

Inhibitive Action of Hydroxylammonium Sulfate on the Corrosion of Carbon Steel in Hydrochloric Acid Medium and their Adsorption Characteristics

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Abstract

The inhibitive action of Hydroxylammonium sulfate ((NH₃OH)₂SO₄) (HAS) on corrosion of carbon steel (CS) in 1M HCl was studied by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and effect of temperature. The measurements show that inhibition efficiencies increase with the increasing of HAS concentrations but decrease with increasing temperatures. This reveals that inhibitive action of the inhibitor was mainly due to adsorption on the carbon steel surface and blocking of the active sites. The above results showed that HAS acted as a mixed-type corrosion inhibitor. The adsorption of HAS on the carbon steel surface obeyed the Langmuir adsorption isotherm. This was supported by the impedance measurements which showed a change in the charge transfer resistance and double layer capacitance, indicating the adsorption of HAS on the carbon steel surface. Thermodynamic parameters of the studied inhibitor were calculated and discussed.

Keywords: *Hydroxylammonium sulfate; Corrosion inhibition; Carbon Steel; Adsorption; EIS.*

1. Introduction

The corrosion of metals remains a world-wide scientific problem as it affects the metallurgical, chemical and oil-industries. Steel has found wide application in a broad spectrum of industries and machinery; however its tendency to corrosion. The corrosion of

steel is a fundamental academic and industrial concern that has received considerable attention. Among several methods used in combating corrosion problems, the use of chemical inhibitors remains the most effective and practical method and could be considered as one of the most economic [1-3]. Also of particular importance is the need to introduce certain compounds as inhibitors into the steel-corrodent environment to prevent corrosion of the steel [4, 5]. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms [6-8]. The effect of the adsorbed inhibitor on metallic surfaces in acid solutions is to slow down the cathodic and anodic process of dissolution of the metal. This is due to the formation of a barrier of diffusion or by means of the blockage of the reaction sites and thereby reducing the corrosion rate [9]. Little work [10-15] appears to have been done regarding the inhibition of steel in HCl solutions by inorganic compounds. The main objective of this paper is to evaluate the corrosion of carbon steel in both the absence and presence of Hydroxylammonium sulfate (HAS) in 1 M HCl. The inhibition effect of HAS on carbon steel in 1 M HCl was studied for the first time by weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation curves methods. Langmuir, as the adsorption isotherm of HAS on carbon steel surface, was tested for its potential relevance to describe its adsorption behaviour.

2. Materials and methods

2.1. Materials

The tested inhibitor, namely, Hydroxylammonium sulfate ((NH₃OH)₂SO₄) (HAS) was obtained from Sigma–Aldrich chemical co. and its chemical structure is presented in Fig. 1. The steel used in this study was a carbon steel (CS) (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder composed of iron (Fe).

The aggressive solutions of 1 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. The concentration range of HAS empl was 10⁻² to 10⁻⁵M.

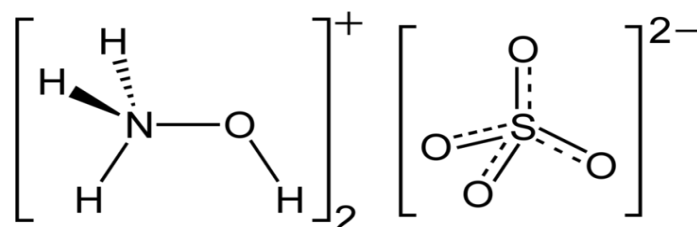


Fig 1: Structure of Hydroxylammonium Sulfate molecule (HAS).

2.2. Measurements

2.2.1. Weight loss measurements

The gravimetric measurements were carried out at definite time intervals of 6 h at room temperature using an analytical balance (precision ± 0.1 mg). The carbon steel specimens used has a rectangular form (length = 1.6 cm, width = 1.6 cm, thickness = 0.07 cm). Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser containing 80 mL of non-de-aerated test solution. After an immersion period, the steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighed. Triplicate experiments were performed in each case and the mean value of the weight loss was calculated.

