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Corrosion Protection of Mild Steel in Petroleum Industry Saline Medium

Rajesh Kumar Singh

Principal, Specialization in Chemistry, JLN, College, Ghorashan, East Champaran, BRAB University, Muzaffarpur, India.

ABSTRACT

Corrosion is major problem with metals. When they come in contact of surrounding corrosive medium to construct a corrosion cell on their interface, metals undergo in corrosion reactions. Such environments metals can be exhibited uniform, galvanic, pitting, stress, crevice, embrittlement, intergranular corrosion etc. The corrosion of phenomenon of rebar steel studied in saline water. It creates corrosive medium for rebar steel due to availability of chloride ions. Rebar steel is used for the construction of bridge, road, airport and building. These components interact with saline medium producing corrosion reactions. Saline water chloride ions attack on rebar steel to form corrosion cell and corrode metals. Rebar steel is covered with concrete and that structure is dipped into saline water by the process of osmosis chloride ions are entered inside the structure creates dissolving and swelling chemical corrosion with nonmetallic components and electrochemical corrosion with metal. For this work synthesized electron rich organic compounds 2-(propan-2-ylidene) propane-1,3-diamine. The corrosion rate of rebar steel was calculated before and after coating by gravimetric method at different temperatures in presence different concentrations of saline water. Potentiostat technique used for the measurement of corrosion potential, corrosion current and corrosion current density in various concentrations of saline water and coating compound.

The surface coverage area and coating efficiency were determined by corrosion rate uncoated and coated rebar steel. The coating compound adhered on the surface of base metal by chemisorptions and it confirmed by thermodynamical parameters like activation energy, heat of adsorption, free energy, enthalpy and entropy. The surface adsorption phenomenon completed by Langmuir, Freundlich and Temkin isotherms. The results of thermodynamical parameters and surface adsorption confirmed that coating compound formed stable passive barrier which increased physical, chemical and mechanical properties of rebar steel saline environment.

*Corresponding author

Dr. Rajesh Kumar Singh, Principal, Specialization in Chemistry, JLN, College, Ghorashan, East Champaran, BRAB University, Muzaffarpur, India.

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Introduction

The fully Corrosion control of materials [1-3] is very difficult task but its effects can be minimized by the applications of suitable techniques [4-5]. In saline water environment different types of constructions activities are going on like housing, bridge, industrialization various manufacturing road railways bridge water transports and development of ports for the completion of such work can be completed by the use of metals [6-13]. Cl- ions play role of chemical and electrochemical reactions with metals and concrete and compel for disintegration inside and outside of materials [14-19]. Atmospheric pollutants produce corrosive environments for metallic and nonmetallic substances thus corrosion reactions take place in sculptures, monuments, antiques, museums, living and nonliving species [20-26]. Biometals are used for bone repairing of humans when it comes under chloride ions medium to start corrosion reactions [27,28]. These pollutants corrode building materials as well as tarnish their facial interface. Industrial effluents contain large amount of acidic which generates corrosive medium for metals, stones and cements. Hostile environments are also created by acid rain,

global warming and greenhouse gases [28-30].

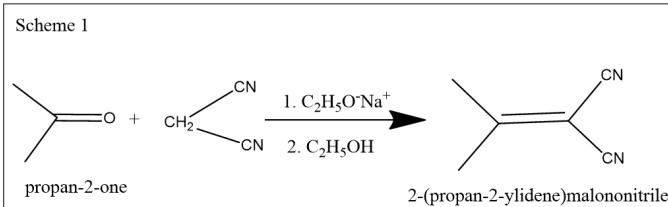
The oxides of carbon, oxides of nitrogen and oxides of sulphur react with moisture to produce acidic medium for materials. Bio-wastes develop microorganisms which release organic acids corrosive medium. Macro-organisms discharge organic acids to form acidic environment [31-33]. Corrosion materials are controlled by metallic and nonmetallic coating but such coatings do not provide good results in corrosive medium [34]. Polymeric and paint coating mitigate reduce corrosion rate of metals [35]. Organic and inorganic inhibitors are used checked the corrosive substances attack on metals [36]. There are some important coatings are applied for corrosion protection materials like electroplating, cladding, spray coating, chemical vapour deposition, structure change etc [37,38]. Nanocoating is an important tool of surface protection of metals but defects of this method is large number of porosities developing on their outer face so corrosive compounds are passed inside materials by osmosis process and accelerating corrosion reactions [39-42]. The organic compound 2-(propan-2-ylidene) propane-1,3-diamine can be used control the corrosion of rebar steel and improve their physical and mechanical properties. It produces good inhibition efficiency and surface coverage area.

