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Corrosion inhibition and adsorption properties of resorcinol with Br - for the corrosion of mild steel in 0.5M H2SO4

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Abstract
Resorcinol as a inhibitor and its adsorption properties with Br- for the corrosion of mild steel were studied using thermometric, gasometric and wight loss monitoring corrosion. The results shows that resorcinol inhibited the corrosion process of mild steel. The inhibitor was found to function by being adsorbed on the surface of mild steel. Resorcinol shows synergism with Br- ion and inhibition increases with concentration of Br- with resorcinol. The adsorption of the resorcinol followed the Langmuir adsorption isotherm. Kinetic and thermodynamic parameters also measured and discussed.

Keywords: corrosion inhibition, mild steel, adsorption

1. Introduction

Acids like HCl and H2SO4 are commonly used in the petrochemical and gas industry for various objective like descaling, pickling and stimulation treatments of gas/oil producer or water injector wells. All of such process exposes metal surfaces in various equipment, such as mixture make up container, pumps, coiled tubing and casing, to severe corrosion, resulting in destroying of the metal parts and other associated other problems also. So that, it is important to control corrosion by the use a proper inhibitor in corrosion system. In general organic molecule used as corrosion inhibitor having hetero atoms in its aromatic or a long carbon chain use as efficient inhibitors in H2SO4 solution [1-10, 30-32]. Those organic molecule containing both sulphur and nitrogen atoms can serve excellent corrosion protection compared with compounds containing either sulphur or nitrogen [1, 2, 11]. On the other hand, triazoles (heterocyclic compounds containing S and N) have been reported as an effective corrosion inhibitors [7-9, 12-14]. The efficiency of such corrosion inhibitor could be increased by synergism; adding a low cost species to the inhibitor for improving the adsorption of the organic inhibitor via the formation of a bridge; a previously adsorbed inorganic anions increased the chance of adsorption of positively charged inhibitors increasing the inhibition efficiency. Synergistic inhibition is also an effective means to improve the inhibitive effect of an inhibitor via enhancing its adsorption through ion-pair interactions, to decrease the extent of usage, to diversify the use of an inhibitor [15-20]. In this work the inhibition efficiency of resorcinol on the corrosion of mild steel in 0.5 M H2SO4 is studied. Also the synergistic action of Br- on the corrosion inhibition of steel by resorcinol is studied.

2. Experimental

2.1 Mild steel sample

Tests were done on mild steel of the composition having (wt. %): 0.08% C, 0.26% Mn, 0.08% Si, 0.014% S, 0.025 % P and the rest iron. Samples of 4x4 cm^2 were used.

2.2. Inhibitor

Resorcinol as inhibitor with Br- was used.

2.3. Solutions

The solution of 0.5 M H2SO4 was prepared by 98% H2SO4. Stock solutions of resorcinol and Br- were prepared in 0.5 M H2SO4 and the required concentrations were made by appropriate dilution.

3. Methodology

Inhibition action of a resorcinol in the with and without of Br- as corrosion inhibitor intensifiers was investigated for mild steel in 0.5 M H2SO4 acid solutions. Potassium Br- was used at a concentration of 10^{-3} M to 10^{-1} for corrosion tests. Various tests were performed on the mild steel coupons for most of the investigation carried out in this study.

3.1 Gasometric method

Hydrogen gas evolution experiment were carried out at 298 K as explained in literature [12]. From the amount of hydrogen gas in term of volume evolved per minute corrosion rate (CR), and degree of surface coverage, inhibition efficiency (%I), were calculated using following equations 1, 2 and 3, respectively.

$$P\% = \left(1 - \frac{V'}{V0}\right) x100 \quad (1)$$

where V' is the volume of H_2 gas at time t for solution with inhibitor and Vo is the volume of H_2 gas evolved at time t for blank solution.

$$CR = \left(\frac{\Delta V}{t}\right) \quad (2)$$

Where ΔV is the volume of H_2 gas evolve at time t.

