percentage coating efficiencies were determined by equation, % CE(Al) = (KAl_o-KAl/KAl) X 100 and their results were written in (Table 1). (Figure 5) indicated the graph between % CE (Al) (percentage coating efficiency) versus T (temperature) which indicated that electro spray compound increased more coating efficiency with respected of nanocoating compound.

Activation energy of coated tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO:

The activation energies of Al without coating and coating with tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO were

obtained by Arrhenius equation $d/dt (\log KAl) = EAl / R T^2$ (where T is temperature in Kelvin, R is universal gas constant and EAl is the activation energy of the reaction) and (Figure 2). Its values were recorded in (Table 2). (Figure 6) plotted against EAl (activation energy) versus T (temperature) and θAl (surface coverage area). Activation energy reduced as temperature enhanced and surface coverage area occupied by nanocoating and electro spray compounds increased. This trend was clearly observed in (Figure 6) and their values indicated that nanocoating and electro spray were attached with Al by chemical bonding. The values of activation energy for tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO were mentioned in (Table 2) which indicated these compounds have less energy so they adhered with base metal by chemical bonding.

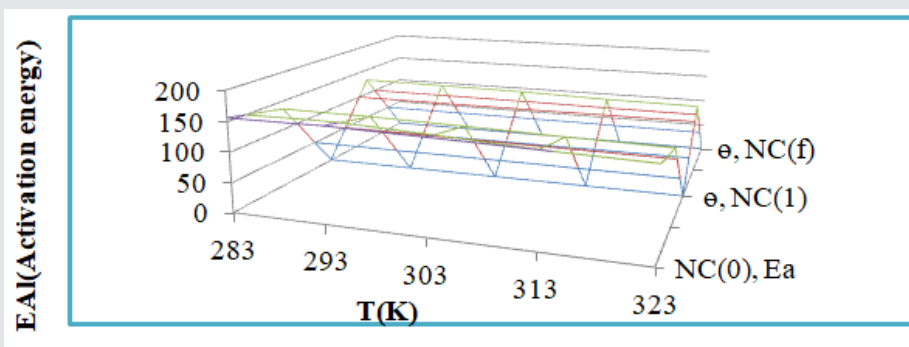


Figure 6: Ea Vs (T, θ) for Al with nanocoating Ct & ZnO

Table 2: Thermal parameters of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO.

Thermal Parameters	283K	293K	303K	313K	323K
EAl(o)	156.13	157.08	153.85	150.43	146.77
Ea, C _t	136.14	135.23	132.51	128.88	126.62
q, C _t	-1.621	-4.241	-4.355	-6.041	-6.679
$\Delta G, C_t$	-240	-234.5	-230.8	-221	-216.7
$\Delta H, C_t$	-119.2	-122.3	-121.1	-119.7	-117.9
$\Delta S, C_t$	-101.8	-104.7	-106.7	-106.8	-108.3
θ, C_t	0.5142	0.5377	0.5402	0.5571	0.5647
Ea,ZnO	128.91	128.05	126.7	123.33	122.24
q,ZnO	-12.43	-16.37	-14.39	-15.32	-12.06
$\Delta G, ZnO$	-231.2	-227.4	-222.8	-216.2	-212.3
$\Delta H, ZnO$	-91.95	-93.36	-93.99	-92.57	-93.31

Heat of adsorption of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO:

The heat of adsorption coating and electro spray compounds were calculated by equation Langmuir equation, $\log (\theta Al / 1-\theta Al) = \log (A . C) - (qAl / 2.303 R T)$ (where T is temperature in Kelvin and qAl heat of adsorption) and (Figure 3). The values of heat of

adsorption of both compounds were recorded in (Table2) and values were found to be with negative. These results confirmed that both compounds were adsorbed on the surface of Al by physical bonding. Heat of adsorption increased at lower to higher temperatures and surface coverage area also enhanced by nanocoating and electro spray compounds as shown in (Figure 7).