Experimental

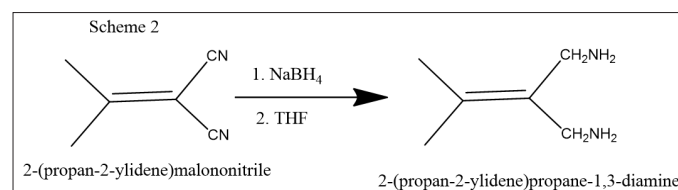
Rebar steel cut into 3cm height and its diameter is 1cm. The outer surface of rubbed with emery paper and washed with acetone to remove dust impurity. The sample immersed into saline water 3mM, 5mM, 7mM, 9mM and 11mM concentrations during mentioned concentrations temperature required 278, 283, 288, 293 and 298 K. On these parameters corrosion rates were calculated. The samples were coated with 2-(propan-2-ylidene) propane-1,3-diamine 2mM, 4mM, 6mM, 8mM and 10mM and their corrosion rate were determined above mentioned saline water concentrations and temperatures. The corrosion rate of metal was calculated by gravimetric method formula $K = 13.56 \times (W_i - W_f) / (D \times A \times t)$ where W_i = initial mass, W_f = final mass, D = density of metal, A = area and t = time. The surface coverage area was determined by formula $\theta = (K_o - K) / K_o$ where K_o = corrosion rate without coating and K = corrosion rate with coating. The percentage coating efficiency was calculated by formula, $\%CE = (K_o - K) / K_o \times 100$. The surface adsorption phenomenon was determined by Langmuir isotherm $\log(\theta / (1 - \theta)) = A C e^{-q} / RT$. Activation energy was calculated by formula $K = A e^{-E_a / RT}$. Free energy of coating compound calculated by formula $-\Delta G = 2.303 R T \log(33.3 K)$. Their enthalpy and entropy were determined by transition state formula transition formula $K = R T / N h \exp(\Delta S^\ddagger / R) \cdot \exp(-\Delta H^\ddagger / R T)$. Stern-Geary equation used to calculate corrosion current $I = \Delta E / \Delta I = \beta_{a1} \times \beta_{c1} / 2.303 I_{o1} (\beta_{a1} + \beta_{c1})$. Corrosion rate of metal was calculated by potentiostat $KC = (0.1288) \times I \times (E_{eq} / \rho)$.

Synthesis of 2-(Propan-2-Ylidene) Propane-1,3-Diamine

Propan-2-one added into solution of methylenedinitrile in presence of ethyl alcohol and sodium ethoxide to form 2-(propan-2-ylidene) malononitrile.



When 2-(propan-2-ylidene) malononitrile used with sodium bromohydrate in presence of THF to produce 2-(propan-2-ylidene) propane-1,3-diamine.