2.2.2. Electrochemical measurements

Electrochemical experiments were conducted using impedance equipment (Tacussel-Radiometer PGZ 100) and controlled with Tacussel corrosion analysis software model Voltmaster 4. A conventional three-electrode cylindrical Pyrex glass cell was used. The temperature was thermostatically controlled. The working electrode was carbon steel with a surface area of 1 cm^2 . A saturated calomel electrode (SCE) was used as a reference. All potentials were given with reference to this electrode. The counter electrode was a platinum plate with a surface area of 1 cm^2 . A saturated calomel electrode (SCE) was used as the reference and a platinum electrode was used as the counter-electrode. All potentials were reported vs. SCE. All electrochemical tests have been performed in aerated solutions at 298 K. For polarization curves, the working electrode was immersed in a test solution for a duration of 30 min until a steady state open circuit potential (E_{ocp}) was obtained. The polarization curve was recorded as a polarization from -800 to -200 mV/SCE with a scan rate of $1 \text{ mV} \cdot \text{s}^{-1}$. AC impedance measurements were carried-out in the frequency range of 100 kHz to 10 mHz, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give intersections with the x -axis.

3. Results and Discussions

3.1. Electrochemical experiment

3.1.1. Polarization curves

The Tafel polarization measurements for carbon steel in 1 M HCl, in the absence and presence of HAS inhibitor are shown in Fig 2. The values of the corrosion current density (I_{corr}) and corrosion potential (E_{corr}), as well as the cathodic Tafel slopes (β_c) were obtained by the linear extrapolation of the Tafel slopes [16]. The corrosion inhibition efficiency, $\eta_{\text{Tafel}} \%$, was calculated by the equation:

$$\eta_{Tafel} \% = \frac{I_{corr}^{\circ} - I_{corr}^i}{I_{corr}^{\circ}} \times 100 \quad (1)$$

Where, I_{corr}° and I_{corr}^i are the corrosion current density in absence and presence of inhibitor, respectively.

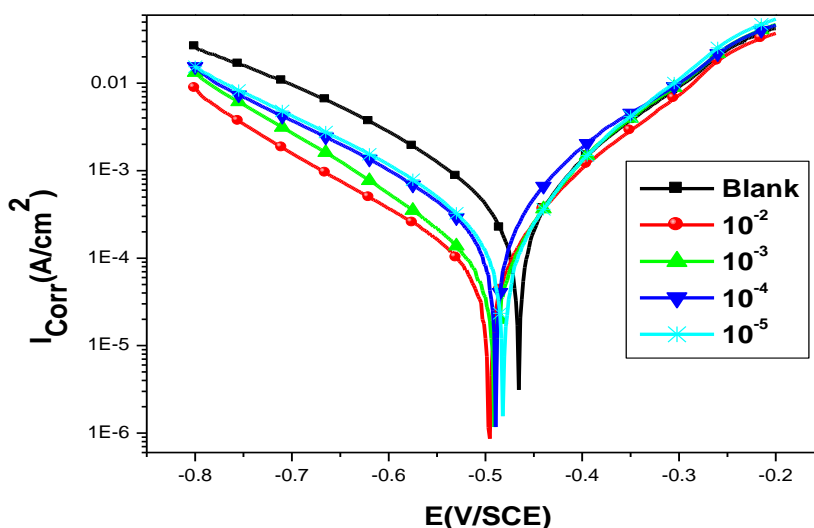


Fig 2: Polarization curve for Carbon Steel in the presence and absence of different concentrations of compound HAS.

The complete electrochemical parameters E_{corr} , I_{corr} and cathodic Tafel slope (β_c), inhibition efficiency are calculated by polarization measurements in 1M HCl solution in the absence and presence of different concentrations of the inhibitor and listed in Table 1. In hydrochloric acid solution the following mechanism is proposed for the corrosion of iron [17].

The anodic dissolution mechanism of iron is:



The cathodic hydrogen evolution mechanism is:



The parallel cathodic Tafel curves in Fig 2 suggest that the hydrogen evolution is activation-controlled and the reduction mechanism is not affected by the presence of the inhibitor. The values of β_c changed with increasing inhibitor concentrations, which indicates the influence of the compound on the kinetics of hydrogen evolution.

Table 1. Electrochemical parameters for carbon steel at various concentrations of HAS in 1 M of HCl and corresponding inhibition efficiency.

