

Inhibition effect of trans-1,2-cyclohexanediaminetetraacetic acid towards C-steel corrosion in sulphuric acid solution

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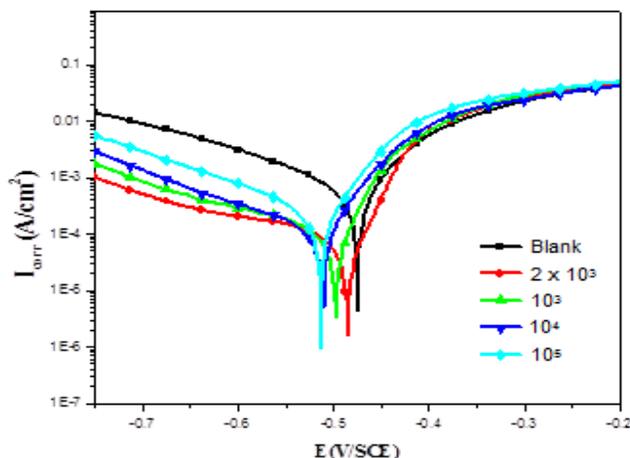
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- **Novelty and Highlights:**

- 1 – Trans-1,2-cyclohexanediaminetetraacetic acid has proved good inhibition properties.
- 2 – Equilibrium analysis has been performed and thermodynamic parameters have been calculated.

- **Graphical Abstract:**



Polarization curves of C-steel in 0.50 M H₂SO₄ in the presence of different concentrations of CyDTA

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The effect of 1,2 cyclohexanediaminetetraacetic (CyDTA) on the corrosion of C-steel in 0.50 M of H_2SO_4 solutions was examined using electrochemical and weight loss methods. It was found that the effectiveness of the inhibitor is increased with the increasing of the inhibitor concentration. The maximum inhibition attained was 91.1%. Temperature effect on the inhibition efficiency was studied by polarization curves method. Inhibition effectiveness decreased with increasing temperature. The thermodynamic activation parameters were determined. Results indicate that the inhibitor under study acts as a cathodic type inhibitor and the adsorption process obeys Langmuir adsorption isotherm.

Key words: C-steel; corrosion; CyDTA; Inhibition

Introduction

Corrosion of metals and alloys is a global concern which influences many industrial activities. The corrosion cost is huge and has been estimated to be about 4 % of the gross national product of the industrial sector. In the field of combating corrosion, both economic and scientific considerations are involved. Acids are commonly used in industrial processes such as cleaning, descaling, pickling and oil well acidizing. Acid solutions usually cause corrosion, so inhibitors are used to diminish the rate of metals dissolution [1-2]. Generally, an inhibitor hinders the corrosion reactions by (i) adsorption of ions/molecules on metal surface (ii) changing the cathodic and/or anodic reactions, and thus reducing the corrosion rate [3]. The efficiency of inhibitor is influenced by many factors such as temperature and concentration. It is well known that the organic compounds having heteroatom like oxygen, nitrogen and sulphur are the best corrosion inhibitors in acid solution as they have large basicity [4-9]. These atoms may work as active centres for sorption on the surface of the metal [10].

Many aminopolycarboxylate compounds are reported to have anticorrosion properties. Ethylene diaminetetraacetic acid (EDTA) was examined as corrosion inhibitor for aluminum in 0.10 M NaCl by using of chronoamperometric and potentiodynamic

methods. EDTA was found to be efficient inhibitor [11]. Evaluation of nitrilotriacetic acid (NTA) as corrosion inhibitor was reported by Kar and Singh [12]. The maximum corrosion inhibition achieved by NTA was 51.9% at concentration of 300 ppm. Abdel Rehim et al. [13] found that some amino polycarboxylic acids, such as diethylenetriaminepentaacetic acid (DTPA), polyacrylic acid, and polymethacrylic acid, are good inhibitors for metal corrosion.

