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Research Article

Coumarin as inhibitor for Steel in Petroleum medium

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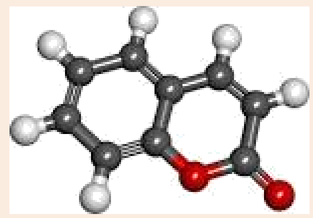
Abstract

This work involves study the corrosion inhibition of steel in petroleum medium using coumarin as inhibitor with four concentrations 10, 40, 70 and 100ppm at four temperatures over the range 323-353K. Inhibition efficiency IE% results show that coumarin gave acceptable efficiencies in petroleum medium. Polarization curves indicate that *coumarin* mixed-type inhibitor through the values of corrosion potential and Tafel slopes. The values of equilibrium constant of the adsorption-desorption process were small indicating the physically adsorption of coumarin. In general, the negative values of the change in free energy confirm the physical adsorption of coumarin. The values of activation energy in the presence coumarin were higher than in the absence of coumarin in petroleum medium except in presence 100 ppm coumarin.



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Introduction

Coumarins occupy an important place in the realm of natural products and synthetic organic chemistry. Coumarins comprise a group of natural compounds found in a variety of plant sources in the form of benzopyrene derivatives. Coumarins have important effects in plant biochemistry and physiology, as they act as antioxidants, enzyme inhibitors, and precursors of toxic substances. In addition, these compounds are involved in the actions of plant growth hormones and growth regulators, the control of respiration, photosynthesis, as well as defense against infection. Coumarins have long been recognized to possess anti-inflammatory, anti-oxidant, anti-allergic, hepatoprotective, anti-thrombotic, anti-viral and anti-carcinogenic activities.

Due to the properties of coumarin, we chose it to inhibit steel 37-2 in petroleum medium in temperatures range 323-353 K using electrochemical studies with three concentrations of coumarin 10, 40, 70 and 100 ppm.

Experimental

Materials and Reagents

Steel 37-2 was used in this work (chemical composition wt%: 0.121 C, 0.22 Si, 0.44 Mn, 0.014 P, 0.016 S, 0.041 Cr, 0.002 Mo, 0.022 Ni, 0.02 Al, 0.002 Co, 0.055 Cu and Fe remain) obtained by SpectroMAX. Cubic steel (10x10x3mm) with a square surface area (1cm^2) was used in all experiments. The specimen was mounted by hot mounting using formaldehyde (Bakelite) at 138^{o}C for 8 minutes to insulate all but one side and made a hole on one side for electrical connection and then the mounted specimens has been grinded with SiC emery papers in sequence of 400, 600, 1000, and 2000 grit to get flat and scratch-free surface and polished to mirror finish using polish cloth and alpha alumina 0.5µm and 1µ m, and then washed with distilled water, degreased with acetone.

The base electrolyte was petroleum medium obtained from Iraqi oil refinery with contents of metals: 48.67% C, 8.73% H, 0.13% N, and 0.71% S. The pH of this medium is 5.25, electrical conductivity is 300 μS/cm, and TDS 296 mg/L.

Electrochemical Measurements

Electrochemical cell was composed of platinum counter electrode, prepared steel specimen as working electrode and saturated calomel electrode (SCE) as a reference electrode according to ASTM standard cell G5-94. The electrochemical behavior of steel in inhibiting and uninhibited solution was studied by WINKING M Lab potentiostat by recording anodic and cathodic galvanodynamic polarization curves. Measurements were carried out by changing the electrode current automatically from -15 to +15 mA at scan rate 1 $mA.sec^{-1}$. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion parameters.

Results and Discussion

Figure 1 shows the galvanodynamic curves for steel 37-2 in petroleum medium at four temperatures, these curves indicate the cathodic and anodic regions. At anodic sites, oxidation of metals can occur according to the following equation:

$$Fe \rightarrow Fe^{2+} + 2e$$

While at cathodic sites, many reactions can occur. The main cathodic reduction in acidic medium is evolution of hydrogen as follows:

$$2H^{+} + 2e \rightarrow H_2$$

Figure 2 shows the Tafel plots of steel in petroleum medium in the presence of four concentrations of coumarin at four temperatures. The values of associated electrochemical parameters such as corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated from the intersection of anodic and cathodic Tafel slopes of the polarization curves as shown in **Table 1**.

The data of Table (1) shows the corrosion parameters for steel in petroleum medium in the absence and presence of coumarin, where they are indicate that corrosion potentials E_{corr} shift either to noble or active direction, i.e. coumarin behaves as mixed-type inhibitor. Corrosion current densities i_{corr} became lower values, in addition to cathodic and anodic Tafel slopes b_c&b_a shift to lower values. The later result enhances the behavior of coumarin as mixed-type inhibitor.

