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Investigation of the Inhibition Effect of N-1-Naphthylethylenediamine Dihydrochloride Monomethanolate on the C38 Steel Corrosion in 0.5M H_2SO_4

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ABSTRACT

Inhibition of the C38 steel corrosion by mean of N-1-Naphthylethylenediamine Dihydrochloride Monomethanolate (N-NEDHME), was studied in 0.5M H_2SO_4 solutions in the temperature range from 298K to 328K using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The results obtained from the both measurement techniques revealed good inhibitor efficiency in the studied concentration range. The inhibition efficiency decrease with rise in temperature. Impedance measurements showed that the double-layer capacitance decreased and charge-transfer resistance increased with increase in the inhibitor concentration and hence increasing in inhibition efficiency. Polarization curves show that N-NEDHME is a anodic-type inhibitor. The results obtained from the different methods are in good agreement. Adsorption followed the Langmuir isotherm with negative values of ΔG°_{ads}, suggesting a stable and a spontaneous inhibition process.

Keywords: C38-Steel, Sulfuric acid, Inhibitor, Polarisation curves, Impedance, Langmuir.

INTRODUCTION

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals and alloys. 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 a considerable amount of attention [1]. Using inhibitors is an important method of protecting materials against deterioration due to corrosion, especially in acidic media [2]. Acid solutions are widely used in industry, some of the important fields of application being acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. As acidic media, the use of hydrochloric acid in pickling of metals, acidization of oil wells and in cleaning of scales is more economical, efficient and trouble-free, compared to other mineral acids [3]. Because of the general aggression of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials. The effect of organic nitrogen compounds on the corrosion behaviour of metallic materials in aggressive solutions has been well documented [4–14]. Their choice is based on their stability as corrosion inhibitors for metallic materials in acidic media. Recently, the excellent inhibitory effect obtained by N-1 Naphthylethylenediamine Dihydrochloride Monomethanolate (N-NEDHME) [15] on copper corrosion in nitric acid, This encouraged us to test this compound in inhibtion of corrosion of steel in H_2SO_4. In this work, the inhibiting action of N-NEDHME compound (Fig. 1) on the corrosion C38 steel in 0.5M H_2SO_4 solution has been investigated. The gravimetric and electrochemical techniques such as potentiodynamic polarization, and impedance measurements were used in this study.

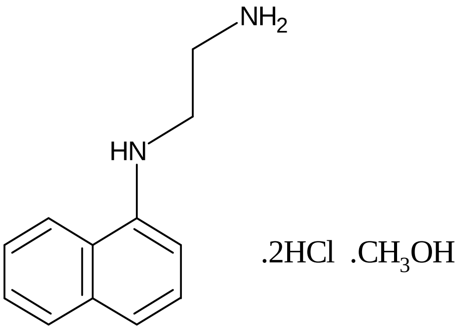

Fig. 1 The molecular structure of N-NEDHME.

MATERIALS AND METHODS

2.1. Materials and reagents

C38 Steel strips containing (0.09 % P; 0.38 % Si; 0.01 % Al; 0.05 % Mn; 0.21 % C; 0.05 % S and the remainder iron) were used for electrochemical and gravimetric studies. Prior to all measurements, are abraded with a series of emery paper from 180 to 1200 grade. The specimens are washed thoroughly with bidistilled water degreased and dried with acetone. The aggressive solution (0.5M H_2SO_4) was prepared by dilution of Analytical Grade 98 % H_2SO_4 with double-distilled water.

2.2. Measurements

2.2.1. Weight loss measurements

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 50 cm^3. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water, degreased and dried with ethanol. The steel specimens used have a rectangular form (1.6cm × 1.6cm × 0.07cm). Three measurements were performed in each case and the mean value of the weight loss has been reported and recorded to nearest. The immersion time for the weight loss is 6h at 298K.

2.2.2. Electrochemical measurements

- *Electrochemical cell*

The electrolysis cell was Pyrex of cylinder closed by cap containing five openings. Three of them were used for the electrodes. The working electrode was C38 steel with the surface area of 1 cm^2. Before each experiment, the electrode was polished using emery paper until 1200 grade. After this, the electrode was cleaned ultrasonically with distillate water. 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 of surface area of 1 cm^2. The aggressive medium used here is 0.5M H_2SO_4 solution was prepared with concentrated H_2SO_4 and distilled water. The organic compound tested is N-1-Naphthylethylenediamine Dihydrochloride Monomethanolate. Its molecule formula is shown in Fig. 1. The concentration range of this compound was 10^{-3} to 10^{-6} M.