In the present study, 1,2 cyclohexanediaminetetraacetic acid (CyDTA) was examined as a chemical corrosion inhibitor in the presence of H_2SO_4 . Mass loss and electrochemical measurements were used to investigate the efficiency of CyDTA as corrosion inhibitor for C-steel in 0.50 M H_2SO_4 and according to our knowledge; no previous study has been performed to evaluate CyDTA as corrosion inhibitor.

Experimental

Electrochemical measurements The electrochemical measurements were performed by using a Gamry Reference 3000 potentiostat. This potentiostat was linked to a corrosion cell with three electrode thermostats. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. The material used for constructing the working electrode was identical to that used for weight loss tests.

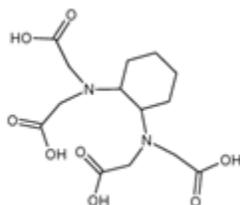


Fig. 1 Chemical structure of trans-1,2 cyclohexanediaminetetraacetic acid

Potentiodynamic polarization curves were obtained at a polarization scan rate of 0.50 mV/s. Potential was stabilized at free potential for 30 minutes before all experiments. Potential was in the range -800 mV to -200 mV. To study the effects of immersion time and temperature on the inhibitor effectiveness, several tests were performed in a temperature range 298–328 K.

The electrochemical impedance spectroscopy (EIS) measurements were achieved by using the same instrument which used for obtaining polarization curves. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 298 K. The impedance diagrams are given in the Nyquist representations. Experiments were repeated three times to ensure the reproducibility.

Weight loss tests Samples of $3.0 \times 3.0 \times 0.08 \text{ cm}^3$ dimensions and consist of (0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe balance) were used for weight loss tests. Before measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers.

Samples were rinsed with deionized water, degreased and dried with ethanol. Weight loss tests were performed in a double walled glass cell equipped with a thermostated cooling condenser. The immersion time for the gravimetric measurements was six hours at 298K.

Results and discussion

Potentiodynamic polarization curves Tafel polarization curves at different concentrations of CyDTA are presented in Fig. 2. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}),

anodic Tafel slope (b_a) and cathodic Tafel slopes (b_c), were obtained from these curves and are listed in Table 1. The inhibition efficiency values ($IE_{\text{I}_{\text{corr}}}$ %) were determined using the following equation:

$$IE_{\text{I}_{\text{corr}}} (\%) = \frac{(I_{\text{corr}}^0 - I_{\text{corr}})}{I_{\text{corr}}^0} \times 100 \quad (1)$$

where I_{corr}^0 and I_{corr} are the values of corrosion current densities of C-steel without and with the inhibitor, respectively, which were calculated by extrapolation of the cathodic Tafel lines to the corrosion potential E_{corr} .

Results in Table 1 prove that I_{corr} values gradually decreased with the increase of the inhibitor concentration with respect to the blank. This can be attributed to the fact that more inhibitor concentration means more molecules that are available to be adsorbed on the C-steel surface.

Table 1. Electrochemical parameters of C-steel at different concentrations of CyDTA in 0.5M H_2SO_4 and corresponding inhibition efficiency

Inhibitor	10^4 Con. (M)	$-E_{\text{corr}}$ mV/SCE	I_{corr} $\mu\text{A cm}^{-2}$	$-b_c$ mV dec $^{-1}$	$-b_a$ mV dec $^{-1}$	$IE_{\text{I}_{\text{corr}}}$ (%)
Blank	-	511	1977	196	252	----
CyDTA	20	524	192	217	267	90.3
	10	507	312	216	261	83.9
	1.0	523	453	196	259	76.6
	0.10	513	598	162	204	69.1

The values of the cathodic Tafel slopes, b_c and anodic Tafel slopes, b_a , were found to vary slightly with the exception of the lowest concentration, indicating that addition of CyDTA has no effect on the mechanism of the proton discharge reaction.