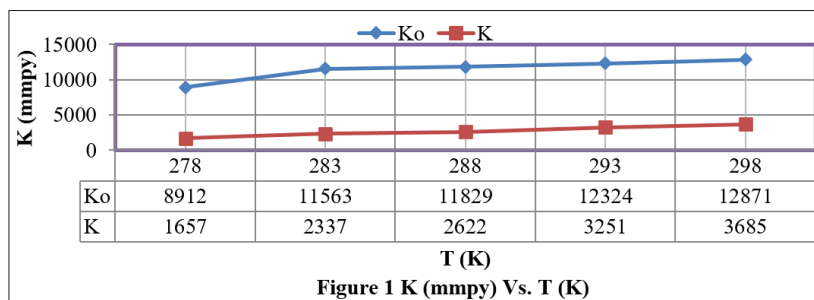


Results and Discussion

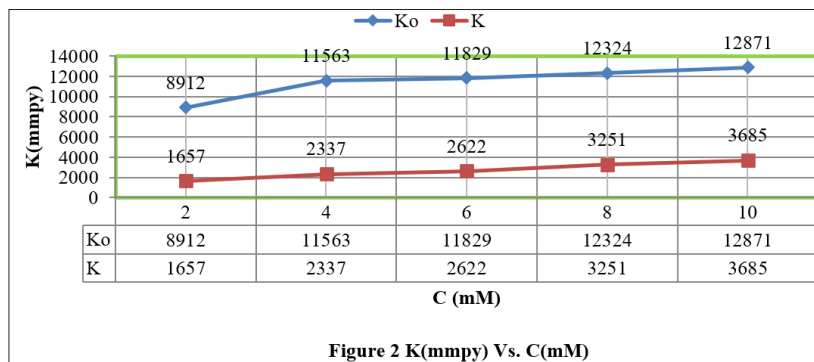
Uncoated and coated rebar steel corrosion rates were recorded in Table 1 at different temperatures, concentration of saline water and coating compound. The results of Table 1 indicated that uncoated rebar steel corrosion rate found to be high. But it coated with 2-(propan-2-ylidene) propane-1,3-diamine then corrosion rate reduced as trends clearly noticed in Table 1 and Figure 1.

Table 1: Corrosion Rates of Uncoated and Coated Rebar Steel in Saline Water

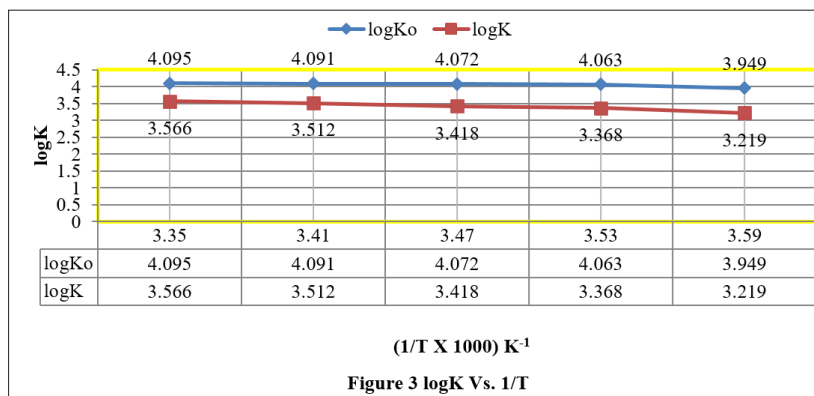
Temperature(K)	278	283	288	293	298
Concentration(mM)	2	4	6	8	10
K_o	8912	11563	11829	12324	12871
$\log K_o$	3.949	4.063	4.072	4.091	4.095
K_o/T	32.057	35.858	39.072	44.061	47.191
$\log(K_o/T)$	1.505	1.554	1.591	1.644	1.673
K	1657	2337	2622	3251	3685
$\log K$	3.219	3.368	3.418	3.512	3.566
K/T	5.961	8.257	9.104	11.095	12.365
$\log(K/T)$	0.775	0.916	0.959	1.045	1.092
$(K_o - K)$	7255	9226	9207	9073	9186
$\theta = (K_o - K / K_o)$	0.8141	0.7978	0.7362	0.7136	0.7013
$\%C$	81.41	79.78	73.62	71.36	70.13
$(1 - \theta)$	0.1859	0.2022	0.2638	0.2864	0.2987
$(\theta / (1 - \theta))$	4.379	4.945	2.791	2.491	2.347
$\log(\theta / (1 - \theta))$	0.641	0.694	0.445	0.396	0.371
$\log \theta$	-0.0893	-0.0981	-0.133	-0.1465	-0.1541
$\log C$	-2.301	-2	-1.824	-1.699	-1.602