- *Polarisation measurements*

The working electrode was immersed in test solution during 30 minutes until a steady state open circuit potential (E_{ocp}) was obtained. The polarization curve was recorded by polarization from -800 mV to -400 mV under potentiodynamic conditions corresponding to 1 mV/s (sweep rate), at frequencies between 100 kHz and 10 mHz was superimposed on the rest potential. The potentiodynamic measurements were carried out using Tacussel Radiometer PGZ 100, which was controlled by a personal computer.

RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization measurements

Fig. 2 show typical Tafel curves obtained for C38 steel in 0.5M H_2SO_4 with and without the compound studied. The values of associated electrochemical parameters, i.e., corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slopes (β_c) and percentage inhibition efficiency (IE (%)) values were calculated from polarization curves and listed in Table 1. The inhibition efficiency IE (%) was calculated from polarization measurements according to the relation given below:

$$E_I(\%) = (\frac{I_{corr} - I'_{corr}}{I_{corr}}) \times 100 \qquad (1)$$

Where I_{corr} and I'_{corr} are uninhibited and inhibited corrosion current densities, respectively. They are determined by extrapolation of Tafel lines to the respective corrosion potentials.

According to the mechanism for the anodic dissolution of Fe in acid solution proposed initially by Bockris et al [16]. Fe electro-dissolution in acidic sulphate solutions depends primarily on the adsorbed intermediate $FeOH_{ads}$ as follows:

$$Fe + OH^- \rightleftharpoons FeOH_{ads} + H^+ + e^- \qquad (2)$$

$$FeOH_{ads} \rightleftharpoons FeH^+ + e^- \qquad (3)$$

$$FeH^+ \rightleftharpoons Fe^{2+} + H_2O \qquad (4)$$

The cathodic hydrogen evolution fellows the steps:

$$Fe + H^+ \rightleftharpoons (FeH^+)_{ads} \qquad (5)$$

$$(FeH^+)_{ads} + e^- \rightleftharpoons (FeH)_{ads} \qquad (6)$$

$$(FeH)_{ads} + H^+ + e^- \rightleftharpoons Fe + H_2 \qquad (7)$$

The corrosion rate of iron in H_2SO_4 solutions is controlled by both hydrogen evolution reaction and dissolution reaction of iron.

Another mechanism, proposed by Ashassi-Sorkhabi and Nabavi-Amri [17] involving two adsorbed intermediates has been used to account for the retardation of Fe anodic dissolution in the presence of an inhibitor.

$$Fe + H_2O \rightleftharpoons Fe.H_2O_{ads} \tag{8}$$

$$Fe.H_2O_{ads} + X \rightleftharpoons FeOH^-_{ads} + H^+ + X \tag{9}$$

$$Fe.H_2O_{ads} + X \rightleftharpoons FeX_{ads} + H_2O \tag{10}$$

$$FeOH^-_{ads} \xrightarrow{r.d.s} FeOH_{ads} + e^- \tag{11}$$

$$FeX_{ads} \rightleftharpoons FeX^+_{ads} + e^- \tag{12}$$

$$FeOH_{ads} + FeX^+_{ads} \rightleftharpoons FeX_{ads} + FeOH^+ \tag{13}$$

$$FeOH^+ + H^+ \rightleftharpoons Fe^+ + H_2O \tag{14}$$

Where « r.d.s » denotes the rate determining step and X represents the inhibitor species. According to the mechanism above, displacement of some adsorbed water molecules on the metal surface by inhibitor species to yield the adsorbed intermediate FeX_{ads} (equation 10) reduces the amount of the species $FeOH^-_{ads}$ available for the rate determining step. Depending on the relative solubility of the adsorbed intermediate, it could either inhibit or catalyze further metal dissolution.