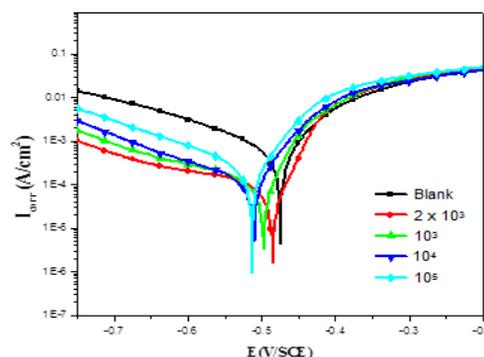


Fig. 2 Polarization curves of C-steel in 0.50M H_2SO_4 in the presence of different concentrations of CyDTA.

The values of inhibition efficiency (IE %) increase with inhibitor concentration reaching a maximum value (90.3%) at $2 \times 10^{-3} \text{ M}$. This (IE %) is the highest among all previously reported polyaminocarboxylates such as EDTA, NTA and DTPA [11-13]. From Fig. 2, it is clear that, the

effect of the inhibitor on the cathodic potential is more profound, so CyDTA can be classified as cathodic type inhibitor.

Electrochemical impedance spectroscopy measurements all plots in Fig. 3 display a single capacitive loop. Impedance parameters derived from the Nyquist plots, percentage of inhibition efficiencies, EI (%) are shown in Table 2.

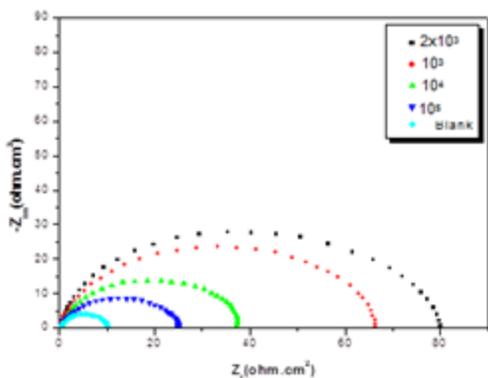


Fig. 3. Nyquist diagrams for C-steel electrode with and without CyDTA at 298K after 30 min of immersion.

Values of R_t were given by subtracting the high frequency impedance from the low frequency one as follow [11]

$$R_t = Z_{re}(\text{at low frequency}) - Z_{re}(\text{at high frequency}) \quad (2)$$

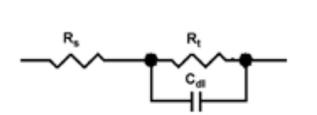


Fig. 4. The electrochemical equivalent circuit used to fit the impedance spectra.

The percentage of inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the equation 3:

$$EI_{R_t} (\%) = \frac{R_t - R_t^0}{R_t} \times 100 \quad (3)$$

where R_t and R_t^0 are the charge transfer resistance values without and with inhibitor, respectively.

It is obvious from the results displayed in Table 2 that the increase in resistance in the presence of CyDTA,

relative to the blank alone is associated to the corrosion protection effect of the molecules.

Table 2. Electrochemical Impedance parameters for corrosion of C-steel in acid medium at various contents of CyDTA

Inhibitor	10^4 Conc. (M)	R_t ($\Omega \cdot \text{cm}^2$)	f_{max} (Hz)	$10^4 C_{dl}$ ($\mu\text{F}/\text{cm}^2$)	EI_{R_t} (%)
Blank	-	11	165	1.0	---
CyDTA	20	98	68	0.33	88.8
	10	64	79	0.30	82.8
	1.0	40	15	0.23	72.5
	0.10	27	66	0.13	59.3

The value of C_{dl} decreases in the presence of the inhibitor. The decrease in C_{dl} , may be ascribed to a decrease in local dielectric constant and/or an increase in the thickness of the electric double layer, suggesting that CyDTA molecules working by adsorption at the metal/solution interface. Thus, the decrease in C_{dl} values and the increase in R_t values and consequently of inhibition efficiency may be due to the gradual replacement of water molecules by the adsorption of the CyDTA molecules on the metal surface, decreasing the extent of dissolution reaction [14,15].