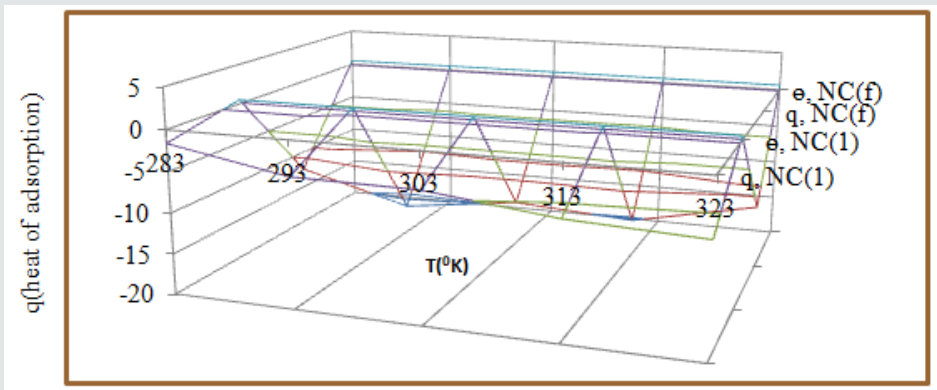


Figure 7: q_{Al} Vs (T, θ) for Al with nanocoating Ct& ZnO

Free energy of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO:

The values of free energy of coating and electro spray compounds were obtained by equation, $\Delta G_{Al} = -2.303RT \log (33.3KAl)$ (where R is universal gas constant, T be temperature and K corrosion rate)

and their values were mentioned in (Table 2). These values were indicated nanocoating and electro spray compounds formed surface film on base material by chemical bonding. (Figure 8) exhibited that free energy reduced at higher temperature and surface coverage area increased with both compounds.

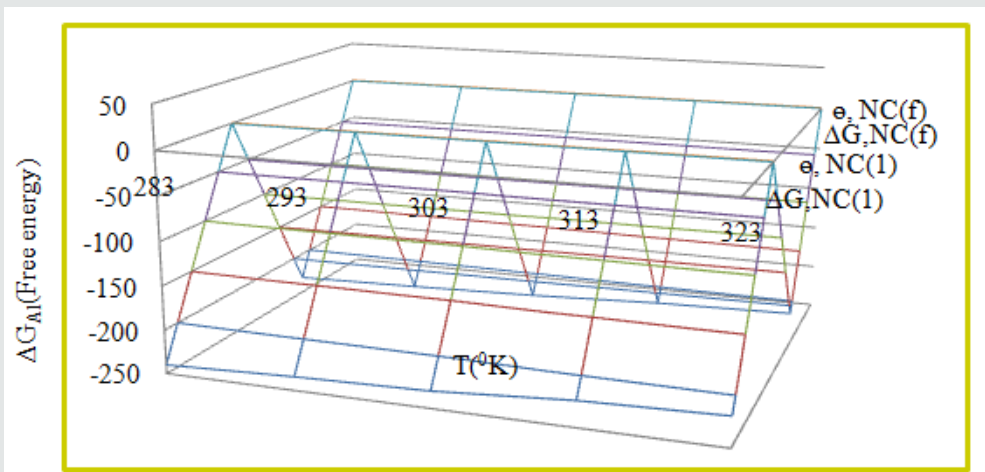


Figure 8: ΔG_{Al} Vs (T, θ) for Al with nanocoating of Ct and ZnO

Enthalpy of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO:

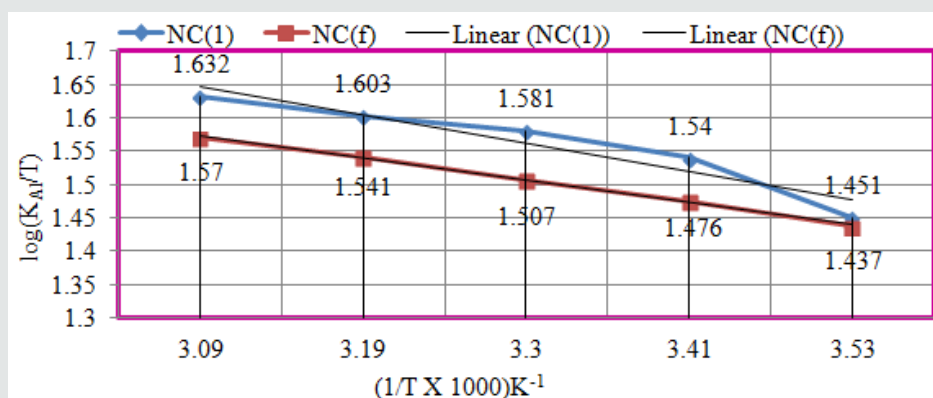


Figure 9: $\log(K_{Al}/T)$ Vs $1/T$ for Al with nanocoating Ct& ZnO

The values of enthalpy of both compounds were calculated by transition equation, $K = R T / N h \log (\Delta S_{Al} \# / R) \times \log (-\Delta H_{Al} \# / R T)$ (where N is Avogadro's constant, h is Planck's constant, $\Delta S_{Al} \#$ is the change of entropy activation and $\Delta H_{Al} \#$ is the change of enthalpy activation) and plot of $\log(K_{Al}/T)$ versus $1/T$ in (Figure 9) and their values were written in (Table 2). The enthalpy of both compounds