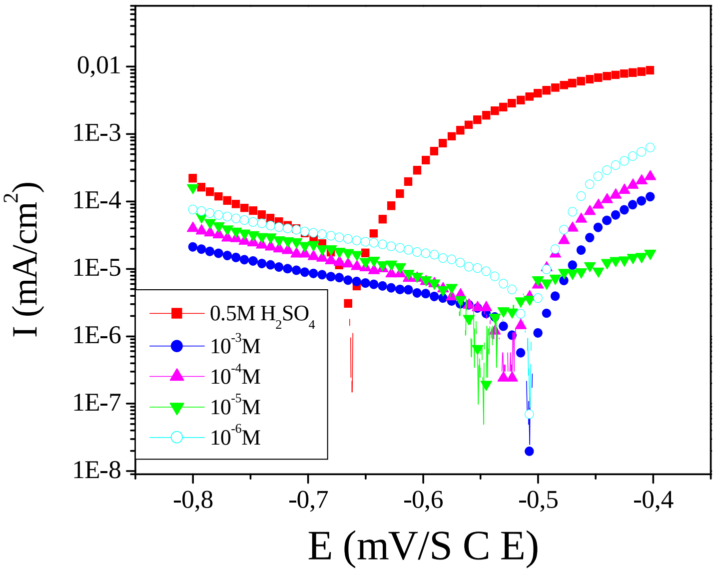

Fig 2. Polarization curves for Steel in 0.5M H_2SO_4 in the absence and presence of different concentrations of N-NEDHME at 298K

As it is show in Fig. 2 and Table 1, the values of I_{corr} decrease with the rise of N-NEDHME concentration.We note that the corrosion current densities were significantly reduced in the presence of N-NEDHME and became only 2.1 μA/cm^2 at 10^{-3} M. The anodic current density decreases with the concentration of this compound however, a slight effect is observed on the cathodic portions. The cathodic Tafel slope increases with presence of inhibitor showed that the addition of inhibitor modifies the mechanism of the hydrogen reduction. This result was obtained in the presence of bis-[2-thiophene carboxylate] di-n-butyl tin in sulfuric acid [18]. The addition of N-NEDHME shifted the E_{corr} value towards the positive direction. This indicates that the N-NEDHME compound acts predominately as a anodic inhibitor.

Table 1. Polarisation data of Steel in 0.5M H_2SO_4 without and with addition of N-NEDHME at 308 K

Inhibitor	Conc (M)	$-E_{corr}$ (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} (μA/cm^2)	E_I (%)
H_2SO_4	0.5	662.9	141.8	17.9	-
N-NEDHME	10^{-3}	508.9	285.5	2.1	**88.3**
	10^{-4}	526.1	253.2	3.3	81.6
	10^{-5}	548.1	295.4	5.5	69.3
	10^{-6}	508.7	298.4	8.1	54.7

3.2. Electrochemical impedance spectroscopic studies

Nyquist plots of N-1 Naphthylethylenediamine Dihydrochloride Monomethanolate compound in 0.5M H_2SO_4 solutions in the absence and presence of various concentrations of N-NEDHME. is given in Fig 3. The impedance spectra show that a single semicircle and the diameter of semicircle increases with increasing inhibitor concentration. These diagrams exhibit that the impedance spectra consist of one capacitive loop at high frequency, the high frequency capacitive loop was attributed to charge transfer of the corrosion process [19]. Various parameters such as charge-transfer resistance (R_{ct}), double layer capacitance (C_{dl}), f_{max} and inhibition efficiency were obtained from impedance measurements and are shown in Table 2. R_{ct} values were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru et al. [20]. C_{dl} values were calculated from the frequency at which the imaginary component of impedance was maximum (Z_{im} max) using the reaction:

$$C_{dl} = \frac{1}{2\pi f_{\max} R_{ct}} \qquad (15)$$

Where f_{max} is the frequency at which the imaginary component of impedance is maximum. The inhibition efficiency got from the charge-transfer resistance is calculated by the following relation:

$$E_{R_{ct}}\% = \frac{R_{ct} - R^{\circ}_{ct}}{R_{ct}} \qquad (16)$$

Where R_{ct} and R°_{ct} represent the resistance of charge transfer in the presence and absence of inhibitor, respectively. R_{ct} is the diameter of the loop. The R_{ct} values of this investigated N-NEDHME derivative increase with increasing inhibitor concentration. At the same time the C_{dl} has opposite trend at the whole concentration range.