3.2 Thermometric method

Eddy and Ebenso [13] describe temperature based method for corrosion rate. By the increase in temperature per unit of time, the reaction number (RN) and inhibition efficiency were calculated using following equations 4 and 5.

$$RN(^{o}C/min) = \left(\frac{Tm - Ti}{t}\right) \quad (4)$$

$$I\% = \left(\frac{RNab - RNpr}{RNab}\right) x100 \quad (5)$$

where

RN_{ab} is the reaction number in the without inhibitors, and RN_{pr} is the reaction number of 0.5 M H2SO4 with resorcinol as inhibitor.

3.3. Mass Loss Measurements

In the mass loss experiment, four glass vessel of capacity 250mL were labeled A to D, each vessel contain 0.5M H2SO4 solution. The first vessel was taken as blank while each of the three remaining vessel contained the inhibitor at different concentrations all placed at normal temperature (about 298K). The mild steel coupons were immersed in the solutions taken for experiment with lass hanger and monitored after 6-6 hours. The mass of the coupons were noted before immersion. After every immersion time of 45 hours, the specimens were taken out, clean with emery papers, washed with double distilled water, degreased by acetone, dried in dry air, and again weighed. From the initial and final mass of the coupons, the loss of mass was calculated, and the corrosion rate (cm/hr) was computed from the following equation [13, 14]:

$$CR = \Delta W/At\rho \quad (6)$$

Where W is the mass lost (grams), A is the surface area of the coupon (cm2), ρ is the density (g/cm3), t is the period of exposure (hours)

The surface coverage (θ) and inhibition efficiency were calculated from the weight loss values according to the equation 2 and 3, respectively. Fig 2 shows the corrosion rate and inhibition efficiency in different concentration of the resorcinol and it is clear that the corrosion rate decreases and % IE increases with the inhibitor concentration.

$$\theta = 1 - \left(\frac{CRpr}{CRab}\right) \quad (7)$$

And

$$\%IE = \theta \times 100 \quad (8)$$

Where CR_{pr} and CR_{ab} are the rates of corrosion in the presence and absence of resorcinol, respectively. It can be noticed that the inhibition efficiency increased and that of corrosion rate decreased as we increased the concentration of inhibitor.

4. Results and discussions

Fig. 1 shows the plot of variation of weight loss and volume of hydrogen gas evolution with concentration of inhibitor during the corrosion process of mild steel in 0.5 M H2SO4 with various concentrations of inhibitor. It was also observed that the addition of resorcinol to the corrodent led to a reduction in weight loss compared to that of the blank. This indicates that resorcinol inhibited the corrosion of mild steel in H2SO4. This is also observe that addition of Br- produce synergistic effect to media and a mix type inhibition takes place in acidic medium.

Table 1: Mass Loss, Evolved Hydrogen Gas For Mild Steel Corrosion In 0.5 M H2SO4 In Presence And Absence Of 0.1M resorcinol with Different Concentration Of Br^-.

Conc.	blanck	0.1M	0.1M+0.001	0.1M+0.01	0.1M+0.1M
ΔW	4.74	4.52	2.6	2.35	1.63
ΔV	3.54	3.21	1.94	1.76	1.22

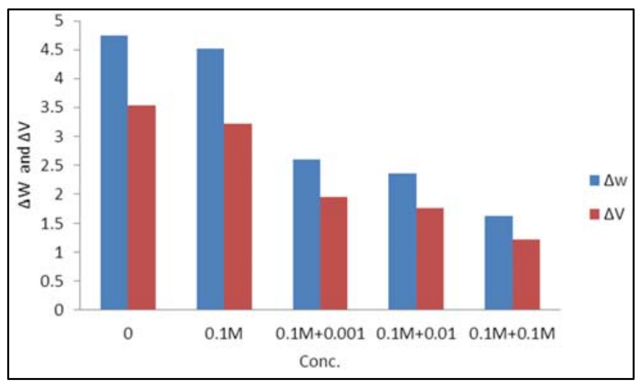

Fig 1: Mass Loss Values And Volume Of Hydrogen Gas Evolved For Mild Steel Corrosion In 0.5 M H2SO4 In Presence And Absence Of 0.1M resorcinol with Different Concentration Of 0.001 to 0.1M Br^- At 298 k.