indicated that they were adsorbed on the surface of Al by chemical bonding. It was observed that enthalpy values decreased when temperatures enhanced and surface coverage area increased as shown in (Figure 10). The enthalpy results were indicated that exothermic process occurred during coating.

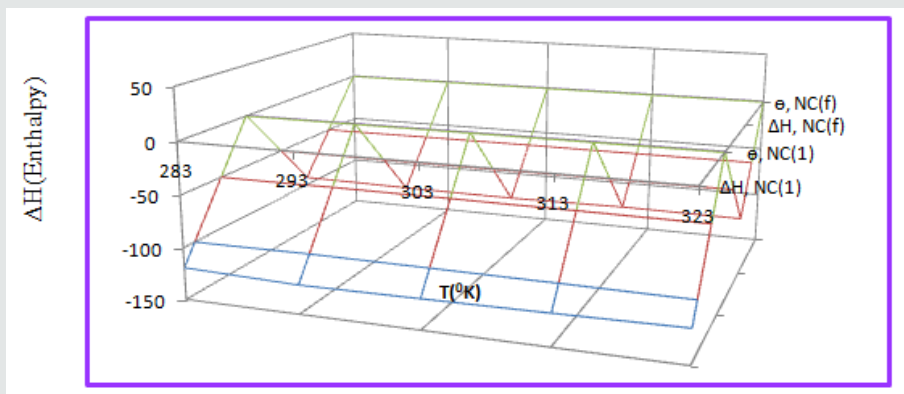


Figure 10: ΔH_{Al} Vs (T, θ) for Al with nanocoating of Ct & ZnO

Entropy of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO:

The values of entropy of both compound mentioned in (Table2). It indicates that nanocoating is an exothermic process. The nanocoating and electro spray compounds were accommodated by chemical bonding. (Figure11) depicted that entropy of both

decreased when temperatures were increased and they enhanced surface coverage area. Nanocoating tetrahydro-dibenzo[a,d][7] annulene-5,11-dioxime and ZnO electro spray were arranged on the surface of Al in order manner. Entropy values of both compounds were shown that nanocoating is an exothermic process. The thin film barrier developed by tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO to mitigate corrosion of Al in SO2 environment.

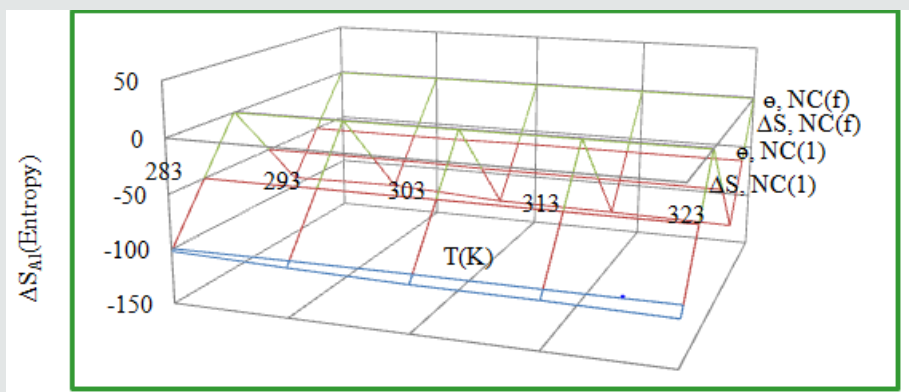


Figure 11: ΔS_{Al} Vs (T, θ) for Al with nanocoating Ct & ZnO

Potentiostatic polarization of tetrahydro-dibenzo [a,d] [7] annulene-5,11-dioxime and ZnO:

The results of electrode potential, corrosion current density, anodic and cathodic polarization were obtained by equation, $\Delta E / \Delta I = \beta_a \beta_c / 2.303 I_{corr} (\beta_a + \beta_c)$ (where $\Delta E / \Delta I$ is the slope with 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/cm²) and Tafel plot between electrode potential (ΔE) versus current density (I) and their values were written in (Table 3). The

results of (Table 3) and Tafel plots shown in (Figure 12) between corrosion potential and corrosion current density informed that Al produced higher corrosion potential but its values were reduced with tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO. It was also observed that Al developed more corrosion current density whereas nanocoating and electro spray compounds reduced their values. The anodic polarization current increased with polymeric-coated Al but cathodic polarization current enhanced by nanocoating and electro spray compounds.