Inhibitor	Conc (M)	$-E_{\text{corr}}$ (mV/SCE)	$-\beta_c$ (mV dec ⁻¹)	I_{corr} ($\mu\text{A cm}^{-2}$)	η_{Tafel} (%)
Blank	1.0	465	588	168	-
HAS	1×10^{-2}	495	83	160	85.88
	1×10^{-3}	491	112	151	80.95
	1×10^{-4}	489	230	180	60.88
	1×10^{-5}	482	245	165	58.33

The results from Fig 2 and Table 1 indicate that the corrosion potential is more negative and the corrosion current density (I_{corr}) decreases in the presence of an inhibitor compared to the blank solution and also with increasing the inhibitor concentration which suggest that the presence of this compound retards the dissolution of carbon steel electrodes in a 1M HCl solution. This result confirms the inhibitive action of the HAS toward acid corrosion of steel [18]. This implies that HAS affected both the anodic dissolution of carbon steel electrodes and its cathodic reduction in hydrogen evolution reactions, indicating that the HAS compound could be classified as a mixed-type inhibitor. This due to the adsorption of the inhibitor over the corroding surface [19, 20]. The cathodic Tafel slope values in the presence of HAS are different of that in its absence; we may deduce that HAS modified the mechanism of the inhibition in the presence and absence of the inhibitor [21]. The inhibition efficiency reaches 85.88% at 10^{-2} M. Consequently, HAS is a good inhibitor.

3.1.2. The electrochemical impedance spectroscopy

3.1.2.1. Effect of concentration inhibitor

The corrosion behavior of carbon steel in a 1M HCl solution in the absence and presence of different concentrations of the inhibitor HAS was investigated by the EIS method at 298K after 30 min of immersion. Fig 3 shows the Nyquist plot for carbon steel in a 1M H solution in the absence and presence of different concentrations of the investigated compound. The impedance spectra containing a depressed capacitive semi circle [15] and the diameter of semicircle increases, with increasing inhibitor concentrations.

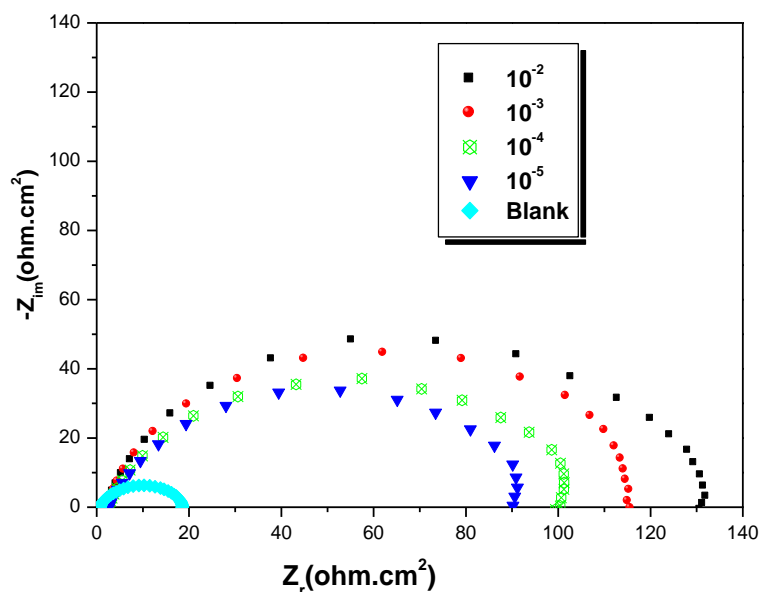


Fig 3: Nyquist plots for the corrosion of CS in 1M HCl in the absence and the presence of different concentrations of HAS inhibitor at 289K.

These diagrams exhibit that the impedance spectra has an approximately semi-circular appearance showing that the corrosion of CS in 1M HCl is controlled by a charge transfer resistance process [22]. It is noticed that the impedance diagram shows a depressed semicircle at the center under the real axis, such phenomenon often referred to as the "frequency dispersion of interfacial impedance", which has been attributed to the roughness; inhomogeneity of the electrode surfaces and adsorption of the inhibitor [23-26]. The impedance of the inhibited steel increases with increasing the inhibitor's concentration. The equivalent circuit model, which describes the metal / electrolyte interface of the present corroding system compatible with the Nyquist diagram recorded in the presence of inhibitors, was depicted in Fig 4.

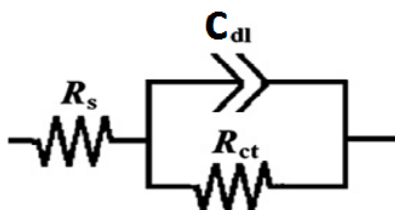


Fig 4: Equivalent circuits compatible with the experimental impedance data in Fig 4.

