

Synergistic Effect of I⁻ on the Corrosion Inhibition of Low carbon Steel in Sulphuric Acid by a Acyl Azide: Kinetics and Thermodynamic Studies

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Abstract:

Acyl Azide as a inhibitor and its adsorption properties with I⁻ for the corrosion of low carbon steel were studied using gasometric weight loss, thermometric monitoring corrosion. The results shows that Acyl Azide inhibited the process of corrosion of low carbon steel. The Acyl Azide was found to function by being adsorbed on the surface of low carbon steel. Acyl Azide shows synergism with I⁻ and inhibition increases with concentration of I⁻ with Acyl Azide. The adsorption of the Acyl Azide followed Langmuir adsorption isotherm. Thermodynamic and kinetic parameter also measured and discussed.

Keywords: low carbon steel, adsorption, corrosion inhibition,

- 1. Introduction:** Acids like hydrochloric acid and sulphuric acid are most commonly used in many petrochemical and gas industry for various objective like descaling, pickling and stimulation treatments of oil/gas 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 inhibitor in sulphuric acid 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 inhibitor [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 inhibitor 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 Acyl Azide on the corrosion of Low carbon steel in 0.5 M sulphuric acid is studied. Also the synergistic action of I⁻ on the corrosion inhibition of steel by Acyl Azide is studied.

2. Experimental

2.1 Low carbon steel sample

Tests were done on Low carbon steel of the composition having (wt. %): 0.09% C, 0.27% Mn, 0.07% Si, 0.015% S, 0.026 % P and the rest of iron. Samples metal of 4x4 cm² were used.

2.2. Acyl Azide

Acyl Azide as Acyl Azide with I⁻ was used.

2.3. Solutions

The solution of 0.5 M sulphuric acid was prepared by 98% sulphuric acid. Stock solutions of Acyl Azide and I⁻ were prepared in 0.5 M sulphuric acid and the required concentrations were made by using appropriate dilution.

3. Methodology

Inhibition action of a Acyl Azide in the with and without of I⁻ as corrosion Acyl Azide intensifiers was investigated for Low carbon steel in 0.5 M SULPHURIC ACID acid solutions. Potassium Iodide was used at a concentration of 10⁻³ M to 10⁻¹ for various corrosion tests. Various tests were performed on the Low carbon steel coupons for most of the investigation that carried out in this study.

3.1 Gasometric method

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

$$P\% = \left(1 - \frac{V'}{V_0}\right) \times 100 \quad (1)$$

where V' is the volume of hydrogen gas at time interval t for solution with Acyl Azide and V₀ is the volume of hydrogen gas evolved at time interval t for blank solution.

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

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

3.2 Thermometric method

Ebenso and Eddy [13] describe temperature based method for determination of rate of corrosion. By the change(increasing) in temperature per unit of time, the reaction number (RN) and inhibition efficiency were calculated using equations 3 and 4 given below:

$$RN(^{\circ}C/min) = \frac{T_{fin}-T_{in}}{t} \quad (3)$$

$$P\% = \left(\frac{RN_{ab}-RN_{pr}}{RN_{ab}}\right) \times 100 \quad (4)$$

where RN_{ab} is reaction number in without Acyl Azides, and RN_{pr} is reaction number of 0.5 M sulphuric acid with Acyl Azide as Acyl Azide.

3.3. Weight Loss Measurements

In the weight loss experiment, four glass container of capacity 250mL were labeled A to D, each container contain 0.5M sulphuric acid solution. The first container was taken as blank while each of the three remaining container contained the Acyl Azide at different concentrations all placed at normal temperature (about 300K). The Low carbon steel coupons were immersed in the solutions taken for experiment with lass hanger and monitored after 5-5 hours. The weight of the coupons were noted before each immersion. After each immersion time of 2 days, all specimens were taken out, clean each with emery papers, washed with doubly distilled water and degreased by acetone, dried in hot dry air and reweighed. From the value of initial and final weight of each coupons, weight loss was calculated, and the corrosion rate (cm/hr) was computed from the equation given [13, 14]:

$$CR = \Delta W / A t \rho \quad (5)$$

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

The value of surface coverage (θ) and inhibition efficiency were calculated from the weight loss values according to equation 6 and 7, respectively. Fig 2 expresses the corrosion rate and inhibition efficiency in verious concentration of Acyl Azide and it is clear that the rate of corrosion decreases and % IE increases with the Acyl Azide concentration.

$$\theta = 1 - \frac{CR_{pr}}{CR_{ab}} \quad (6)$$

And

$$\%IE = \theta \times 100 \quad (7)$$

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

4. Results and discussions

Fig. 1 shows the plot of change in weight loss and volume of hydrogen gas evolution with various concentration of Acyl Azide during the corrosion process of Low carbon steel in 0.5 M sulphuric acid with various concentrations of Acyl Azide. It was also observed that the addition of Acyl Azide to the corrodent led to a reduction in weight loss compared to that of the blank. This indicates that Acyl Azide inhibited the corrosion of Low carbon steel in sulphuric acid. This is also observe that addition of I- produce synergistic effect to media and a mix type inhibition takes place in acidic medium.

