Technical paper

Effect of Diaminoalkane Derivatives on Steel Corrosion in HCL Media

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Abstract

Some diamine compounds have been tested as corrosion inhibitors on steel in 1 M hydrochloric acid. The study is carried out using weight loss measurements. Results obtained show that the inhibition efficiency (E %) increases with concentration. The effect of carbon chain length between the two amino groups shows that the efficiency increases with the number of $–CH_2$. A correlation between quantum energies and efficiency is obtained. Adsorption of inhibitors on the mild steel surface in 1 M HCl follows the Langmuir isotherm model.

Keywords: diamine; steel; hydrochloric acid; corrosion; inhibition.

1. Introduction

Acid solutions are generally used for the removal of rust and scale in industrial processes. Inhibitors are often used in these processes to control the metal dissolution. Hydrochloric acid is widely used in the pickling, cleaning and descaling of steel and ferrous alloys. Most of the well known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms. There has been a growing interest in the use of organic compounds as inhibitors for the aqueous corrosion of metals. The study of corrosion inhibition processes by organic compounds is a very active field of research.[1–4] Adsorbed organic molecules prevent steel corrosion by blocking the active sites on the metal surfaces [5] and the inhibition efficiency (E%) of an inhibitor depends strongly on the chemical structure or the functional groups on the inhibitor molecule.[6] Furthermore, the molecular-level structure and composition of materials can dramatically affect their bulk and interfacial properties.

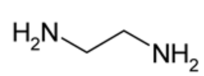
Nitrogen-containing organic compounds, such as amines[7–12] and diamine derivatives[13–15] on the corrosion for many metals in acidic solutions offer good protection of metallic materials. Due to the presence of the $–NH_2$ group, electronegative nitrogen atom in the molecule, amines should be good corrosion inhibitors.

The corrosion inhibition efficiency in relation with molecular properties for different kinds of organic compounds has successfully linked to some quantum mechanical studies.[16–21] Quantum chemical parameters are usually used to explore the relationship between the inhibitor molecular properties and its corrosion inhibition efficiency. The properties include orbital energy, charge density and combined energy, etc ...

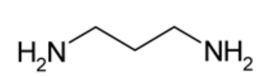
The objective of this work is to study by weight loss method some aminoalkane as corrosion inhibitor of steel in molar hydrochloric acid solution. The inhibition efficiency is correlated to the number of CH_2 group between amine function and also to some quantum parameters.

2. Experimental

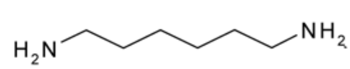
The three diaminoalkanes (diaminoethane (DAE), diaminopropane (DAP) and diaminohexane (DAH)) are analytical grade. The molecular structures are shown below:



Diaminoethane (DAE)



Diaminopropane (DAP)



Diaminohexane (DAH)

The steel samples (0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and Fe balance) were polished with different emery paper up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and drying at room temperature. Molar HCl was prepared by dilution of Analytical Grade 37 % HCl with distilled water.

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 ml. The steel specimens used had a rectangular form (2.5 cm × 2 cm × 0.05 cm). The immersion time for the weight loss was 6 h at 308 K. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Triplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in $mg.cm^{-2}\ h^{-1}$.

The computation of the energies of the molecular orbital, E_{HOMO} (high occupied molecular orbital energy) and E_{LUMO} (lowest unoccupied molecular orbital energy), energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) has been determined by using the PETRA program[22], (http://www2.chemie.uni-erlangen.de/software/petra/ manual/)

3. Results and Discussion

3.1. Weight Loss Study

The effect of concentration of diaminoalkane studied on the corrosion behaviour of steel was investigated in 1 M HCl by gravimetric measurements at 6 h of immersion at 308 K (Table 1). The inhibition efficiency (Ew, %) was calculated by the following relation:

$$E_w\,\% = \frac{W_{corr} - W_{corr\,(inh)}}{W_{corr}} \times 100 \qquad (1)$$

where W_{corr} and $W_{corr\,(inh)}$ are the corrosion rates of steel in the absence and presence of the organic compound, respectively.

It is clear that the corrosion rate decreases with the concentration of diaminoalkane (Table 1). Then inhibition efficiency (E_w %) increases with the inhibitor concentration to reach 85.2 % at 10^{-3} M DAH. The inhibitory action is due to the presence of two NH_2 group in the molecule. E% obtained increases linearly with the number of CH_2 group between the two NH_2 (Fig. 1). The effect of chain length is studied by several authors. We cited Touhami et al. in studying the effect of chain length between two pyrazolic rings.[6] The molecular weight of the inhibitor has a direct influence on its inhibition efficiency. The increase in molecular weight of the inhibitor is due to an increase in the length of the hydrocarbon chain of amines,[23] nitriles[24] or mercaptants.[25] The rise of the inhibition efficiency is due to the inductive effect of the methyl groups.