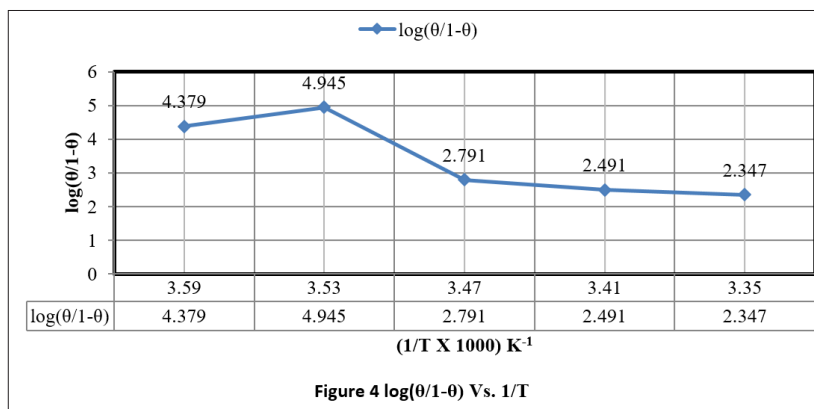
The concentrations of coating compounds increased on surface the surface of rebar and coated metal dipped into different concentrations of saline water and their results were depicted in Table. Such trends were observed in Figure2.



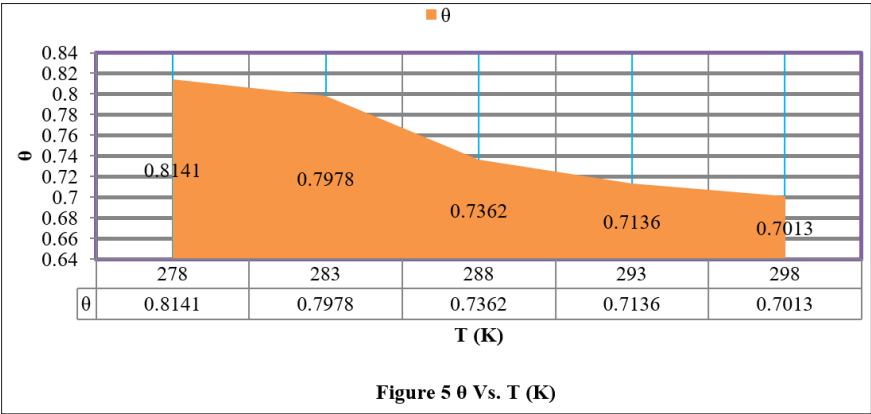
The results of logKo uncoated rebar steel and logK values coated rebar steel with 2-(propan-2-ylidene) propane-1,3-diamine at different temperatures mentioned in Table1 and Figure3. It observed that corrosion rate enhanced with uncoated metal after coating its corrosion rate decreased.