Weight loss, corrosion rates and inhibition efficiency The effect of the addition of different concentrations of CyDTA on the corrosion of C- steel in 0.50M H_2SO_4 solutions was investigated by using weight loss test at 298 K. Inhibition efficiency E_w (%) was calculated as follows:

$$EI_w (\%) = \frac{W_{corr} - W'_{corr}}{W_{corr}} \times 100 \quad (4)$$

where W_{corr} and W'_{corr} are the corrosion rates of C-steel in the absence and the existence of various concentrations of CyDTA, respectively.

It is clear from the results that presented in Table 3 that the effectiveness of CyDTA increases as its concentration increases.

Table 3. Effect of CyDTA concentration on corrosion data of C-steel in 0.5 M H_2SO_4

Inhibitor	10^4 Conc. (M)	W_{corr} ($\text{mg} \cdot \text{cm}^{-2}$)	E_w (%)
Blank	-	17.56	---
CyDTA	20	2.03	88.4
	10	3.90	77.8
	1.0	5.75	67.3
	0.10	7.42	57.7

It is obvious that the required concentration of inhibitor to achieve the maximum efficiency was determined as 2×10^{-3} M (88.4 %). Results found by weight loss technique are in excellent agreement with the values of inhibitor efficiency determined by electrochemical method.

Adsorption isotherms the aim of adsorption isotherms is to explain the relation between the equilibrium concentration of the inhibitor and the adsorbed quantity on the sorbent surface. It is necessary to calculate the coverage of the surface, θ ; in order to determine the best adsorption isotherm model. Experimental data were fitted to two isotherm models.

Langmuir isotherm model the linear form of Langmuir isotherm can be represented by Eq. 5

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process that expresses the relative adsorption capacity of the sorbent which is associated to the bonding energy and C_{inh} the inhibitor concentration. Value of K_{ads} was determined from the intercept of Fig. 6.

The surface coverage (θ) can be obtained from weight loss measurements, it calculated by the following equation:

$$\theta = \frac{W_{corr} - W'_{corr}}{W_{corr}} \quad (6)$$

The linear form of Langmuir is shown in Fig. 5. It gives a straight line with slope value of 0.93. This slope is close to 1, and the strong correlation ($R^2 > 0.9995$) proved clearly that the adsorption of CyDTA onto the C-steel obeys the Langmuir adsorption isotherm.

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G^0_{ads}}{RT}\right) \quad (7)$$

The value of equilibrium adsorption constant obtained from this isotherm is about $5.1 \times 10^3 \text{ M}^{-1}$, suggesting a chemically adsorbed film [16]. Moreover, the largest negative value of ΔG_{ads} , (-54.0 kJ/mol) for CyDTA, indicate that this inhibitor is strongly adsorbed onto the C-steel surface. It is well known that values of $-\Delta G_{ads}$ of the order of 20 kJ/mol or lower indicate a physisorption; those of order of 40 kJ/mol or higher indicate chemisorption process [18-19].

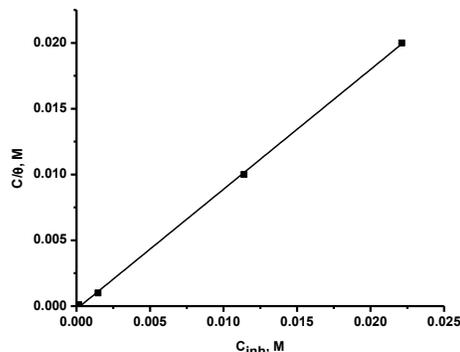


Fig. 5. Langmuir adsorption of CyDTA on the C-steel surface in 0.5 M H_2SO_4 solution.