Table 1: Weight Loss, Evolved Hydrogen Gas For Low carbon Steel Corrosion In 0.5 M Ssulphuric acid In Presence And Absence Of 0.1M Acyl Azide with Different Concentration Of I - .

Conc	blank	0.1M	0.1M+0.001M	0.1M+0.01M	0.1M+0.1M
ΔW_{gm}	4.82	4.66	3.36	2.12	1.56
Δv_{lit}	2.91	2.82	2.03	1.28	0.94

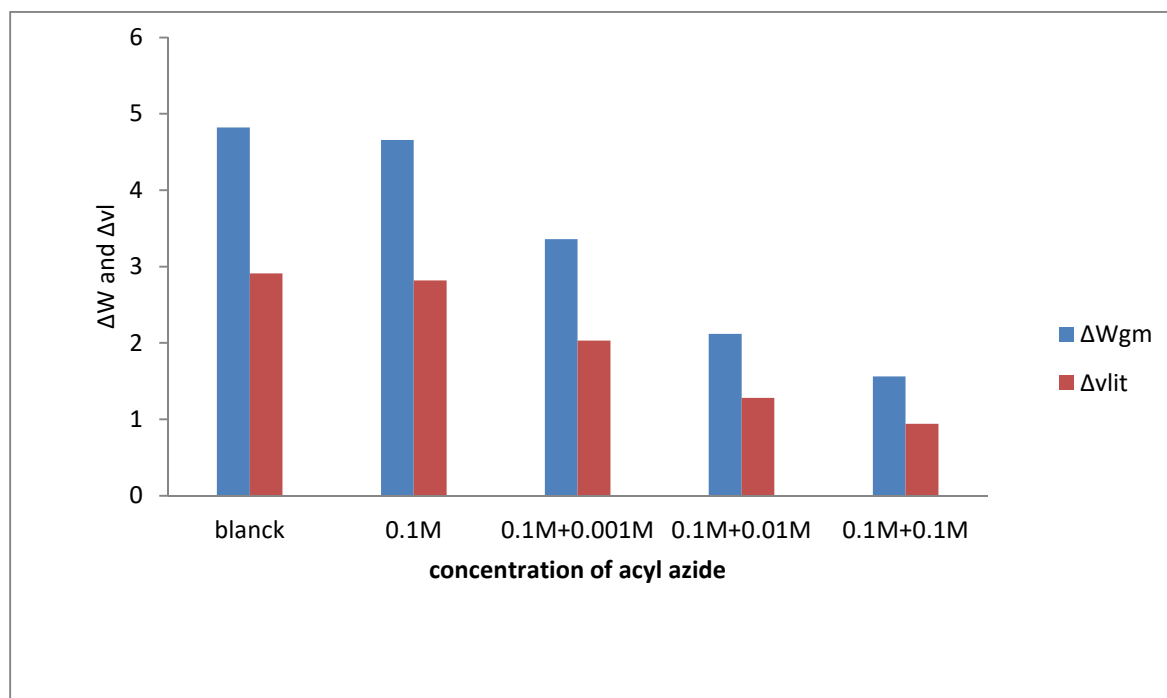


Fig 1: Weight Loss Values And Volume Of Hydrogen Gas Evolved For Low carbon Steel Corrosion In 0.5 M sulphuric acid In Presence And Absence Of 0.1M Acyl Azide with Different Concentration Of 0.001 to 0.1M I - At 298 k.

Table 2: Corrosion Rate value, Acyl Azide Efficiency and Surface Coverage for Low carbon Steel Corrosion In 0.5 M sulphuric Acid In presence and Absence of Various Concentration of Mixed Acyl Azide.