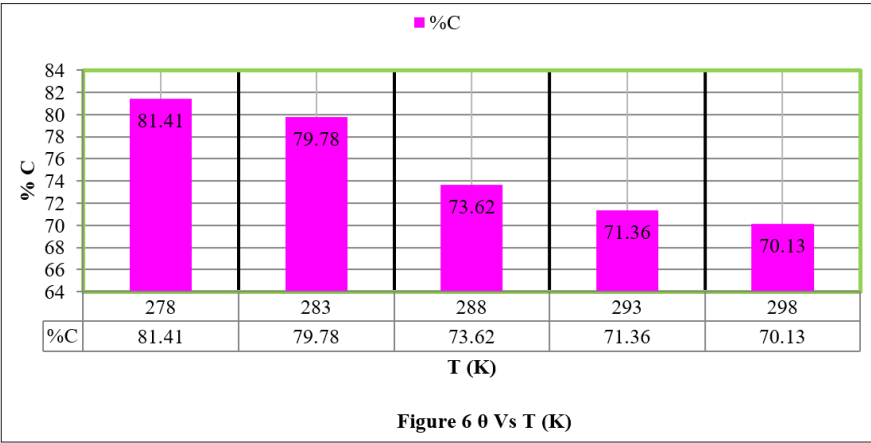
The coating compound 2-(propan-2-ylidene) propane-1,3-diamine log($\theta/1-\theta$) values at various temperatures were given in Table1. These results indicated that log($\theta/1-\theta$) decreased as temperatures enhanced which observed in Table1 and Figure4.



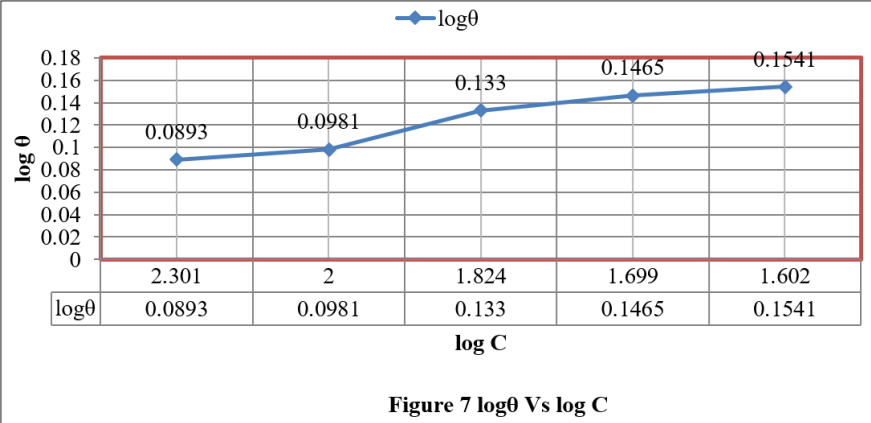
The surface coverage areas occupied by 2-(propan-2-ylidene) propane-1,3-diamine at various temperatures were written in Table1 and Figure5. It observed that at low temperature it covered more surfaces with respect of higher temperature.



The coating efficiencies of 2-(propan-2-ylidene) propane-1,3-diamine were given in Table1 at different temperatures and Figure6. These results were shown that lower temperature coating efficiencies found to be as notice at higher temperatures.



The plot between log θ versus log C found to be straight line as shown in Figure7 that line confirmed about Freundlich isotherm so coating compound 2-(propan-2-ylidene) propane-1,3-diamine adsorbed on base metal surface.



The graph plotted between θ (surface coverage area) versus log C for 2-(propan-2-ylidene) propane-1,3-diamine compound produced by straight line as noticed in Figure8 which indicated Temkin isotherm so this compound accommodated on rebar steel.