Table 2: Corrosion Rate value, Inhibitor Efficiency and Surface Coverage for Mild Steel Corrosion In 0.5 M H2SO4 In presence and Absence of Various Concentration of Mixed Inhibitor.

conc.	CR(mm/yr)	P	θ
0	37.92	---	---
0.1M	36.44	3.92	0.03
0.1M+0.001	20.92	44.8	0.44
0.1M+0.01	18.92	50.11	0.5
0.1M+0.1M	13.13	65.35	0.65

It is clear from table no. 2 that the with concentration of inhibitor inhibition efficiency increases and corrosion rate decreases. The maximum value of inhibition efficiency reported was 65.35 %**.** It could be considered that Resorcinol with Br- act as inhibitor of mild steel to 0.5M sulphuric acid solution.

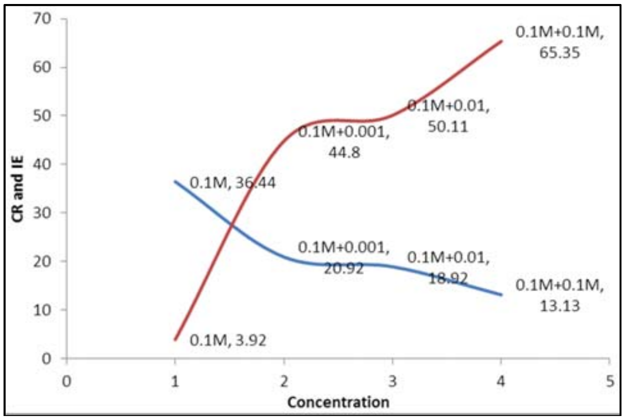

Fig 2: Corrosion Rate and Inhibitor Efficiency for Mild Steel Corrosion In 0.5 M H2SO4 In Presence of Different Concentration of Inhibitor.

Corrosion rates and values of inhibition efficiency (%I) obtained from weight loss, thermometric and gasometric method are recorded in Table 3. The results shows that efficiency of inhibitor obtained from weight loss measurement are close than those obtained from gasometric and thermometric methods. However, data obtained from thermometric and gasometric methods strongly correlated with those obtained from mass loss measurements, confirming that resorcinol is a good inhibitor for the corrosion of mild steel in H2SO4.

Table 3: Values of inhibition efficiency and rate of corrosion for the inhibition of the corrosion of mild steel at various concentrations of resorcinol and Br-.

Gasometric		Thermometric		Mass Loss	
CR(cm3/min)	%IE	RN(C/min)	%IE	CR(mm/yr)	%IE
17.7	--	0.05	--	37.92	--
16.05	9.32	0.048	3.79	36.44	3.92
9.7	45.19	0.029	41.3	20.92	44.8
8.8	50.28	0.024	51.19	18.92	50.11
6.1	65.53	0.016	66.72	13.13	65.35

3.3. Adsorption Isotherm behavior

In this experiment the value of the correlation (R^2) is 0.961, used to find out the best fit isotherm obtained by Langmuir.