Conc	CRmm/yr	φ	P
blanck	39.08		
0.1M	37.77	0.03	3.35
0.1M+0.001M	27.25	0.3	30.27
0.1M+0.01M	17.17	0.56	56.06
0.1M+0.1M	12.62	0.67	67.7

It is clear from table no. 2 that the with concentration of Acyl Azide inhibition efficiency increases and corrosion rate decreases. The maximum value of inhibition efficiency reported was 67.70 %. It could be considered that Acyl Azide with I- act as Acyl Azide of Low carbon steel to 0.5M sulphuric acid solution.

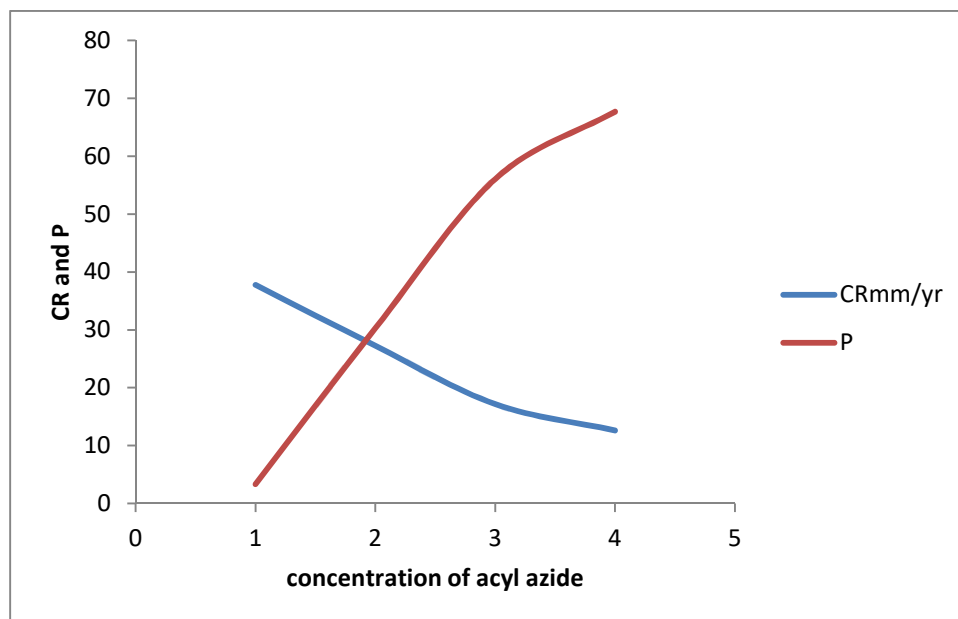


Fig 2: Corrosion Rate and Inhibitor Efficiency for Low carbon Steel Corrosion In 0.5 M SULPHURIC ACID In Presence of Different Concentration of Acyl Azide.

Rate of corrosion and inhibition efficiency (%I) obtained from weight loss, thermometric and gasometric method are reported in following table 3. The results tells that efficiency of Acyl Azide obtained from weight loss measurement are nearly close than those obtained from gasometric and thermometric methods. However, data obtained from thermometric and gasometric methods strongly correlated with those obtained from weight loss measurements,

confirming that Acyl Azide is a good Acyl Azide for the corrosion of Low carbon steel in sulphuric acid.

Table 3: Values of inhibition efficiency and rate of corrosion for the inhibition of the corrosion of Low carbon steel at various concentrations of Acyl Azide and I-

Conc	CR(cm3/min)	P	RN(C/min)	P	CRmm/yr	P
0	2.91		0.058		39.08	
0.1M	2.82	3.09	0.053	8.62	37.77	3.35
0.1M+0.001M	2.03	30.24	0.035	39.65	27.25	30.27
0.1M+0.01M	1.28	43.98	0.026	55.17	17.17	56.06
0.1M+0.1M	0.94	67.69	0.018	68.96	12.62	67.7

3.3. Adsorption Isotherm behavior:

The value of the correlation (R^2) in this experiment is 0.99, used to find out the best fit isotherm obtained by Langmuir by thermomeric method.