Table 2. Corrosion parameters obtained by impedance measurements for steel in 0.5M H_2SO_4 at various concentrations of N-NEDHME

Inhibitor	Conc (M)	R_{ct} (Ω.cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	E_{Rct} (%)
H_2SO_4	0.5	560.2	63.33	4.488	-
N-NEDHME	10^{-3}	3479	25.00	1.829	83.9
	10^{-4}	2324	31.65	2.165	75.9
	10^{-5}	1638	40.00	2.429	65.8
	10^{-6}	1145	50.00	2.781	51.1

These observations clearly bring out the fact that the corrosion of C38 steel in 0.5M H_2SO_4 is controlled by a charge transfer process. The decrease in C_{dl} is due to the gradual replacement of water molecules by the adsorption of the organic molecules at metal/solution interface, leading to a protective film on the steel surface, then decreasing the extent of dissolution reaction [21].

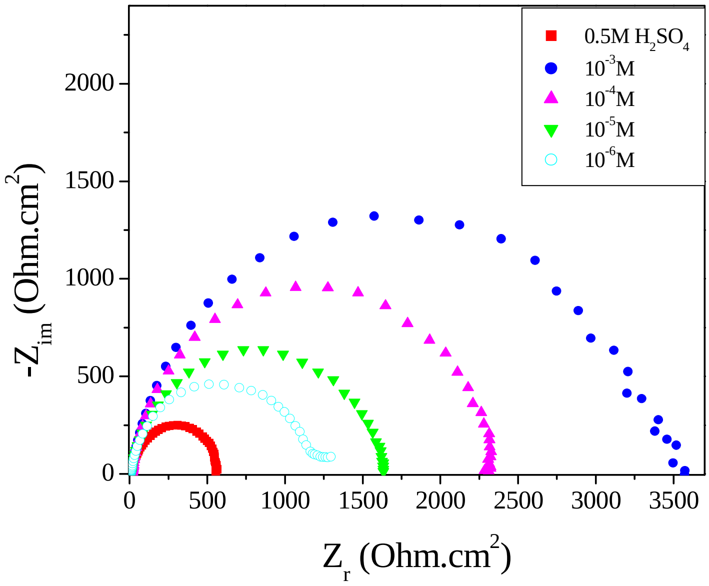

Fig.3 Nyquist diagrams for C38 steel in 0.5M H_2SO_4 containing different concentrations of N-NEDHME at 298K.

3.3. Gravimetric measurements

3.3.1. Effect of concentration

Three parallel rectangular C38 steel specimens of were used for the determination of corrosion rate. The coupons, initial weight using an analytic balance was recorded before immersion in 80 ml open beakers containing 50 ml of corrodent (0.5M H_2SO_4) without and with different concentrations of N-NEDHME. The specimens were taken out, washed, dried, and reweighed accurately. The average weight loss of the three parallel C38 steel specimens could be obtained. The corrosion rates of have be C38 steel en determined for 6h immersion period at 298K from mass loss, using Eq. (17) where Δm is the mass loss, S is the area, and t is the immersion period [22]. The percentage protection efficiency E_w (%) was calculated according the relationship Eq. (18) where W and W_{inh} are the corrosion rates of steel without and with the inhibitor, respectively [23]:

$$W = \frac{\Delta m}{S.t} \tag{17}$$

$$E_w\% = \frac{W - W_{inh}}{W} \tag{18}$$

$$\Theta = 1 - \frac{W_{inh}}{W} \tag{19}$$

The value of percentage inhibition efficiency (%IE), corrosion rate (W) and Θ (Eq. (19)) the degree of surface coverage of the inhibitor obtained from weight loss method at different concentrations of N-NEDHME in 0.5M H_2SO_4 at 298K are summarized in Table 3. It is evident from the Table 3 that the corrosion rate decreases and inhibition efficiency increases with increase in N-NEDHME concentration.

Table 3. Corrosion parameters for steel in aqueous solution of 0.5M H_2SO_4 in absence and presence of different concentrations of N-NEDHME from weight loss measurements at 298K for 6h

Inhibitor	Conc (M)	W (mg/cm^2.h)	E_w (%)	Θ
H_2SO_4	0.5	1.789	-	-
N-NEDHME	1×10^{-3}	0.182	89.8	0.898
	5×10^{-4}	0.274	84.7	0.847
	1×10^{-4}	0.392	78.1	0.781
	5×10^{-5}	0.472	73.6	0.736
	1×10^{-5}	0.603	66.3	0.663
	1×10^{-6}	0.921	48.5	0.485

The variations in the degree of surface coverage and corrosion rate with N-NEDHME concentration shown in Fig 4 suggest that N-NEDHME inhibits steel at all the concentration range used in the study. Maximum degree of surface coverage was reported at 10^{-3}M concentration of this compound.