Table 1: Gravimetric results of steel in acid without and with addition of diamines at 6h.

Inhibitor (M)		W ($mg.cm^{-2}.h^{-1}$)	% E
	Blank	1,439	–
	10^{-5}	1,25	13,8
DAE	5×10^{-5}	1,025	28,8
	10^{-4}	0,8566	40,5
	5×10^{-4}	0,499	65,3
	10^{-3}	0,349	75,7
	10^{-6}	1,09	24,2
	10^{-5}	0,761	47,1
	5×10^{-5}	0,693	51,8
DAP	10^{-4}	0,458	68,1
	5×10^{-4}	0,326	77,3
	10^{-3}	0,301	79,1
	10^{-6}	0,72	50,0
	10^{-5}	0,593	58,8
	5×10^{-5}	0,574	60,1
DAH	10^{-4}	0,552	63,7
	5×10^{-4}	0,246	82,9
	10^{-3}	0,213	85,2

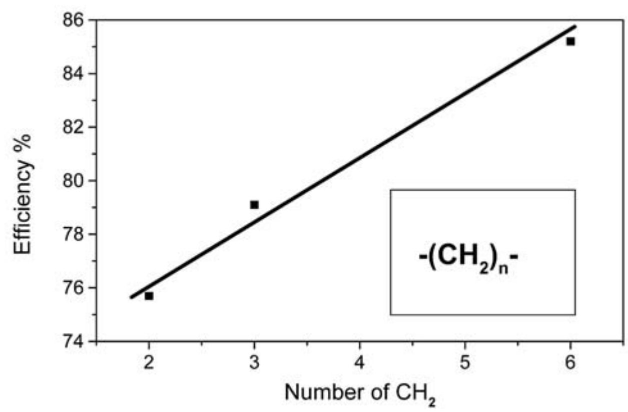


Fig. 1: Variation of efficiency with the number of CH_2 between NH_2 groups

3.2. Quantum Calculation

The reactive ability of the inhibitor is closely linked to their frontier molecular orbitals (MO), including highest occupied molecular orbital HOMO and lowest unoccupied molecular orbital LUMO. Higher HOMO energy (E_{HOMO}) of the molecule means a higher electron donating ability[26] and Low LUMO energy (E_{LUMO}) indicates that the acceptor accepts electrons easily.

In the tested inhibitors, diaminoalkane compounds as Lewis bases are electron donators, so E_{HOMO} is an important tool to interpreting their inhibitions. Moreover these amines in acidic solution are readily protonated and the quantum parameters are evaluated. Results obtained in Table 2 show that $(DAH)H_2^{2+}$ has the highest HOMO energy, it donates electrons easily, and DAH is the best inhibitor. It is known that in the chemical adsorption an increase in E_{HOMO} causes the significant increase in inhibition efficiency of inhibitors. E% increases linearly with E_{HOMO} (Fig. 2). Moreover, the negative sign of the coefficient of E_{HOMO} can be concluded that the adsorption of these diamines on the steel surface has not chemical mechanism and it may be physical.[26,27] Physical adsorption results from electrostatic interaction between the charged centres of inhibitor and charged metal surface. The energy gap between LUMO and HOMO ($\Delta E = E_{LUMO} - E_{HOMO}$) may be also an important parameter and shows a linear behaviour with efficiency (Fig. 3). The smaller value of ΔE indicates that the molecule is the more probable to give higher inhibition efficiency.[28]

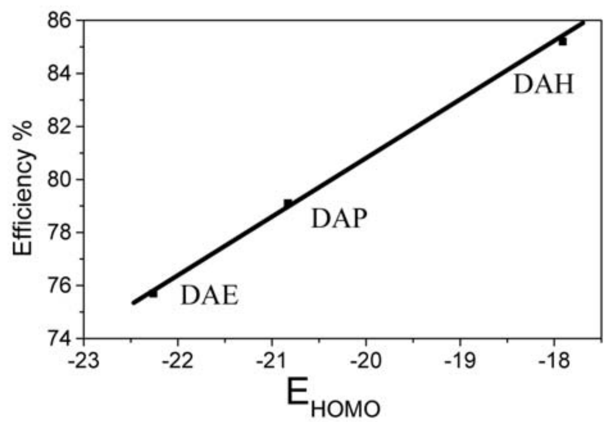


Fig. 2: Variation of efficiency against the HOMO energy of diamine compounds.