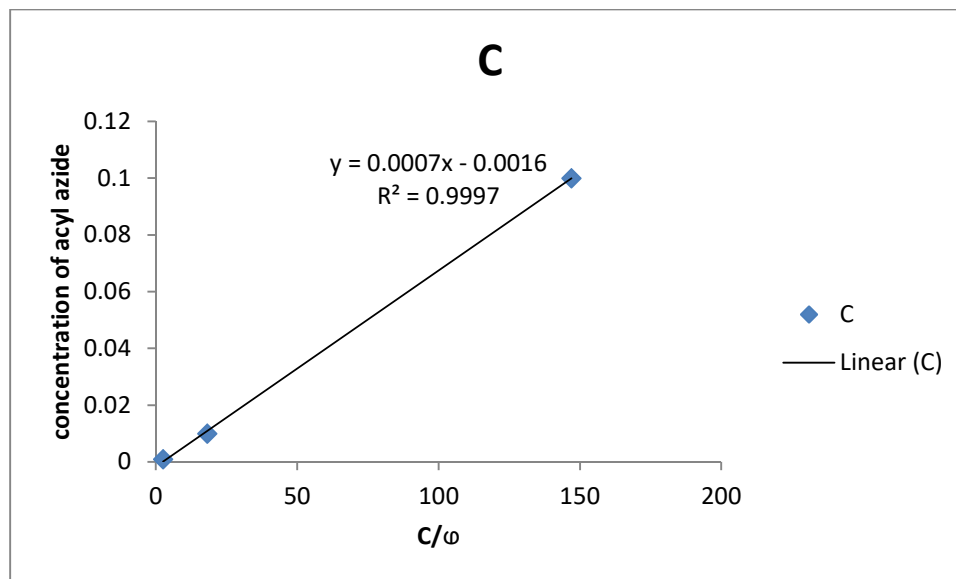


Fig 3: Langmuir Adsorption Isotherm of I- with 0.1M Acyl Azide on Low carbon Steel In 0.5 M sulphuric acid.

The Langmuir isotherm is most commonly used to find out equilibrium constant k . Equation given below shows the relationship between total surface coverage and the Acyl Azide concentration.

$$\frac{c}{\theta} = \frac{1}{K} + C \quad 8$$

Where C is the concentration of Acyl Azide, θ is total surface coverage. Figure 3 tells that a plot of c/θ versus c yields a straight line with $R^2 = 0.999$. This plot follows Langmuir adsorption isotherm, is the plot has linearity and having very good correlation coefficient. The R^2 values are nearly unity, tells a good adherence to Langmuir adsorption isotherm. From equation 9 the value of rate constant K is found to be 21.25. Gibb’s free energy of adsorption was calculated with the help of equation 10.

$$\Delta G = - RT\ln(55.5k) \quad (10)$$

Where R is universal gas constant having value 8.314 kJ/mol; and T is the absolute temperature(300K). The value of ΔG_{ads} for the Acyl Azide (and I-) on the surface of Low carbon steel is given -17.63 kJ/mol. ΔG_{ads} is below 40 kJ/mol, it indicated that the adsorption is physisorption. The negative value of ΔG_{ads} indicate spontaneous adsorption of the mixed Acyl Azide [21-24] on the steel surface.

3.4. Synergism:

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

$$S\theta = 1-\theta_1+2 / 1-\theta_1+2..... (8)$$

Acid/Acyl Azide System	I-	CR(mpy)	ω	$S\omega$
blank	nil	39.08		
0.1M	nil	37.77	0.37	
blank	0.1M	26.22	0.32	
0.1M	0.1M	12.62	0.67	2.88

Table 4: $S\theta$ value of I- at 0.1M Acyl Azide.

Where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$; θ_1 and θ_2 in equation are the degrees of surface coverage in the presence of the iodideion and the Acyl Azide, respectively, and θ_{1+2} is the degree of surface coverage in the presence of both species. The $S\theta$ values are found to be 2.88, suggesting a real synergistic action of I- ion with the Acyl Azide. The above results suggest that Acyl Azide can act as an effective Acyl Azide in the presence of I- ions.

3.5 Thermodynamic and kinetic parameters:

Effect of temperature on the inhibition efficiency was studied in the temperature range of 300 K, 310K and 320 K in 0.5 M sulphuric acid both in the absence and presence of Acyl Azide. Values of corrosion rate, surface coverage and %P are given in table 5.

	300K			310K			320K		
Conc	CRmm/yr	ω	P	CRmm/yr	ω	P	CRmm/yr	ω	P
blanck	39.08			77.25			151.25		
0.1M	37.77	0.03	3.35	72.2	0.06	6.53	146.3	0.03	3.27
0.1M+0.001M	27.25	0.3	30.27	53.6	0.3	30.61	108.4	0.28	28.33
0.1M+0.01M	17.17	0.56	56.06	32.35	0.58	58.12	63.3	0.58	58.14
0.1M+0.1M	12.62	0.67	67.7	22.8	0.7	70.48	42.1	0.72	72.16

Table 5: Corrosion Data of Low carbon Steel In 0.5 M Sulphuric Acid Solution Without And With different Concentration of Acyl Azide and I- at the Temperature 300K, 310K and 320k For 2 days.