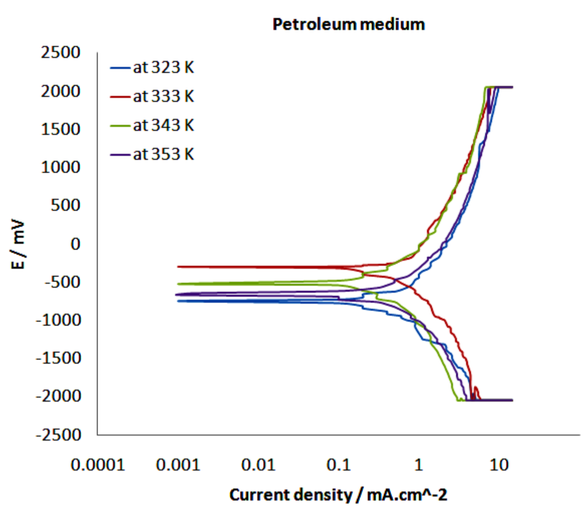

Figure 1 Tafel plot of carbon steel in petroleum medium at four temperatures

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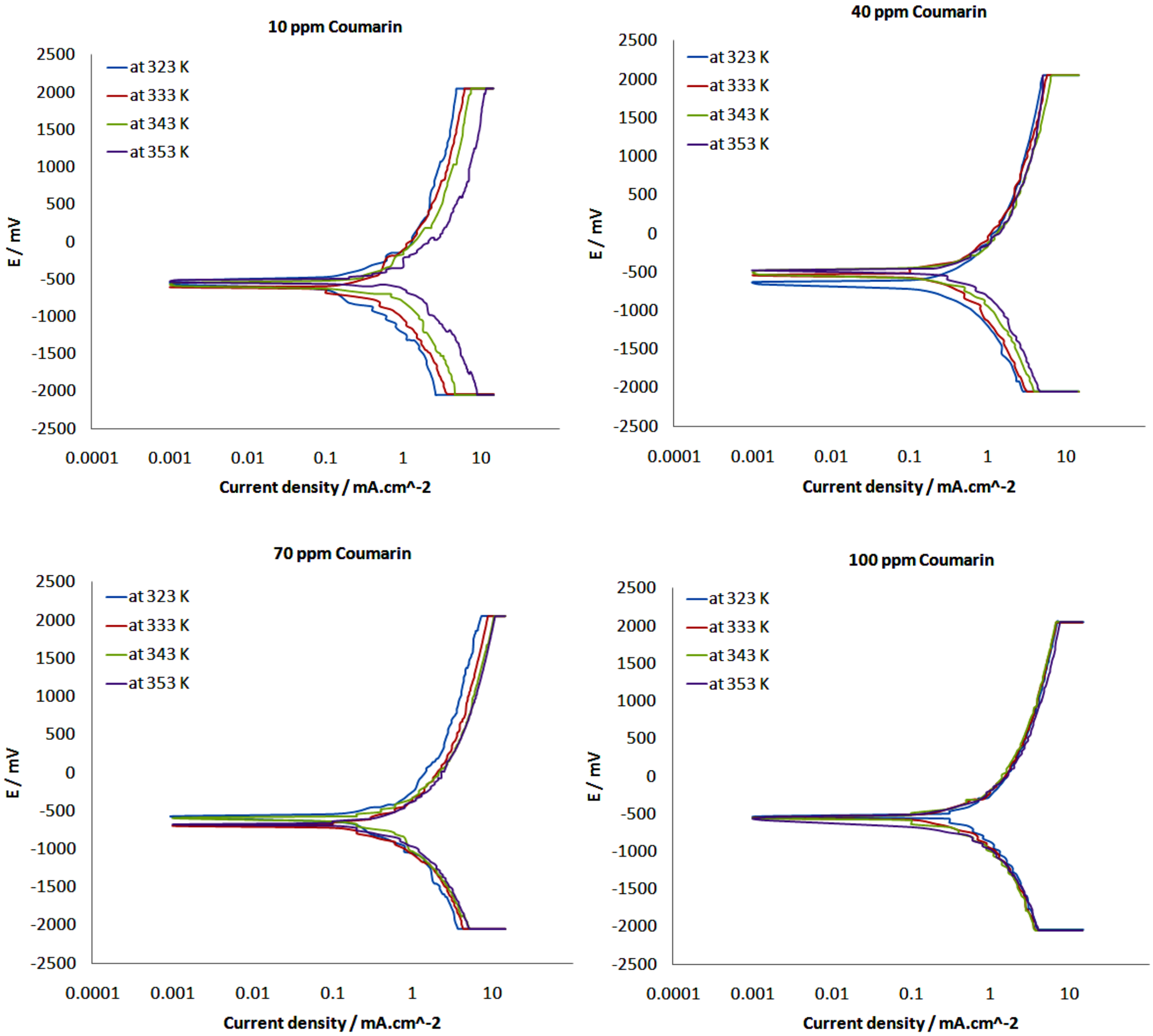

Figure 2 Tafel plots of carbon steel in petroleum medium in the presence of four concentrations of coumarin at four temperatures.