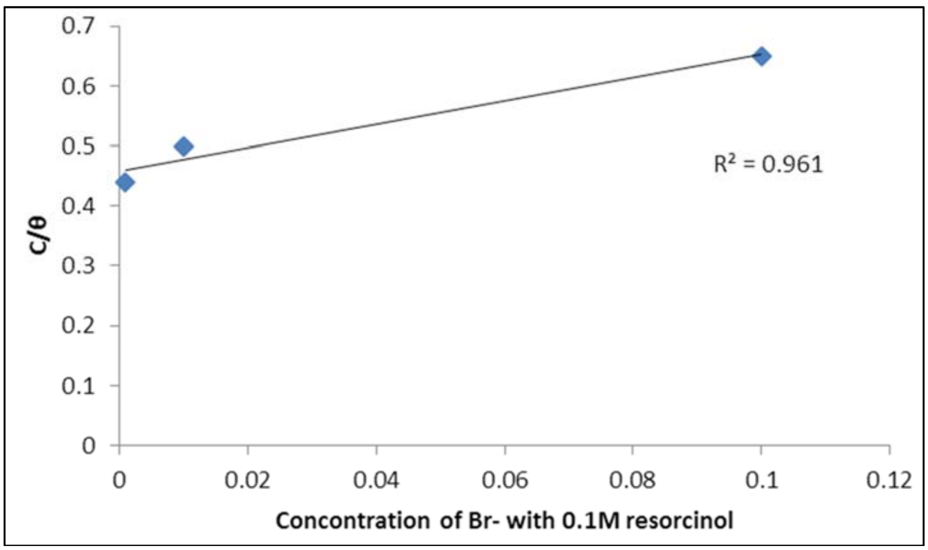

Fig 3: Langmuir Adsorption Isotherm of Br^- with 0.1M Resorcinol on Mild Steel In 0.5 M H2SO4

The Langmuir isotherm, which is given in Equation 9. Langmuir isotherm generally used to find the equilibrium constant k. Equation gives the relationship between surface coverage and the inhibitor concentration.

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (9)$$

Where C is the concentration of inhibitor, θ is the surface coverage. Figure 3 shows that a plot of c/ θ versus c yields a straight line with R^2 = 0.961. The plot obeys Langmuir adsorption isotherm, is the plot has linearity and having good correlation coefficient. The R^2 values are very close to unity, tells the high adherence to Langmuir adsorption isotherm. From equation 9 the value of rate constant K is found to be 2.27. Gibb's free energy of adsorption was calculated by using equation 10.

$$\Delta G = - RTln(55.5k) \qquad (10)$$

Where R is the universal gas constant (8.314 kJ/mol); and T is the absolute temperature. The value of ΔG_{ads} for the resorcinol (and Br-) on the surface of mild steel is given -11.97 kJ/mol since ΔG_{ads} is below 40 kJ/mol, it suggest that the adsorption is physisorption. The negative value of ΔG_{ads} indicate spontaneous adsorption of the mixed inhibitor [21-24] on the steel surface.

3.4. Synergism

The adsorption of a anionic inhibitor generally enhanced by increasing of negative charge density on the surface of metal. Therefore the pre-adsorption of a bromide ions could enhance the adsorption of the cationic inhibitor due to ion–pair interactions between the molecules and the bromide ions, resulting in what is the so-called inhibition synergism. Synergism parameter is given by equation 8.

$$S_\theta = 1-\theta_{1+2} / 1-\theta'_{1+2} \ldots\ldots\ldots\ldots (8)$$

Table 4: S_θ value of Br^- at 0.1M Resorcinol.

Acid/Resorcinol system	Br-	CR(mm/yr)	θ	S_θ
Blank	nil	37.92		
0.1M	nil	36.44	0.03	
Blank	0.1M	27.16	0.28	
0.1M	0.1M	13.13	0.65	1.99

Where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$; θ_1 and θ_2 are the degrees of surface coverage in the presence of the bromide ion and the inhibitor, respectively, and θ'_{1+2} is the degree of surface coverage in the presence of both species. The S_θ values are found to be 1.99, suggesting a real synergistic action of Br- ion with the inhibitor. The above results suggest that resorcinol can act as an effective inhibitor in the presence of Br- ions.

3.5 Thermodynamic and kinetic parameters:

Effect of temperature on the inhibition efficiency was studied in the temperature range of 298 K,308K and 318 K in 0.5 M H2SO4 both in the absence and presence of inhibitor. Values of corrosion rate, surface coverage and %*P* are listed in table 5.

Table 5: Corrosion Data of Mild Steel In 0.5 M H2SO4 Solution Without And With different Concentration of Inhibitor and Br- at the Temperature 298k, 308K and 318k For 2 days.