The model consists of the solution resistance (R_s), the charge-transfer resistance of the interfacial corrosion reaction (R_{ct}), and the double layer capacitance (C_{dl}). Table 2 shows the

Table 2. Impedance parameters for corrosion of steel in 1 M HCl in the absence and presence of different concentrations of HAS at 298 K.

Inhibitor	C (M)	R_{ct} ($\Omega \cdot \text{cm}^2$)	f_{\max} (Hz)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	$\eta_z\%$
Blank	1.0	18	40	221.16	-
HAS	1×10^{-2}	132	63	19.15	86.36
	1×10^{-3}	116	63	21.79	84.48
	1×10^{-4}	101	40	39.41	82.18
	1×10^{-5}	92	40	43.27	80.43

As it can be seen from Table 2 (EIS data) where the C_{dl} values decrease and the R_{ct} values increase; in comparison with that in blank with the increase of the inhibitor concentrations solution. This is due to the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface, and decreasing the extent of the dissolution reaction. The decrease in the C_{dl} can result from the decrease of the local dielectric constant and/or from the increase of thickness of the electrical double layer [27] suggesting that the inhibitor molecules function by adsorption and formation of the protective layer at the metal surface. The inhibition efficiency $\eta_z\%$ in various concentrations of HAS is calculated by charge transfer resistance as followed [28]:

$$\eta_z \% = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (9)$$

where R_{ct} and $R_{ct(inh)}$ were the values of polarization resistance in the absence and presence of inhibitor, respectively.

The charge transfer resistance (R_{ct}) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [29]. The double layer capacitance (C_{dl}) values were obtained at maximum frequency (f_{\max}), at which the imaginary component of the Nyquist plot is maximum and calculated using the following equation:

$$C_{dl} = \frac{1}{2 \cdot \pi \cdot f_{\max} \cdot R_{ct}} \quad (10)$$

With C_{dl} : double layer capacitance ($\mu\text{F} \cdot \text{cm}^{-2}$); f_{\max} : maximum frequency (Hz) and R_{ct} : Charge transfer resistance ($\Omega \cdot \text{cm}^2$). From Table 2 we can see that the inhibition efficiency increases with the increasing inhibitor concentration. At this purpose, one observes that the optimum concentration of inhibitor HAS required to achieve the great efficiency ($\eta_z\% = 86.88\%$) is found to be 10^{-2}M . The results obtained by this method are in good agreement with the values of inhibitor efficiency obtained from polarization measurements.

3.1.2.2. Effect of temperature

We intended to investigate the mechanism of inhibition and to calculate the kinetic and thermodynamic parameters for the inhibition and the adsorption processes. These parameters

are useful in interpreting the type of adsorption by the inhibitor. The effect of temperature on the inhibition efficiencies of HAS was also studied by EIS in the temperature range 298–328K. Fig 5 and Fig 6 give the Nyquist plots for C-steel in the absence and presence of 10^{-2} M HAS at different temperatures.

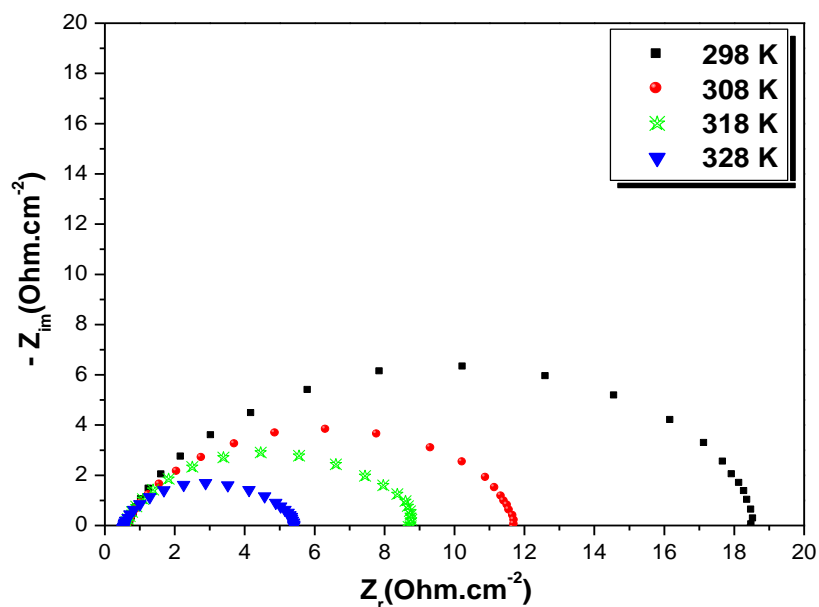


Fig 5: Nyquist diagrams for carbon steel in 1 M HCl at different temperatures.