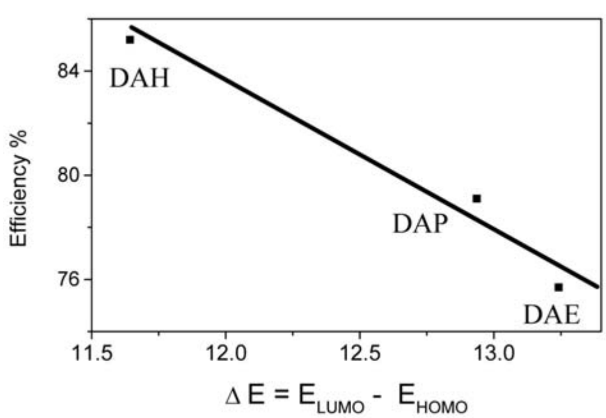


Fig. 3: Variation of efficiency against the gap energy of diamine compounds.

3.3. Adsorption Isotherm

Action of inhibitors on metal surface is often expressed by an adsorption isotherm. Many adsorption isotherms were proposed to calculate the thermodynamic parameters pertaining to inhibitor adsorption. The models considered were:[29]

Langmuir isotherm $\theta/(1-\theta) = k_{ads}C$ (2)

Temkin isotherm $\exp(f.\theta) = k_{ads}C$ (3)

Frumkin isotherm $\theta/(1-\theta).\exp(-2f.\theta) = k_{ads}C$ (4)

and Freundluich isotherm $\theta = k_{ads}\, C$ (5)

where k_{ads} is the equilibrium constant of the adsorption process, C the inhibitor concentration and f the factor of energetic inhomogeneity. The simplest one is that of Langmuir which involves assumptions of (a) no interactions between the absorbed species on the electrode surface, (b) no heterogeneity of the surface, and (c) at high bulk activities, saturation coverage of the electrode by adsorbate (e.g., to form a monolayer) of surface coverage θ. The Langmuir adsorption isotherm is the best fitted plot (Fig. 4) expressed by the following equation:[30]

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (6)$$

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant.

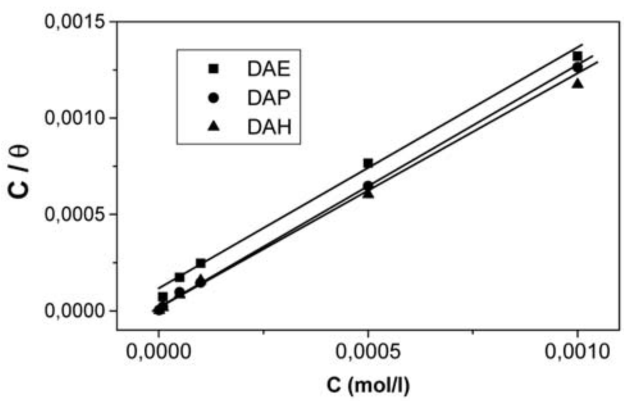


Fig. 4: The relationship between C/θ and C of diaminoalkanes.

The linear regression between C/θ and C is calculated by the computer, and the slope and the linear correlation coefficient are close to unity. The obtained values of K lead to the adsorption free energy (ΔG°_{ads}) obtained according to the equation:[31]

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^\circ}{RT}\right) \qquad (7)$$

The negative values of ΔG°_{ads} for DAE, DAP and DAH, respectively, suggest that the adsorption of diamines onto the steel surface is a spontaneous process. The relatively small and negative values of ΔG°_{ads} show

Table 2: Adsorption parameters of diamines on the surface of steel in molar HCl solution.

	slope	R	K ($l.mol^{-1}$)	ΔG°_{ads} ($kJ\ mol^{-1}$)
DAE	1,239 ± 0.046	0.9979	9560	–33.78
DAP	1,251 ± 0.014	0.9998	58480	–38.42
DAH	1,161 ± 0.018	0.9995	55556	–38.29

that adsorption of studied amines may have physical mechanism. The obtained values of the adsorption free energy, ΔG°_{ads}, may be indicative of physical adsorption.[32,33]

4. Conclusion

From the above results and discussion, the following conclusions are drawn:

- The inhibition efficiency increases with the inhibitor concentration to reach 85.2%.
- The inhibition increases with the chain length between amine groups.
- The adsorption of aminoalkanes on the steel surface from 1M HCl obeys the Langmuir adsorption isotherm.
- A good correlation is obtained between HOMO and gap energies and efficiency.

5. Acknowledgements

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Povzetek

Z meritvami izgube mase smo proučevali nekatere diaminske spojine kot inhibitorje korozije jekla v 1 M HCl. Dobljeni rezultati kažejo, da učinkovitost inhibicije raste tako s povečevanjem koncentracije diamina v raztopini kot tudi s številom $–CH_2$ skupin med amino skupinama. Pokazali smo tudi na korelacijo med kvantnimi energijami in učinkovitostjo inhibicije, ki jo lahko opišemo z Langmuirjevo izotermo.