The inhibition efficiency IE (%) can be calculated using the equation given below [1]:

$$IE\% = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100$$

Where $(i_{corr})_a$ and $(i_{corr})_p$ are the corrosion current density ($\mu A.cm^{-2}$) in the absence and the presence of the inhibitor, respectively.

The values of IE% in **Table 1** are acceptable due to presence of carbonyl group (C=O) in the lactone ring of coumarin. The little efficiency due to benzene ring which shares by its electrons with carbonyl group by resonance effect. This phenomenon reduces the electronic density on oxygen atom of carbonyl group.

Table 1 Corrosion parameters for polarization of steel in petroleum medium in the absence and presence of coumarin at four temperatures

Conc. of coumarin	*Temp. K*	*E_{corr} mV*	*i_{corr} $\mu A.cm^{-2}$*	*$-b_c$ $mV.dec^{-1}$*	*$+b_a$ $mV.dec^{-1}$*	*IE%*
0	323	-759.8	497.68	1095.3	1087.7	-
	333	-322.0	682.72	1632.2	1647.9	-
	343	-496.2	694.09	2321.5	1957.9	-
	353	-665.1	719.78	1606.6	1597.8	-
10 ppm	323	-560.5	76.820	501.8	341.3	**84.56438**
	333	-636.8	256.42	665.8	938.9	62.44141
	343	-554.7	387.02	632.6	1012.7	44.24066
	353	-514.3	476.53	400.3	832.2	33.79505
40 ppm	323	-643.8	208.19	769.5	677.5	58.1679
	333	-547.9	218.52	736.6	675.0	67.99273
	343	-501.3	227.72	635.4	500.6	67.19157
	353	-478.9	331.18	725.3	744.3	53.98872
70 ppm	323	-567.8	102.51	454.0	204.5	**79.40243**
	333	-701.1	182.36	476.0	432.0	**73.28920**
	343	-599.4	222.40	457.6	396.6	67.95805
	353	-679.3	240.01	461.1	461.8	66.65509
100 ppm	323	-343.9	199.13	81.2	99.1	59.98835
	333	-358.1	289.25	92.5	108.5	57.6327
	343	-547.3	177.48	541.6	440.7	**74.42983**
	353	-552.1	224.57	653.4	494.6	68.80019

Langmuir isotherm was tested for its fit to the experimental data. The plots of *C/θ* against *C* in the presence coumarin as inhibitor at four temperatures in the range 323 – 353 K were straight lines (**Figure 3**) indicating that the coumarin obeys Langmuir adsorption isotherm which given by the following equation[2]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

where, K_{ads} is the equilibrium constant of the adsorption-desorption process, θ is the degree of surface coverage and C is concentration of inhibitor in the bulk solution. The linear regression coefficient close to unity, hence, adsorption of inhibitor followed Langmuir adsorption isotherm. R^2 values were 0.950, 0.969, 0.996 and 0.995 at 323, 333, 343 and 353K respectively. The Langmuir isotherm is based on the assumption that each site of metal surface holds one adsorbed species. Therefore, one adsorbed H_2O molecule is replaced by one molecule of the inhibitor adsorbate on the steel surface. The apparent free energy of adsorption (ΔG^o_{ads}) is calculated from the following relation [2]:

$$\Delta G^o_{ads} = -2.303RT\ log55.5\ K_{ads}, \quad where\ K_{ads} = \frac{\theta}{C(1-\theta)}$$

The values of K_{ads} and ΔG^o_{ads} are shown in **Table 2**.

The negative values of ΔG^o_{ads} indicated the spontaneous adsorption of coumarin. The values of K_{ads} are relatively small indicating that the interaction between the coumarin molecules and steel surface is physically adsorbed. This is also supported by lower negative (ΔG^o_{ads}) values.

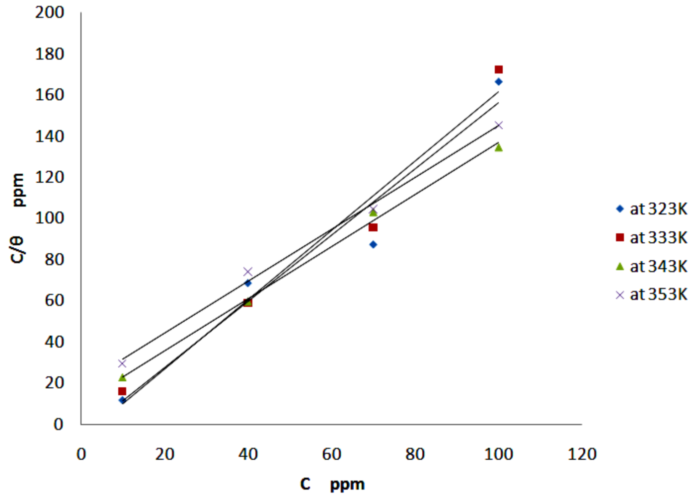

Figure 3 Langmuir adsorption plots for steel in petroleum medium with different concentrations of *Coumarin* at four temperatures.