The corresponding data are given in Table 3. In the temperature range studied (298–328K) the values of R_t decrease with increasing temperature both in uninhibited and inhibited solutions and the efficiency of inhibition by HAS decreases with increasing temperature. The R_t value of C-steel increases more rapidly with temperature in the presence of the inhibitor; the results confirm that HAS acts as an efficient inhibitor in the range of temperature studied.

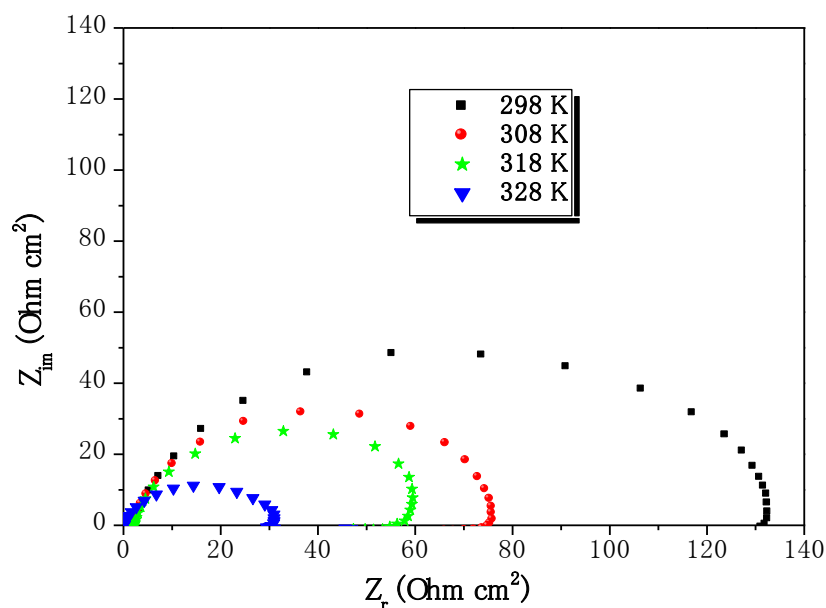


Fig 6: Nyquist diagrams for carbon steel in 1 M HCl + 10^{-2} M of HAS at different Temperatures.

Table 3. Thermodynamic parameters for the adsorption of HAS in 1M HCl on the carbon steel at different temperatures.

Inhibitor	T (K)	R_{ct} ($\Omega \text{ cm}^2$)	C_{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	η_z (%)
Blank	298	18	221.16	-
	308	11	229.78	-
	318	8	199.04	-
	328	5	201.56	-
HAS	298	132	19.15	86.36
	308	79	20.15	86.00
	318	54	29.49	85.18
	328	31	32.53	83.87

On the other hand, the values of R_{ct} were employed to calculate values of the corrosion current density (I_{corr}) at various temperatures in the absence and presence of HAS using the following equation [30]:

$$I_{corr} = R.T.(z.F.R_{ct})^{-1} \quad (11)$$

where R is the universal gas constant ($R = 8.31 \text{ J K}^{-1}\text{mol}^{-1}$), T is the absolute temperature, z is the valence of iron ($z = 2$), F is the Faraday constant ($F = 96485 \text{ coulomb}$) and R_{ct} is the charge transfer resistance.

The activation energy for the corrosion process was calculated from Arrhenius type plot according to the following equation:

$$\log I_{corr} = -\frac{E_a}{2.303RT} + \log A \quad (12)$$

where E_a is the apparent activation corrosion energy, T is the absolute temperature, A is the Arrhenius pre-exponential constant and R is the universal gas constant. Plotting $(\ln I_{corr})$ versus $1/T$ gives straight lines as revealed from Fig 7.

