



# Electrochemical and theoretical studies of adsorption and corrosion inhibition of aniline violet compound on carbon steel in acidic solution



Hojat Jafari<sup>a,\*</sup>, Koray Sayin<sup>b</sup>

<sup>a</sup>Abadan Faculty of Petroleum Engineering, Petroleum University of Technology, Abadan, Iran

<sup>b</sup>Department of Chemistry, Institute of Science, Cumhuriyet University, 58140 Sivas, Turkey

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## ABSTRACT

The inhibition ability of 4-[bis[4-(dimethylamino)phenyl]methyl]-*N,N*-dimethylaniline (Mv10B) on carbon steel in 1 M HCl solution was studied by electrochemical techniques. Mv10B inhibited carbon steel corrosion in 1 M HCl solution significantly and the inhibition efficiency increased with Mv10B concentration. Potentiodynamic polarization results showed that Mv10B was a mixed-type inhibitor. The adsorption of Mv10B on steel surface followed Langmuir adsorption isotherm. The inhibition performance of Mv10B was also evidenced by AFM images. Computational investigations of studied inhibitor are performed by using HF method with 6-31++G(d,p) and 6-311++G(d,p) basis sets.

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## 1. Introduction

Over the years, a number of protection measures have been suggested to delay, slow, or stop the corrosion process, the use of corrosion inhibitors is an important method to protect metallic materials against corrosion in acidic medium. The acid solutions are widely used in industry for various purposes, such as acid pickling, acidification of petroleum wells, among others [1]. Most well-known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms.

The choice of the inhibitor is based on two considerations, first economic consideration and second, should contain the electron cloud on the aromatic ring or the electronegative atoms such as N, O in the relatively long chain compounds. Generally the organic compounds containing hetero atoms like O, N, S, and P are found to work as very effective corrosion inhibitors. The efficiency of these compounds depends upon electron density present around the hetero atoms, the number of adsorption active centers in the molecule and their charge density, molecular size, mode of adsorption, and formation of metallic complexes [2–5].

Adsorption of inhibitors on the metal surface involves the two types of interaction (physical adsorption and chemical adsorption). Physical adsorption is associated with the electrostatic interaction between charged molecules and the charged metal surface. The second one, chemisorption process involves charge sharing or charge

transfer from the inhibitor molecules to the metal surface to form a co-ordinate type bond and takes place in the presence of heteroatoms (P, N, S, O, etc.) with lone pairs of electrons and/or aromatic ring in the molecular structure [6–8].

Density functional theory (DFT) has grown to be a useful theoretical method to interpret experimental results, enabling one to obtain structural parameters for even huge complex molecules, and it can explain the hard and soft acid base (HSAB) behavior of organic molecules, *i.e.*, DFT connects some traditional empirical concepts with quantum mechanical interpretations [9,10]. Therefore, DFT is a very powerful technique to probe the inhibitor/surface interaction and to analyze experimental data. These are the reasons why we selected both electrochemical and DFT methods to evaluate the efficiency of 4-[bis[4-(dimethylamino)phenyl]methyl]-*N,N*-dimethylaniline.

In this work, we report the successful use of 4-[bis[4-(dimethylamino)phenyl]methyl]-*N,N*-dimethylaniline as eco-friendly corrosion inhibitor for corrosion of steel in 1 M HCl solutions by using several electrochemical techniques like: electrochemical impedance spectroscopy and potentiodynamic polarization; corrosion kinetic parameters were evaluated and surface topology was studied using AFM images. Quantum chemical calculations have been performed using DFT, and several quantum chemical indices are calculated and correlated with the inhibitive effect of inhibitor.

## 2. Experimental

### 2.1. Materials

The carbon steel used had the following chemical composition (wt.%): 0.11 C, 0.56 Mn, 0.03 Si, 0.007 P, 0.005 S, 0.07 Cr,

\* Corresponding author. Tel.: +98 9137118405.

E-mail address: [hojatjafari80@yahoo.com](mailto:hojatjafari80@yahoo.com) (H. Jafari).

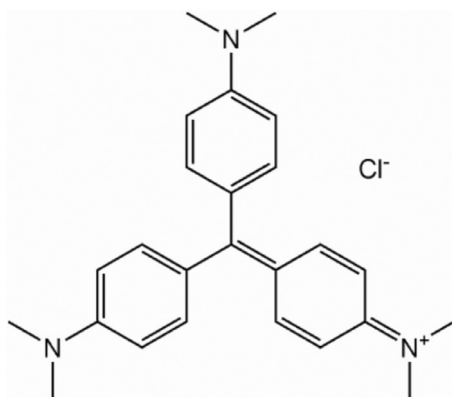


Fig. 1. Chemical structure of Mv10B.

0.03 Ni and balance Fe. The specimens of dimension 1 cm × 1 cm (exposed) × 0.5 cm (isolated with polyester resin) were used for polarization and electrochemical impedance methods. They were polished mechanically using different grade emery papers up to 1200, and washed thoroughly with triple distilled water and degreased with acetone before being immersed in the acid solution.