	298K			308K			318K		
Concentration	CR(mm/yr)	θ	P	CR(mm/yr)	θ	P	CR(mm/yr)	θ	P
blank	37.92	---	---	73.18			146.13		
0.1M	36.44	0.03	3.92	71.14	0.02	2.78	143.12	0.02	2.05
0.1M+0.001	20.92	0.44	44.8	40.66	0.44	44.43	78.68	0.46	46.15
0.1M+0.01	18.92	0.5	50.11	39.32	0.46	46.26	74.91	0.48	48.73
0.1M+0.1M	13.13	0.65	65.35	27.65	0.62	62.21	55.37	0.62	62.1

It is clear from above data that the protection efficiency decreases at high temperature. The decrease in %*P* with temperature at high concentration of Br- shows that physical adsorption is the predominant [33, 34]. The energy of activation was calculated from the Arrhenius plots as shown in Fig. 4.

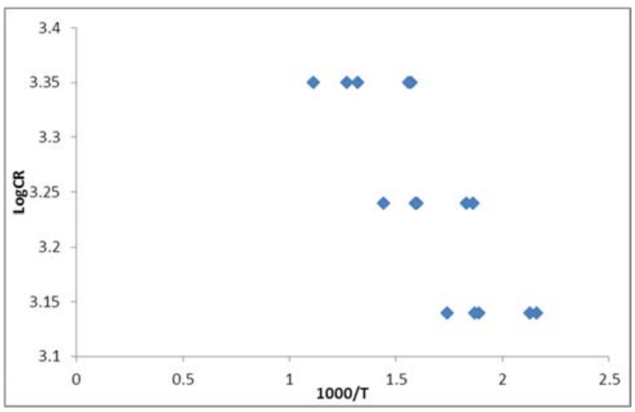

Fig 4: Arrhenius Plots of log CR Versus 1/T At Different Concentration Of Resorcinol.

The activation energy (*E*a) for the corrosion of given steel in the presence and absence of different concentrations of resorcinol and bromides, were calculated using Arrhenius-type equation:

$$CR=A\ exp(-Ea/RT)..................(6)$$

Where *E*a is the activation energy for corrosion process; *R* is the universal gas constant; *A* is the Arrhenius pre exponential factor, *T* is the absolute temperature and *CR* is corrosion rate. The data obtained in Tables 5 shows that the addition of inhibitor leads to an increase in the activation energy *E*a and enthalpy of reaction Δ*H* to values greater than that of the solution without inhibitor. Most of the times, the average difference value of the *E*a − Δ*H* is 2.55 kJ/mol which tells that the process of corrosion is a unimolecular reaction as described by the known perfect gas equation [23]:

$$Ea - \Delta H = RT.....................(5)$$

It is clear that positive sign of the enthalpies shows endothermic nature of the metal dissolution process. The presence of resorcinol (and Br-) tested suggest that the corrosion process becomes more endothermic when compared with blank.

Table 6: Activation Energy and Enthalpy of Corrosion process of Mild Steel In 0.5 M H2SO4 Solution in Absence and Presence of Inhibitor and Br-.

Concentration	Blank	0.1M	0.1+0.001M	0.1M+0.01M	0.1M+0.1M
Eact	50.15	51.03	50.69	55.8	56.81
Δ H (KJ/mol)	40.6	48.48	48.14	53.25	54.26

4. Conclusion

From the above study the following points were concluded;

1. Resorcinol and Br- act as a mixed inhibitor for the corrosion of mild steel in 0.5 M H2SO4 and it retarded both cathodic and anodic corrosion to different extents.
2. Protection efficiency of Resorcinol was increased by adding bromide ions due to co-operative adsorption of the inhibitor and halide ions.
3. Adsorption of resorcinol and Br- on the surface of mild steel is spontaneous and occurs by physical adsorption.
4. Temperature effect suggest that mixture of resorcinol and Br- exhibits constant efficiency until 318 K which is recommended for industrial use.

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