It is clear from above data that the protection efficiency increases at high temperature . Activation energy was calculated from the Arrhenius plots as shown in following Fig. 4.

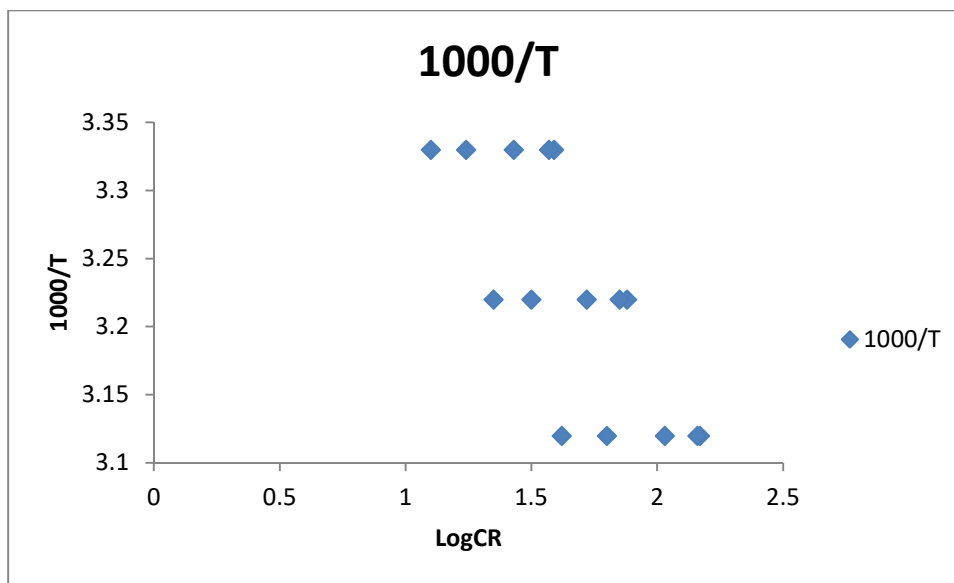


Fig 4: Arrhenius Plots of log CR Versus 1/T At Different Concentration Of Acyl Azide.

Energy of activation (Ea) for the corrosion process of given steel in the presence and absence of different concentrations of Acyl Azide and iodide, were calculated using following Arrheniustype equation:

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

Where E_a is energy of activation for corrosion ; R is universal gas constant; A is Arrhenius pre exponential factor, T is the absolute temperature and CR is rate of corrosion. The data obtained in Tables 5 shows that the addition of Acyl Azide leads to an increase in the activation energy E_a and enthalpy of reaction involved is ΔH to values greater than that of the solution without Acyl Azide and maximum value of activation energy and enthalpy were recorded at 0.001M amount of I- in 0.1M Acyl Azide . Many times, the value of average difference value of the $E_a - \Delta H$ is 2.55 kJ/mol that tells that corrosion is a unimolecular reaction as described perfect gas equation [23]:

$$E_a - \Delta H = RT \dots \dots \dots (5)$$

It is clear that positive sign of the enthalpies tells endothermic nature of the metal i.e. low carbon steel dissolution process. The presence of Acyl Azide (and I-) tested suggest that the corrosion process becomes more endothermic when compared with blank.

Table 6: Activation Energy and Enthalpy of Corrosion process of Low carbon Steel In 0.5 M sulphuric acid Solution in Absence and Presence of Acyl Azide and I-.

Conc.of inhibitor system	blanck	0.1M	0.1M+0.001M	0.1M+0.01M	0.1M+0.1M
Eact(KJ/mol)	51.34	54.13	55.15	52.13	48.12
ΔH (KJ/mol)	48.79	51.58	52.6	49.58	45.57

4. Conclusion:

From the above research work the following points were concluded:

1. Acyl Azide and I- act as a mixed Acyl Azide for the corrosion of Low carbon steel in 0.5 M sulphuric acid and it retarded both cathodic and anodic corrosion to various extents.
2. Protection efficiency of Acyl Azide was increased by adding iodide ions due to co-operative adsorption of the Acyl Azide and iodide ions.
3. Adsorption of Acyl Azide and I- on the surface of Low carbon steel is spontaneous and it occurs by physical adsorption.
4. Temperature effect suggest that mixture of Acyl Azide and I- exhibits constant efficiency until 320 K which is recommended for industrial use.
5. Optimum concentration of I- in Acyl Azide is 0.001M.

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