ARTICLE IN PRESS

Arabian Journal of Chemistry (2011) xxx, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

# Adsorption and corrosion inhibition of carbon steel in hydrochloric acid medium by hexamethylenediamine tetra(methylene phosphonic acid)

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Received 13 January 2011; accepted 27 March 2011

**KEYWORDS**

Carbon steel;
Thermodynamic parameters;
Phosphonic acid;
Acid inhibition

**Abstract** The inhibitive effect of the hexamethylenediamine tetra(methylene phosphonic acid) (HMDTMPA) on the corrosion of carbon steel in 1.0 M HCl solution has been investigated by weight loss measurement, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The presence of (HMDTMPA) reduces remarkably the corrosion rate of carbon steel in acidic solution. The effect of temperature on the corrosion behavior of carbon steel was studied in the range of 298–328 K. Results clearly reveal that the (HMDTMPA) behaves as a mixed type corrosion inhibitor with the highest inhibition at $4 \times 10^{-3}$ M. The adsorption of HMDTMPA on the carbon steel surface obeys to the Langmuir's adsorption isotherm. Surface analysis via scanning electron microscope (SEM) shows a significant improvement on the surface morphology of the carbon steel plate.



## 1. Introduction

Acid solutions are widely used in industries such as pickling, cleaning and descaling which lead to corrosive attack. The commonly used acids are hydrochloric acid, sulfuric acid and nitric acid. Since acids are aggressive, inhibitors are usually used to minimize the corrosive attack on metallic materials. A wide variety of compounds are used as corrosion inhibitors for metals in acids media (Schmitt, 1984; Mernari et al., 1998; Onuchukwu, 1988; Ashassi-Sorkhabi and Nabavi-Amri, 2000; Ebenso, 2002; Gomma, 1998). Their inhibitive action is related to several factors including the structure and

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Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2011.03.018

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charge distribution of the molecule, the number and types of adsorption sites, and the nature of interaction between the molecule and the metal surface. Corrosion inhibition occurs via adsorption of the organic molecule on the metal surface following some known adsorption isotherms with the polar groups acting as the reactive centers in the molecules. The resulting adsorption film acts as a barrier that isolates the metal from the corrosive media.

Recent works involve the study of corrosion inhibition of Aramco iron and carbon steel in different media using phosphonic acid and monofluorophosphate compounds (Laamari et al., 2010a,b, 2001, 2004; Amar et al., 2008).

The aim of this study is to evaluate the inhibitive effect of hexamethylenediamine tetra(methylene phosphonic acid) (HMDTMPA) as a corrosion inhibitor of carbon steel in 1 M HCl solution. The assessment of the corrosion behavior was studied using weight loss, potentiodynamic polarization measurement, electrochemical impedance spectroscopy (EIS) and the scanning electron microscope (SEM). Thermodynamic data were also obtained from adsorption isotherms and Arrhenius plots.

## 2. Experimental

### 2.1. Electrochemical cell

Electrochemical experiments were performed using a conventional three electrode cell assembly. The working electrode is a carbon steel rotating disk with surface area of 1 $cm^2$. It is abraded with different emery papers up to 1200 grade, washed thoroughly with double-distilled water, degreased with AR grade ethanol, acetone and drying at room temperature.

A saturated calomel electrode (SCE) was used as the reference electrode. All the measured potentials presented in this paper are referred to this electrode. The counter electrode was a platinum plate with a surface area of 2 $cm^2$.

The aggressive solutions were made of AR grade 37% HCl. Appropriate concentration of acid is prepared using double distilled water. The inhibitor is added to freshly prepared 1.0 M HCl in the concentration range of $10^{-4}$–$4\times10^{-3}$ M.

The corrosion inhibitor used in this work is hexamethylenediamine tetra(methylene phosphonic acid) (HMDTMPA). The organic compound is synthesized by the micro-wave technique. The obtained product is purified and characterized by $^{1}H$, $^{13}C$, $^{31}P$ NMR spectroscopy and IR techniques. The molecular structure is shown in Fig. 1.

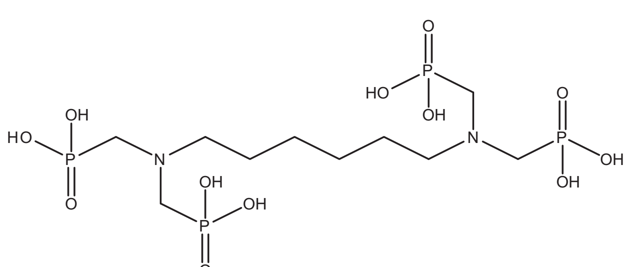


**Figure 1** Structure of hexamethylenediamine tetra(methylene phosphonic acid) (HMDTMPA).

### 2.2. Methods

#### 2.2.1. Gravimetric measurements

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 mL of 1.0 M HCl with and without addition of different concentrations of inhibitor. The carbon steel specimens used have a rectangular form (2 × 2 × 0.05 cm). The immersion time for the weight loss was 24 h at 298 K and 6 h at the other temperatures. After the corrosion test, the specimens of carbon 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 inhibition efficiency (IE%) was determined by using the following equation:

$$IE\% = \frac{CR_0 - CR}{CR_0} \times 100 \quad (1)$$

where, CR and $CR_0$ are the corrosion rates of carbon steel with and without the inhibitor, respectively.

#### 2.2.2. Electrochemical measurements

Two electrochemical techniques, namely DC-Tafel slope and AC-electrochemical impedance spectroscopy (EIS), were used to study the corrosion behavior. All experiments were performed in one-compartment cell with three electrodes connected to a Voltalab 10 (Radiometer PGZ 100) system controlled by the Volta master 4 corrosion analysis software model.

Polarization curves were obtained by changing the electrode potential automatically from −800 to 0 mV versus open circuit potential ($E_{ocp}$) at a scan rate of 1 $mVs^{-1}$. The inhibition efficiency is calculated by the following equation:

$$IE\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (2)$$

Where $i^0_{corr}$ and $i_{corr}$ are the corrosion current density values without and with inhibitor, respectively.EIS measurements were carried out under potentiostatic conditions in the frequency range 100–0.1 Hz, with an amplitude of 10 mV peak-to-peak, using AC signal at $E_{ocp}$. All experiments were performed after immersion for 60 min in 1.0 M HCl with and without addition of inhibitor.

#### 2.2.3. Surface morphology

For morphological study, surface features (0.9 × 0.8 × 0.2 cm) of carbon steel were examined after exposure to 1 M HCl solution after 1 day with and without inhibitor. JEOL JSM-5500 scanning electron microscope was used for this investigation.

## 3. Results and discussion

### 3.1. Weight loss measurements

#### 3.1.1. Effect of inhibitor concentration

Table 1 collects the corrosion rates and Fig. 2 shows the variation of inhibition efficiencies evaluated from weight loss measurements for different inhibitor concentrations in 1.0 M HCl.