Table 2 Thermodynamic function for adsorption of *coumarin* in petroleum medium

Conc.	*Temp. K*	R^2	K_{ads}	ΔG^o_{ads}/kJ.mol^{-1}
10 ppm	323	0.950	0.547852	-9.171
	333		0.166251	-6.153
	343		0.079342	-4.228
	353		0.051046	-3.057
40 ppm	323	0.969	0.034763	-1.765
	333		0.053107	-2.993
	343		0.051200	-2.979
	353		0.029335	-1.431
70 ppm	323	0.996	0.055071	-3.001
	333		0.039197	-2.152
	343		0.030299	-1.482
	353		0.028557	-1.352
100 ppm	323	0.995	0.014993	0.494
	333		0.013603	0.778
	343		0.029108	-1.368
	353		0.022051	-0.593

The activation energies (E_a^*) for the corrosion process in absence and presence of *Tobacco* extract was evaluated from Arrhenius equation [3]:

$$\log C_R = \log A - \left[\frac{E_a^*}{2.303\ RT}\right]$$

Where, C_R is the corrosion rate and represents corrosion current densities, A is the constant frequency factor and E_a^* is the apparent activation energy, R is the gas constant (8.314 $J.mol^{-1}K^{-1}$) and T is the absolute temperature. By plotting of logarithm of the corrosion rate of steel in petroleum medium in absence and presence of coumarin versus the reciprocal of absolute temperature range (323 – 353 K), give straight lines with slope equal to ($-E_a^*/2.303R$) as represented in **Figure 4**. The data of activation energy are listed in **Table 3** which demonstrate that, the presence of coumarin in petroleum medium increase the values of E_a^* comparing to its unhibited except in the presence of 100ppm coumarin. Adsorption of the organic molecules occurs as the interaction energy between molecule and metal surface is higher than that between the H_2O molecule and the metal surface. The protection efficiency and the degree of surface coverage θ change with temperature [4].

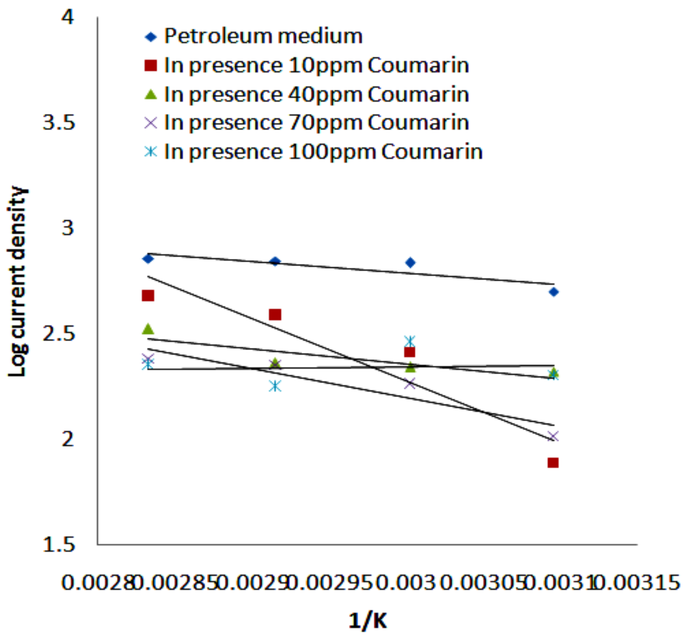

Figure 4 Arrhenius plots of the corrosion rate for steel in petroleum medium in absence and presence of coumarin.

Table 3 Activation energies for adsorption of coumarin in petroleum medium

Extract	***Conc./ppm***	***E_a^*/ kJ.mol^{-1}***
Petroleum medium	-	10.80494
Coumarin	10	56.34778
	40	13.40651
	70	26.34758
	100	2.308426

Conclusions

Corrosion inhibition properties for steel in petroleum medium has been investigated using coumarin with four concentrations 10, 40, 70 and 100 ppm at four temperatures over range 323 – 353 K. Coumarin gave acceptable efficiencies by physical adsorption as predicted through the values of equilibrium constant of the adsorption-desorption process and the change in free energy. The activation energies of adsorption of coumarin were increased except in presence of 100ppm compared with uninhibited medium.

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