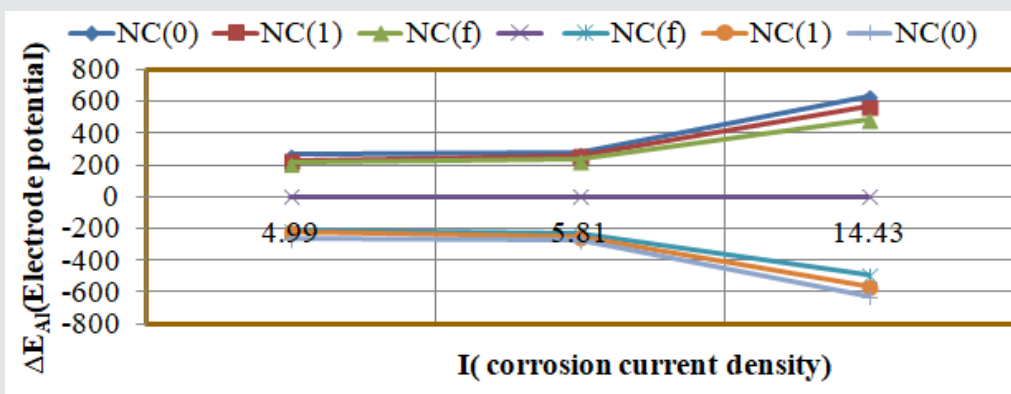


Figure 12: ΔE_{Al} Vs I for Al with nanocoating of Ct & ZnO

Table 3: potentiostatic polarization of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO nanocoating on Al.

C	ΔE_{Al}	ΔI	β_a	β_c	I _{corr} (mA/cm ²)	KAI (mmpy)
	(mV)					
Ct(0)	-630	239	286	126	14.43	620.53
Ct	-275	90	57	144	5.81	249.83
ZnO	-265	80	51	149	4.99	211.13

Putting the values of corrosion current density of polymeric-coated Al, nanocoating tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO electro spray in equation, $C. R (mmpy) = 0.1288 I (mA/cm^2) \times Eq. Wt (g) / \rho (g/cm^3)$ (where I is the corrosion current density ρ is specimen density and Eq.Wt is specimen equivalent weight) produced corrosion rate of material in each case and their values were given in (Table 3). In these results it was noticed that corrosion rate enhanced with polymeric-coated Al but nanocoating and filler compounds reduced the same. Gravimetric results were produced by Al, tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO were confirmed by the result of potentiostat. The results of potentiostat obtained for nanocoating of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO electro spray, it could shown that they produced high current density and neutralized the attack of SO₂. The surface coverage area and percentage coating efficiency tetrahydrodibenzo[a,d][7]annulene-5,11-dioxime and ZnO were confirmed that electro spray enhanced more these values and provide coating barrier thermal, chemical, physical and mechanical stability.

Mechanism of tetrahydro-dibenzo [a,d] [7]annulene-5,11-dioxime and ZnO

It is electron rich compound because it contains di-oxime functional groups and benzene ring. Coating of this compound, it is bonded with Al metal through chemical bonding. After coating of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime lots of porosities develop on base metal. These porosities block with electro spraying of ZnO thus a composite barrier is produced. The composite barrier of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO stop diffusion of SO₂ and base metal can be protected.

Conclusion

The nanocoating of tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO is an exothermic process. These compounds adsorbed on Al metal through chemisorptions process that is confirmed by activation energy, heat of adsorption, free energy, enthalpy and entropy. The composite barrier created by tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO which produced strong chemical bonding. Both compounds reduced corrosion rate and enhanced surface coverage area and coating efficiency. The composite barrier developed by tetrahydro-dibenzo[a,d][7]annulene-5,11-dioxime and ZnO work as repeller for SO₂ and checked its diffusion process.

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