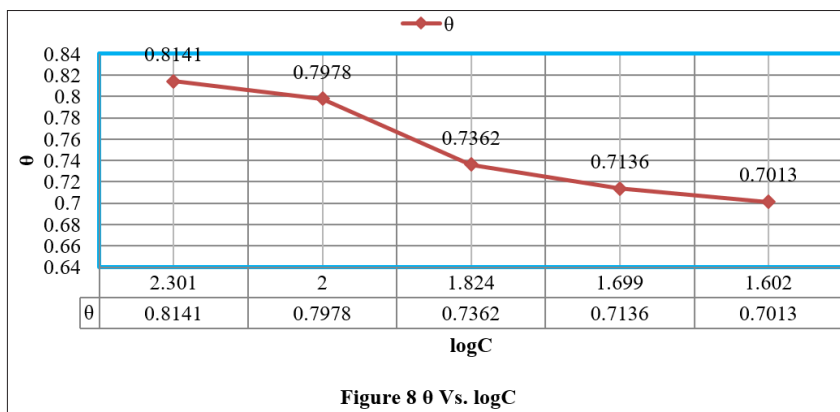
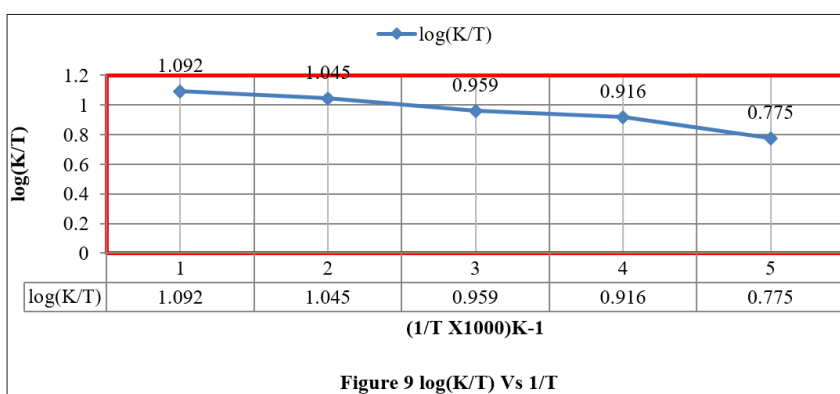


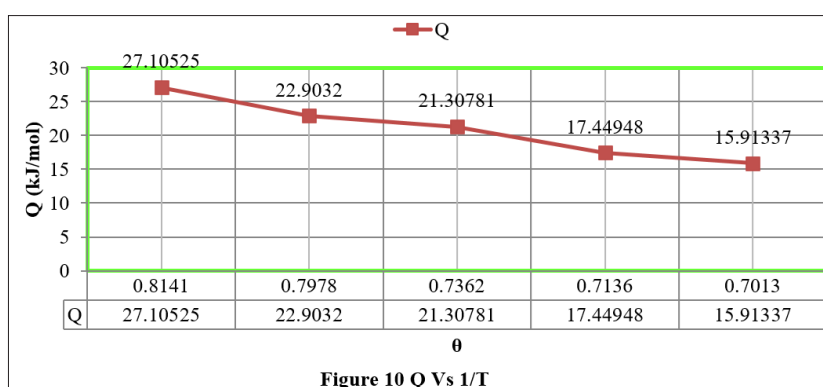
Figure9 exhibited the plot between $\log(K/T)$ versus $1/T$ found to be straight line with help of that graph calculated enthalpy of 2-(propan-2-ylidene) propane-1,3-diamine.



The coating compound 2-(propan-2-ylidene) propane-1,3-diamine activation energy, heat of adsorption, free energy, enthalpy and entropy were calculated on their absence and presence at different temperatures and concentrations in saline water medium. Their values were noticed that coating compound adhered with rebar steel by chemisorptions. Their thermal parameters values decreased after coating and surface coverage areas increased as shown in Table2 and Figure10.