Frenudlich isotherm the linear form of Frenudlich isotherm model is given by Eq.8.

$$\ln\theta = \ln K_{ads} + n \ln C_{inh} \quad (8)$$

where n is the heterogeneity factor expressing the deviation from linearity of adsorption which determines the degree of non-linearity between solution concentration and adsorption in this manner: if $n = 1$, then adsorption is linear; if $n > 1$, then adsorption is a chemical process; if $n < 1$, adsorption is considered as a physical process [17]. n value for adsorption of CyDTA on the surface of C-steel was determined from slope of Fig. 6 as 0.08. n value is less than 1 indicating the adsorption is a physical process.

3.5. Effect of temperature

The corrosion behaviour of C-steel in the acid media was investigated at various temperatures in order to calculate the thermodynamic activation parameters of the corrosion process.

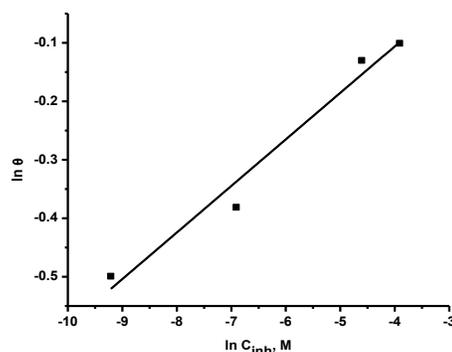


Fig. 6 Freundlich adsorption isotherm of CyDTA on the C-steel surface in 0.50 M H_2SO_4 solution.

Table 4. Effect of temperature on different corrosion parameters for C-steel in 0.50 M H₂SO₄ in absence and presence of CyDTA

	T K	E _{corr} mV/SCE	I _{corr} mA/cm ²	-b _c mV/dec	b _a mV/dec	E %
0.50 M H ₂ SO ₄	298	-511	1977	196	254	-
	308	-497	2786	175	265	-
	318	-506	3718	211	260	-
	328	-514	4555	188	251	-
2 x 10 ⁻³ M of CyDTA	298	-524	192	247	189	91.3
	308	-510	417	217	178	85.0
	318	-528	797	233	184	79.3
	328	-536	1258	221	181	72.9

Tafel polarization curves were carried out at temperature range (298-328 K) in the absence and existence of CyDTA of concentration 2.0 x 10⁻³ M. Results shown in Table 4, Figs. 7 and 8 reveal that I_{cor} is directly proportional to temperature. Although these results prove that CyDTA can be considered as an effective inhibitor, but it is clear that the efficiency of CyDTA decreases as temperature increases; this may be attributed to desorption of adsorbate as the temperature increases.

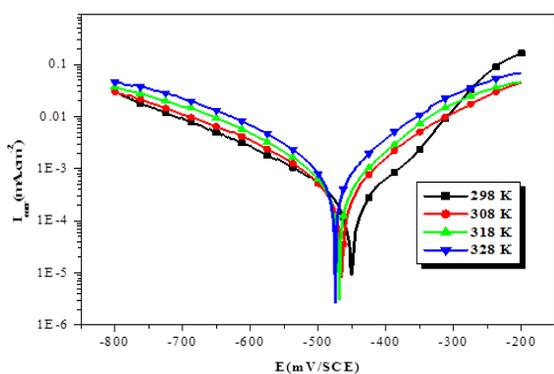


Fig. 7. Polarization diagrams for C-steel in 0.50 M H₂SO₄ at various temperatures.

Thermodynamic activation parameters for the corrosion process were determined by using Arrhenius and Eyring equations which are represented by Eqs. 9 and 10 respectively

$$\ln(I_{cor}/T) = -\Delta H/RT + \ln(k_B/h) + \Delta S/R \quad (9)$$

$$\ln I_{cor} = (-E_a)/RT + \ln A \quad (10)$$

where k_B is the Boltzmann's constant (1.381 x 10⁻²³ J/K), T is the absolute temperature in Kelvin (K), h is Planck's constant (6.626 x 10⁻³⁴ Js), E_a is the activation energy, A is the frequency factor, R is the gas constant and ΔH_a is the enthalpy of activation. The E_a, ΔH_a and ΔS_a values were determined from the slopes of these plots. The calculated values of E_a, ΔH_a and ΔS_a in the absence and the presence of 2.0 x 10⁻³ M of CyDTA are given in Table 5.