The aggressive solution of 1 M HCl was prepared by dilution of Merck Product HCl. The concentration range of inhibitors employed was varied from  $1 \times 10^{-4}$  M to  $5 \times 10^{-3}$  M. All chemicals used in present work were of reagent-grade Merck product and used as received without further purification. Fig. 1 shows the chemical structure of Mv10B.

## 2.2. Methods

The apparatus for electrochemical investigations consists of computer controlled Auto Lab potentiostat/galvanostat (PGSTAT302N) corrosion measurement system at a scan rate of 1 mV/s. The electrochemical experiments were carried out using a conventional three electrode cell assembly at 25 °C. A rectangular platinum foil was used as counter electrode and saturated calomel electrode as the reference electrode. The EIS experiments were conducted in the frequency range of 100 kHz to 0.01 Hz at open circuit potential. The AC potential amplitude was 10 mV. Time interval of 25 min was given for steady state attainment of open circuit potential. Fitting of experimental impedance spectroscopy data to the proposed equivalent circuit was done by means of home written least square software based on the Marquardt method for the optimization of functions and Macdonald weighting for the real and imaginary parts of the impedance [9].

The specimens of size 1 cm × 1 cm × 0.5 cm were abraded with emery paper (up to 1200) to give a homogeneous surface, then washed with distilled water and acetone. The specimens were immersed in 1 M HCl prepared with and without addition of  $5 \times 10^{-3}$  M at 25 °C for 6 h, cleaned with distilled water. The surface morphology of the electrode surface was evaluated by metallographic microscope Neophot32 and atomic force microscopy Nan Surf easyscan2.

Computational progresses were done by using GaussView 5.0.8 [11], Gaussian 09 AM64L-G09RevD.01 package programme [12], ChemBioDraw Ultra Version (13.0.0.3015) [13]. HF method was selected as method with 6-31++G(d,p) and 6-311++G(d,p) basis sets for studied inhibitor. All calculations were performed *in vacuo*. The vibration frequency analyses were indicated that optimized structures of all inhibitors are at stationary points corresponding to local minima without imaginary frequencies. Mentioned quantum chemical descriptors were calculated by using Eqs. (1)–(17) [14–19].

$$E_{\text{GAP}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

$$I = -E_{\text{HOMO}} \quad (2)$$

$$A = -E_{\text{LUMO}} \quad (3)$$

$$\eta = \frac{I - A}{2} \quad (4)$$

$$\sigma = \frac{1}{\eta} \quad (5)$$

$$\chi = \frac{|E_{\text{HOMO}} + E_{\text{LUMO}}|}{2} \quad (6)$$

$$\mu = -\chi \quad (7)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (8)$$

$$N = \frac{1}{\omega} \quad (9)$$

$$f_k^+ = P_k(N + 1) - P_k(N) \quad (10)$$

$$f_k^- = P_k(N) - P_k(N - 1) \quad (11)$$

$$f_k^0 = \frac{P_k(N + 1) - P_k(N - 1)}{2} \quad (12)$$

$$\sigma^+ = \sigma \chi f_k^+ \quad (13)$$

$$\sigma^0 = \sigma \chi f_k^0 \quad (14)$$

$$\sigma^- = \sigma \chi f_k^- \quad (15)$$

$$E_{\text{H}^+} = E_{\text{H}_3\text{O}^+} - E_{\text{H}_2\text{O}} \quad (16)$$

$$PA = E_{\text{pro.inh.}} - (E_{\text{non-pro.inh.}} + E_{\text{H}^+}) \quad (17)$$

where  $E_{\text{H}^+}$ ,  $E_{\text{H}_3\text{O}^+}$ ,  $E_{\text{H}_2\text{O}}$ ,  $E_{\text{pro.inh.}}$ ,  $E_{\text{non-pro.inh.}}$  and PA are total energy of proton, total energy of hydronium, total energy of water, total energy of protonated inhibitor, total energy of non-protonated inhibitor, proton affinity, respectively.

## 3. Results and discussion

### 3.1. Electrochemical results

Polarization curves were obtained for steel in 1 M HCl solution with and without inhibitors. The polarization exhibits Tafel behavior. Tafel lines which obtained in various concentrations of Mv10B in 1 M HCl solutions were shown in Fig. 2, at 25 °C respectively. The corresponding electrochemical parameters, *i.e.*, corrosion potential ( $E_{\text{corr}}$  versus SCE), corrosion current density ( $I_{\text{corr}}$ ), cathodic and anodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ ) and the degree of surface coverage ( $\theta$ ) values were calculated from these curves and are given in Table 1. The degree of surface coverage for different concentrations of inhibitor is calculated using the following equations [20,21]:

$$\theta = \frac{I - \dot{i}}{I} \quad (18)$$

where  $I$  and  $\dot{i}$  are the corrosion current densities without and with corrosion inhibitor, respectively, determined by the intersection of the extrapolated Tafel lines at the corrosion potential for steel in uninhibited and inhibited acid solution. The presence of Mv10B shifts

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