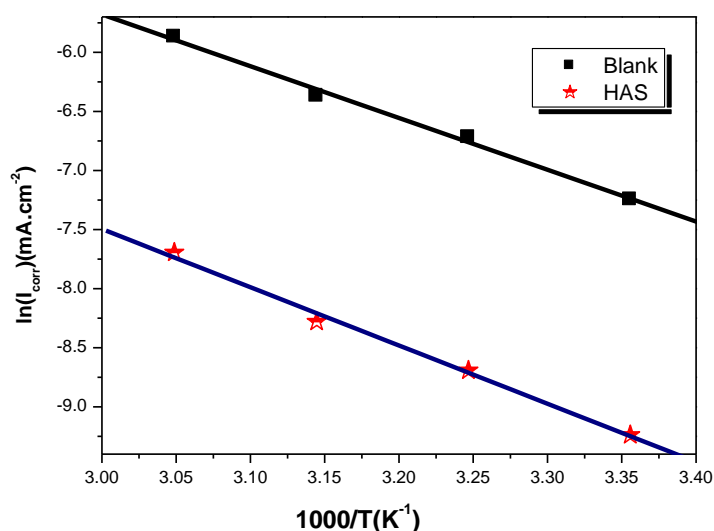


Fig 7: Arrhenius plots of carbon steel in 1M HCl with and without 10^{-2} M of HAS.

The activation energy values obtained (Table 4) are 40.95 and 36.39 kJ/mol for 10^{-2} M of HAS and free acid, respectively. It's observed that E_a increases with addition of HAS concentration to the acid medium; that indicates the good performance of this inhibitor at higher temperatures. The increase in E_a in the presence of this inhibitor may be interpreted as physical adsorption that occurs in the first stage [31].

And the an alternative formulation of Arrhenius equation is:

$$I_{corr} = \frac{RT}{Nh} \cdot \exp\left(\frac{\Delta S_a}{R}\right) \cdot \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (13)$$

where h is Planck's constant, N is Avagadro's number, ΔS_a is the entropy of activation and ΔH_a is the enthalpy of activation.

Fig 8 shows a plot of $\ln(I_{corr}/T)$ against $1/T$ for HAS. Straight lines are obtained with a slope of $(-\Delta H_a/R)$ and an intercept of $(\ln R/Nh + \Delta S_a/R)$ from which the values of ΔH_a and ΔS_a are calculated respectively and listed in Table 4.

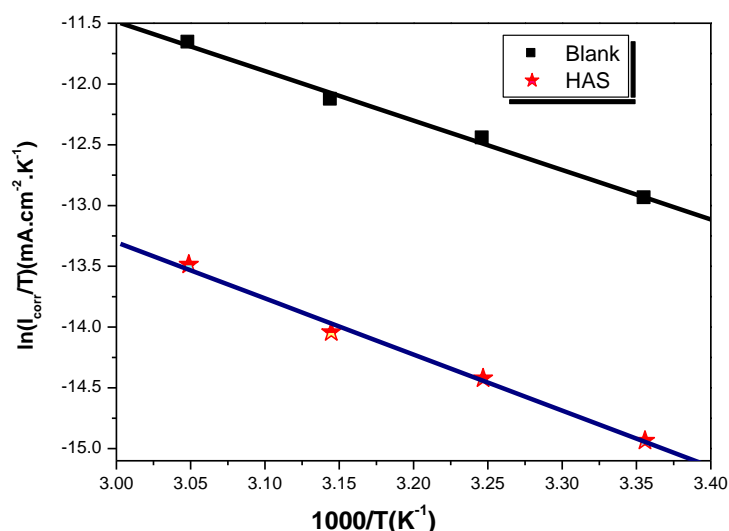


Fig 8: Arrhenius plots of carbon steel in 1 M HCl with and without 10^{-2} M of HAS.

Table 4. The value of activation parameters for carbon steel in 1 M HCl in the absence and presence of 10^{-2} M of HAS.

Inhibitor	E _a (kJ/mol)	ΔH _a (kJ/mol)	ΔS _a (J/mol K)	E _a - ΔH _a (KJ/mol)
Blank	36.39	33.80	-76.69	2.60
HAS	40.95	38.35	-192.94	2.60

From this table 4: The positive sign of the enthalpie ΔH_a reflects the endothermic nature of the steel dissolution process, which means that the dissolution of steel is difficult [32]. In this act some authors [33-35] have attributed this result to the inhibitor species being physically adsorbed on the metal surface. We remark that E_a and ΔH_a values vary in the same way (Table 4). This result permit to verify the known thermodynamic reaction between the E_a and ΔH_a as shown in Table 4 [36]:

$$\Delta H_a = E_a - RT \quad (14)$$

The negative value of entropic ΔS_a in the presence of an inhibitor implies that the activated complex in the rate determining step represents an association, rather than a dissociation step, meaning that an increase in disordering takes place in going from reactants to the activated complex [37].