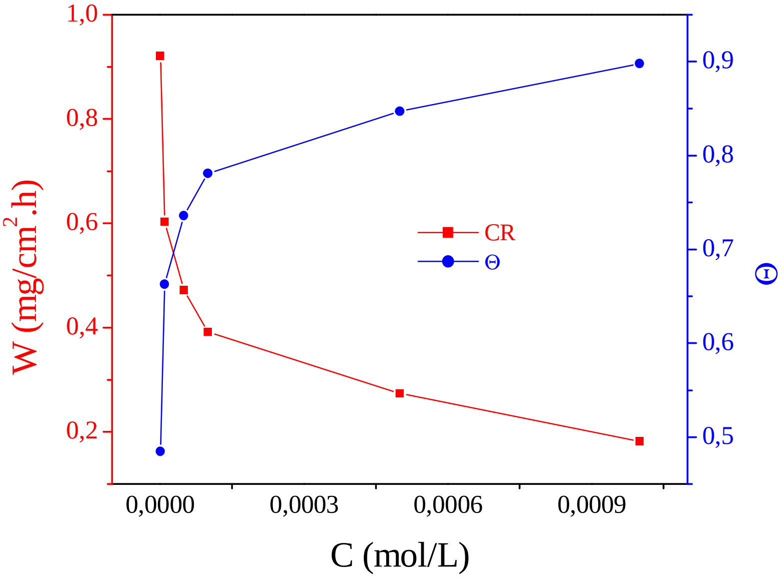

Fig 4. Variation of inhibition efficiency and corrosion rate in 0.5M H_2SO_4 on C38 steel surface without and with different concentrations of N-NEDHME.

A comparison may be made between inhibition efficiency *E* (%) values obtained by different methods (weight loss, polarisation curves and EIS methods). Fig 5 shows a curve that compares the *E* (%) values obtained. One can see that whatever the method used, no significant changes are observed in *E* (%) values. We can then conclude that there is a good correlation with the three methods used in this investigation at all tested concentrations and that N-NEDHME is an efficient corrosion inhibitor.

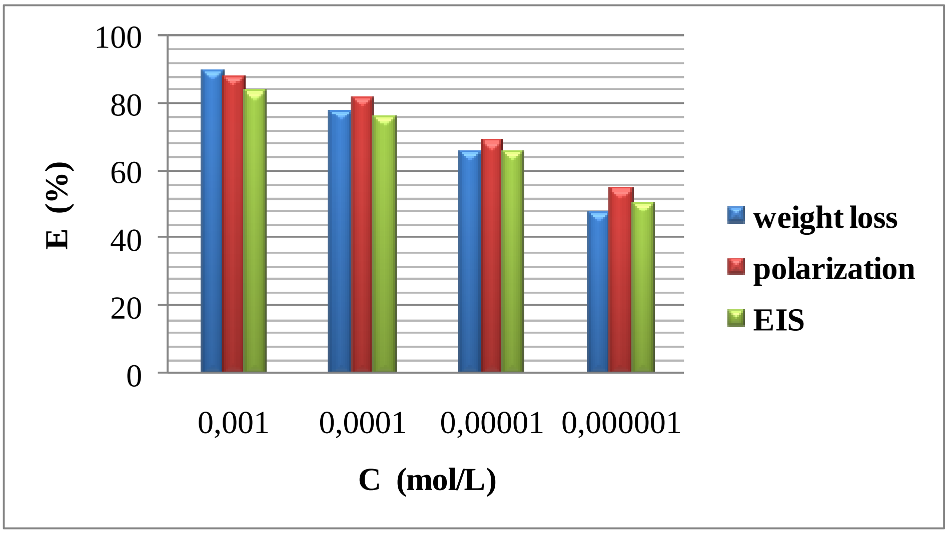

Fig 5. Comparison of inhibition efficiency (E %) values obtained by weight loss, polarisation and EIS methods

