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.\(^1\) 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\(^7\) and diamine derivatives\(^13\) on the corrosion for many metals in acidic solutions offer good protection of metallic materials. Due to the presence of the \(-\text{NH}_2\) 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.\(^16\) 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 \(\text{CH}_2\) group between amine function and also to some quantum parameters.

2. Experimental

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

\[
\text{Diaminoethane (DAE)} \quad \text{Diaminopropane (DAP)}
\]

\[
\text{Diaminohexane (DAH)}
\]
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:

$$E_w \% = \frac{W_{corr} - W_{corr\ (inh)}}{W_{corr}} \times 100$$  \hspace{0.5cm} (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.\textsuperscript{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,\textsuperscript{23} nitriles\textsuperscript{24} or mercaptants.\textsuperscript{25} The rise of the inhibition efficiency is due to the inductive effect of the methyl groups.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Inhibitor (M) & W (mg.cm$^{-2}$·h$^{-1}$) & \% E \\
\hline
Blank & 1.439 & \textemdash \\
$10^{-3}$ & 1.25 & 13.8 \\
$5 \times 10^{-5}$ & 1.025 & 28.8 \\
$10^{-4}$ & 0.8566 & 40.5 \\
$10^{-3}$ & 0.499 & 65.3 \\
$10^{-6}$ & 0.349 & 75.7 \\
$10^{-5}$ & 0.199 & 24.2 \\
$5 \times 10^{-5}$ & 0.0693 & 51.8 \\
$10^{-4}$ & 0.458 & 68.1 \\
$5 \times 10^{-4}$ & 0.326 & 77.3 \\
$10^{-3}$ & 0.301 & 79.1 \\
$10^{-6}$ & 0.72 & 50.0 \\
$10^{-5}$ & 0.593 & 58.8 \\
$5 \times 10^{-5}$ & 0.574 & 60.1 \\
$10^{-4}$ & 0.552 & 63.7 \\
$5 \times 10^{-4}$ & 0.246 & 82.9 \\
$10^{-3}$ & 0.213 & 85.2 \\
\hline
\end{tabular}
\caption{Gravimetric results of steel in acid without and with addition of diamines at 6h.}
\end{table}

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\textsuperscript{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)H2+ 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 $E_{\text{HOMO}}$ causes the significant increase in inhibition efficiency of inhibitors. $E\%$ increases linearly with $E_{\text{HOMO}}$ (Fig. 2). Moreover, the negative sign of the coefficient of $E_{\text{HOMO}}$ 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 ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) may be also an important parameter and shows a linear behaviour with efficiency (Fig. 3). The smaller value of $\Delta E$ 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: $\theta/(1 - \theta) = k_{\text{ads}} C$ (2)
- Temkin isotherm: $\exp(f, \theta) = k_{\text{ads}} C$ (3)
- Frumkin isotherm: $\theta/(1 - \theta) \exp(-2f, \theta) = k_{\text{ads}} C$ (4)
- Freundlich isotherm: $\theta = k_{\text{ads}} C$ (5)

where $k_{\text{ads}}$ 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 $\theta$. The Langmuir adsorption isotherm is the best fitted plot (Fig. 4) expressed by the following equation:30

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

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

The linear regression between $C/\theta$ 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 ($\Delta G^o_{\text{ads}}$) obtained according to the equation:31

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

The negative values of $\Delta G^o_{\text{ads}}$ 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 $\Delta G^o_{\text{ads}}$ show
that adsorption of studied amines may have physical mechanism. The obtained values of the adsorption free energy, $\Delta G_{\text{ads}}^\circ$, 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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### 6. References

Povzetek

Z meritvami izgube mase smo proučevali nekatere diaminske spojine kot inhibitorje korozije jekla v 1 M HCl. Dobitni rezultati kažejo, da učinkovitost inhibicije raste tako s povečevanjem koncentracije diamina v raztopini kot tudi s številom –CH₂ skupin med amino skupinama. Pokazali smo tudi na korelacijo med kvantnimi energijami in učinkovitostjo inhibicije, ki jo lahko opišemo z Langmuirjevo izoteremo.