3.2. Gravimetric study

The figure 9 shows the variation of η_{WL}(%) against the concentration for the HAS inhibitor. The values of percentage inhibition efficiency (η_{WL}) and the surface coverage (θ) that represents the weight of the metal surface covered by inhibitor molecules obtained from the

weight loss experiment for the corrosion of carbon steel in 1 M HCl, in the presence of different concentrations of HAS compounds at 298K are given in Table 5.

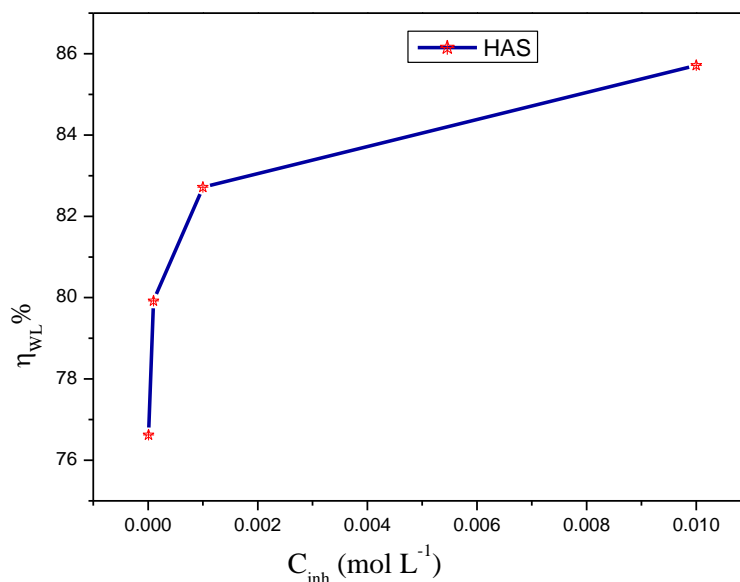


Fig 9: Corrosion inhibitor efficiency of HAS for C-Steel in 1 M HCl as a function of concentration and temperature.

Table 5. Corrosion parameters obtained from weight loss measurements for carbon steel in 1M HCl containing various concentration of inhibitor at 298 K.

Inhibitor	Conc. (M)	P (mg cm ⁻² h ⁻¹)	η_{WL} (%)	Θ
Blank	1.0	1.001	-----	-----
HAS	1×10^{-2}	0.143	85.71	0.857
	1×10^{-3}	0.173	82.72	0.827
	1×10^{-4}	0.201	79.92	0.799
	1×10^{-5}	0.234	76.62	0.766

It was observed from Table 5 that the corrosion rate was decreasing with increasing inhibitor concentrations, whereas inhibition efficiency was increased with increasing amounts of the inhibitor. The η_{WL} (%) increases with increasing the inhibitor concentration, indicating that more inhibitor molecules are adsorbed on the metal surface, thus providing a wider surface coverage. The optimum concentration required to achieve an efficiency of 85.71% was found to be 10^{-2} M for HAS inhibitor. The η_{WL} (%) values were calculated using equation (14) as shown below [38] .

$$\eta_{WL} \% = \left(1 - \frac{w}{w_0}\right) \times 100 \quad (12)$$

where w° and w are weight loss in the absence and presence of inhibitor. The rate of corrosion ρ ($\text{g cm}^{-2} \text{h}^{-1}$) was calculated from equation, where S is surface area of steel plate and t is immersion time.:

$$\rho = \frac{w^\circ - w}{St} \quad (13)$$

3.3. Adsorption and thermodynamic considerations

Basic information about the properties of the tested compound may be provided from the kind of adsorption isotherm. The values of surface coverage θ , corresponding to different concentrations of inhibitors at 298K have been used to explain the best isotherm to determine the adsorption isotherm. Several adsorption isotherms were tested and the Langmuir adsorption isotherm was found to provide the best description of the adsorption behaviour of the investigated inhibitor. The Langmuir isotherm is given by the equation [39]:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (14)$$

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{\text{ads}}}{RT}\right) \quad (15)$$

Where C is the inhibitor concentration, θ the fraction of the surface covered determined by $\eta_{\text{WL}}(\%) / 100$, K_{ads} the equilibrium constant, ΔG_{ads} is the standard free energy of adsorption reaction, R is the universal gas constant, T is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution in mol/L. Fig 10 shows the dependence of the ratio C/θ as function of C .