3.3.2. Adsorption isotherm and thermodynamic parameters

The adsorption on the corroding surfaces never reaches the real equilibrium and tends to reach an adsorption steady state. However, when the corrosion rate is sufficiently small, the adsorption steady state has a tendency to become a quasi-equilibrium state. In this case, it is reasonable to consider the quasi-equilibrium adsorption in thermodynamic way using the appropriate equilibrium isotherms [24]. The efficiency of this compound as a successful corrosion inhibitor mainly depends on its adsorption ability on the metal surface. So, it is essential to know the mode of adsorption and the adsorption isotherm that can give valuable information on the interaction of inhibitor and metal surface. The surface coverage values, Θ ($\Theta =$ IE/100) for different concentrations of N-NEDHME was used to explain the best adsorption isotherm. A plot of C/Θ versus C (Fig. 6) gives a straight line with an average correlation coefficient of 0.99959 and a slope of nearly unity (1.11) suggests that the adsorption of N-NEDHME molecules obeys Langmuir adsorption isotherm, which can be expressed by the following equation:

$$\frac{C_{inh}}{\Theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (20)$$

Where C_{inh} is inhibitor concentration and K_{ads} is the equilibrium constant for the adsorption–desorption process.

The thermodynamic parameters from the Langmuir adsorption isotherm are listed in Table 4, together with the value of the Gibbs free energy of adsorption ΔG°_{ads} calculated from the equation:

$$\Delta G^{\circ}_{ads} = -RTLn(55.5K_{ads}) \qquad (21)$$

Where R is the universal gas constant, T the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution [25].

The value K_{ads} calculated from the reciprocal of intercept of isotherm line as $6.028693 \times 10^4\ M^{-1}$. The high value of the adsorption equilibrium constant reflects the high adsorption ability of this inhibitor on C38 steel surface.

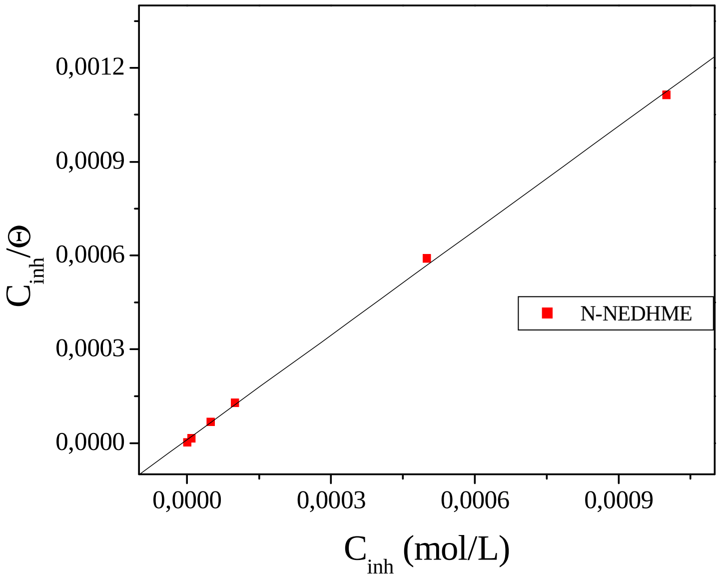

Fig 6. Langmuir adsorption isotherm of N-NEDHME on the steel surface

Table 4. Thermodynamic parameters for the adsorption of N-NEDHME in 0.5M H_2SO_4 on the C38 steel at 298K

Inhibitor	Slope	K_{ads} (M^{-1})	R^2	ΔG°_{ads} (KJ/mol)
N-NEDHME	1.11	60286.93	0.99959	-38.22

From Eq. (21), the ΔG°_{ads} was calculated as -38.22 kJ mol^{-1}. The negative value of standard free energy of adsorption indicates spontaneous adsorption of N-NEDHME molecules on C38 steel surface and also the strong interaction between inhibitor molecules and the metal surface [26, 27]. Generally, the standard free energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface (physical adsorption); those of -40 kJ mol^{-1} or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [28, 29]. The value of ΔG°_{ads} in our measurement is -38.22 kJ mol^{-1} (in Table 4), it is suggested that the adsorption of this N-NEDHME derivative involves two types of interaction, chemisorption and physisorption [30].

CONCLUSION

The following main conclusions are drawn from the present study :

- Inhibition efficiencies increase with increasing inhibitor concentration.
- Adsorption mechanism of the N-NEDHME on C38 steel in a 0.5M H_2SO_4 solution at 298K was a combination of both physisorption and chemisorption.
- Polarization curves indicated that the N-NEDHME behaves mainly as anodic-type inhibitor.
- Impedance method indicates that N-NEDHME adsorbs on the C38 steel surface with increasing transfer resistance and decreasing of the double-layer capacitance.
- The inhibition efficiencies determined by weight loss, potentiodynamic polarization and EIS techniques are in reasonably good agreement.

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