Table 2: Thermal parameters of 2-(propan-2-ylidene) propane-1,3-diamine

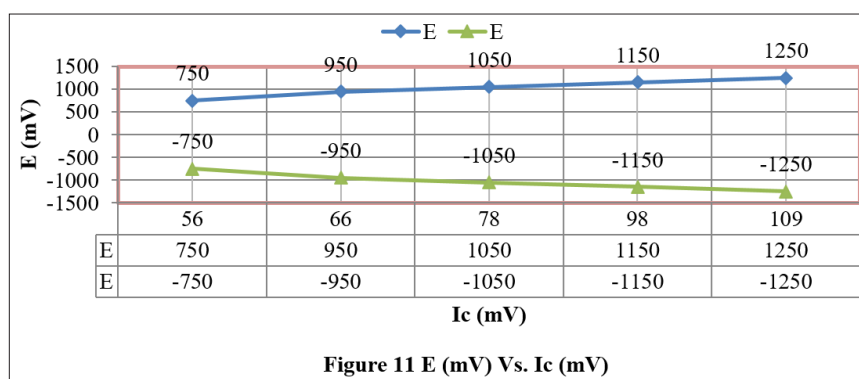
Con	2mM	4mM	6mM	8mM	10mM
T(K)	278	283	288	293	298
Eo	273.7561	276.9516	272.8472	269.3805	264.8994
E1	223.1504	229.5774	229.0255	231.255	230.6792
Q1	-27.10525	-22.9032	-21.30781	-17.44948	-15.91337
ΔG1	-338.5195	-340.5541	-338.8208	-336.629	-332.1285
ΔH1	-53.72525	-62.4385	-64.25847	-68.81022	-70.63984
ΔS1	-148.0204	-158.9127	-161.9014	-167.5284	-169.7827
θ	0.8141	0.7978	0.7362	0.7136	0.7013



Potentiostatic polarization used to determine without and with coating electrode potential and corrosion current density and their results were written in Table3. It observed that without coating electrode potential increased but its values reduced after coating with 2-(propan-2-ylidene) propane-1,3-diamine. The corrosion current enhance without coating but it values can be decreased after coating as shown in Figure11. The corrosion current density increased when rebar steel coated with 2-(propan-2-ylidene) propane-1,3-diamine as results depicted in Table3 and Figure11. The corrosion rate obtained by gravimetric method was matched with corrosion rate of potentiostat.

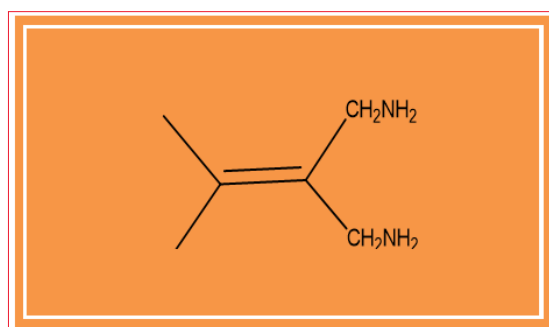
Table 3: Potentiostat Polarization Results Uncoated and Coated Rebar Steel in Saline Water

	ΔE	ΔI	R_p	ρ_a	ρ_c	$\rho_a \cdot \rho_c$	$\rho_a + \rho_c$	$\frac{\rho_a \rho_c}{\rho_a + \rho_c}$	$\Delta I / \Delta E$	I_c	K_{cr}
Co	950	625	1.52	552	401	221352	953	232	0.65	66	281
	1050	725	1.44	621	451	280071	1072	261	0.69	78	332
	1150	925	1.24	651	501	326151	1152	283	0.81	98	419
	1250	1025	1.21	700	552	386400	1252	308	0.82	109	466



Mechanism

The coating compound 2-(propan-2-ylidene) propane-1,3-diamine is highly electron rich substance. It contains two π -electrons and two amino functional groups so it forms a protective thin film barrier with base metal as shown in its structure. This protective barrier checks the attack of chloride ions.



Conclusion

The organic compound 2-(propan-2-ylidene) propane-1,3-diamine used for corrosion mitigation of rebar steel in saline water medium. This compound anticorrosive activity studied in different temperatures and concentrations. Thermal results were shown that 2-(propan-2-ylidene) propane-1,3-diamine formed chemical bonding with base metal. The protective barrier suppressed the attack of Cl^- ions and its physical, chemical and mechanical properties saline water environment. Surface adsorption theory like Langmuir, Freundlich and Temkin isotherms confirmed that 2-(propan-2-ylidene) propane-1,3-diamine adsorbed on metal by chemisorptions phenomenon. The coating produced good results of efficiency and surface coverage area.

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707/2010(SR). The author thanks other people who provided data collection and graph plotting.

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