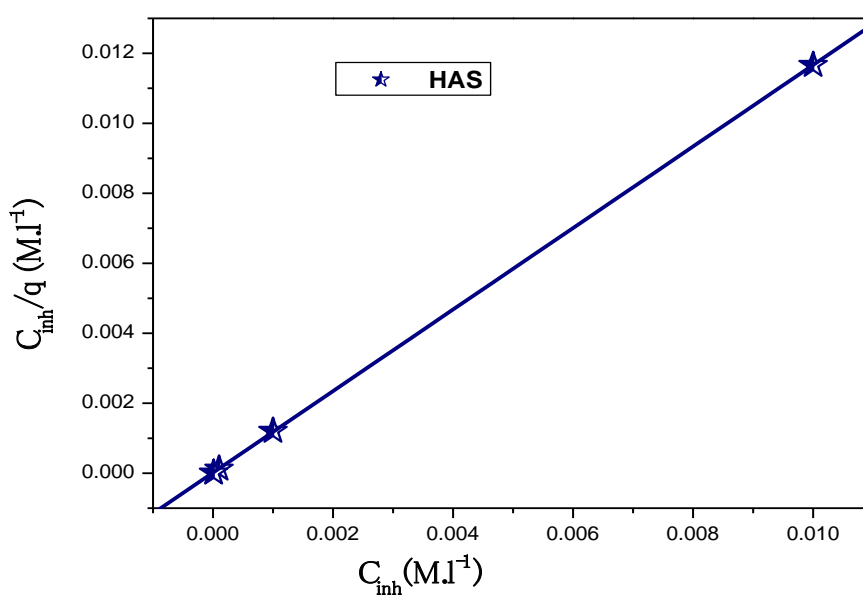


Fig 10: Langmuir adsorption of HAS on the carbon steel surface in 1HCl solution.

Table 6. Thermodynamic parameters for the adsorption of HAS in 1M HCl on the carbon steel at 298K.

Inhibitor	Slope	K_{ads} (M ⁻¹)	R ²	ΔG_{ads}° (kJ/mol)
HAS	1.2	58600.00	0.99	-37.135

According to the Langmuir isotherm [40], K_{ads} values can be calculated from the intercepts of the straight lines on the C_{inh}/θ axis, the K_{ads} is related to the standard free energy of adsorption ΔG_{ads}° , with the following equation:

$$\Delta G_{ads}^{\circ} = -RTL \ln(55.5K_{ads}) \quad (16)$$

Thermodynamic parameters for adsorption processes obtained from Langmuir's adsorption isotherm for the studied inhibitor are given in Table 6. The value of $\Delta G_{ads}^{\circ} = -37.135 \text{ kJ mol}^{-1}$ is too negative indicating that HAS is strongly adsorbed on the steel surface [41, 42] and ensuring the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface. The value of ΔG_{ads} is found to be around -40 kJ.mol^{-1} ; meaning that the adsorption mechanism of HAS on C-steel surface is mainly the chemisorption. Noticeably, it is generally accepted that physical adsorption is a preceding stage of chemisorption of inhibitor on metal surface [43]. In other words, chemisorption is always accompanied by physisorption [44].

4. Conclusion

Hydroxylammonium Sulfate is found to be good inhibitor for carbon steel corrosion in 1M HCl. The inhibition is accomplished by adsorption of HAS molecules on the steel surface, and the adsorption of HAS on the steel surface obeyed the Langmuir isotherm.

The thermodynamic parameters (K_{ads} , ΔG_{ads}°) of adsorption for the studied inhibitor were calculated from their adsorption isotherm.

The negative values of free energy of adsorption indicated that the adsorption of the inhibitor molecule is a spontaneous process.

The inhibition efficiency of HAS increases with the increase in the inhibitor concentration and decreases with the increase in temperature of the corrosion medium. Energy of activation for the corrosion process increases in the presence of the inhibitor.

The polarization curves appears as if the Tafel behaviour indicates that HAS are a mixed - type inhibitor.

EIS measurement results indicated that the resistance of the carbon steel electrode increased greatly and its capacitance decreases by increasing the inhibitor concentration.

The inhibiting efficiencies obtained by polarization, EIS and weight loss measurements are all in good agreement.

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