Table 5. Values of activation parameters for C-steel corrosion in 0.50 M H₂SO₄ in the absence and presence of 2.0 x 10⁻³ M of CyDTA.

Inhibitor	E _a (kJ/mol)	ΔH _a (kJ/mol)	ΔS _a (J/mol)	E _a - ΔH _a (KJ/mol)
Blank	22.82	20.15	-78.35	2.6
CyDTA	51.23	48.63	-113.5	2.6

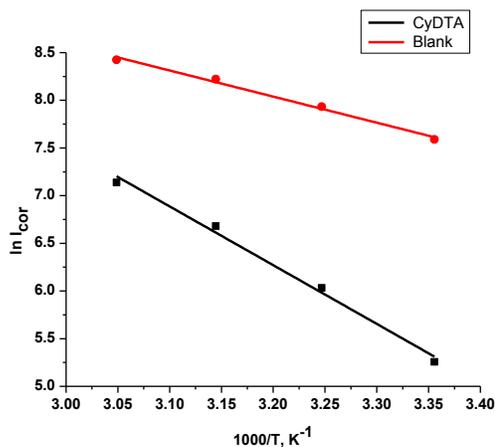


Fig. 8. Arrhenius plots of C-steel in 0.50 M H₂SO₄ with and without 2.0 x 10⁻³ M of CyDTA.

Values of activation energy E_a in the absence and presence of the CyDTA; reveals that addition of CyDTA to the acid solution increases the activation energy.

On the other hand, the inspection of the Table 4 revealed that the thermodynamic parameters (ΔS_a and ΔH_a) for corrosion process of C-steel in 0.50 M H₂SO₄ in the presence of inhibitor was lower than that obtained in the absence of inhibitor. The positive sign of ΔH_a reflects the endothermic nature of the C-steel dissolution process suggesting that the dissolution of C-steel is slow [20] in the presence of inhibitor. Large and negative value of entropies (ΔS_a) imply that the

activated complex in the rate determining step represents an association rather than a dissociation step [18, 19], meaning that a decrease in disordering takes place on going from reactants to the activated complex [20-22].

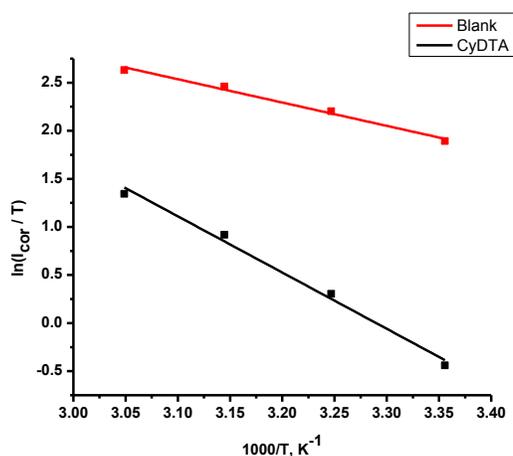


Fig. 9. Eyring plots of C-steel in 0.50 M H₂SO₄ with and without 2.0 x 10⁻³M of CyDTA

Conclusions

CyDTA proved its effectiveness as corrosion inhibitor for the corrosion of C-steel at various temperatures in 0.5 M H₂SO₄. The inhibition efficiency increases as the inhibitor concentration increases. Thermodynamic activation parameters were calculated proving that adsorption of inhibitor on the metal surface is considered be chemical process. Results were analyzed by using Langmuir adsorption isotherm.

Notes and references

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