



# Sodium diethyldithiocarbamate as a corrosion inhibitor of cold rolled steel in 0.5 M hydrochloric acid solution

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## ARTICLE INFO

### Article history:

Received 6 August 2011

Accepted 2 March 2012

Available online 12 March 2012

### Keywords:

A. Steel

B. Polarization

B. EIS

C. Acid inhibition

## ABSTRACT

Sodium diethyldithiocarbamate (DDTC) as a corrosion inhibitor for cold rolled steel (CRS) in 0.5 M HCl solution was investigated by Tafel polarization and electrochemical impedance spectroscopy (EIS). All the data indicate that DDTC can inhibit the corrosion of CRS in HCl solution. Polarization data show that DDTC mainly acts as a good inhibitor though it can accelerate the anodic reaction somewhat. Adsorption of DDTC is found to follow the Langmuir adsorption isotherm. Thermodynamic analysis indicates that both physisorption and chemisorption probably occur in the adsorption process. SEM and FTIR results further validate that DDTC can adsorb on CRS surface.

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## 1. Introduction

Hydrochloric acid (HCl) solutions are widely used for acid cleaning, industry acid pickling, oil well acidizing and acid descaling [1–3], but HCl solutions are also highly corrosive to any metals. Addition of inhibitor remains the necessary procedure to secure the metal against acid attack. Therefore, corrosion inhibitors for HCl solutions have attracted more attention [1–10]. Inhibitors are compounds that control, reduce or prevent reactions between a metal and its surroundings when added to the medium in small quantities [11]. The efficiency of an inhibitor mainly depends on its structure characteristics and properties such as the number of adsorption active centers in the molecule, their charge density, the molecule size, the mode of adsorption, the formation of metallic complexes, and the projected area on the metallic surface, etc. [12]. Therefore, it is well known that most of the acid inhibitors are organic compounds containing nitrogen, oxygen, and sulfur, which generally tend to interact with metallic surface and form a protective film by means of surface adsorption [13–25].

Sodium diethyldithiocarbamate (DDTC) is a member of the dithiocarbamate family and a potent metal-chelating agent containing nitrogen and sulfur function group [26]. From the structure

of DDTC shown in Fig. 1, it is easy to see that DDTC is an organo-sulfur compound with the formula  $\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$  which has characteristics suitable for its application as a corrosion inhibitor. Liao et al. [27] studied the inhibitive behaviour of DDTC as a new corrosion inhibitor for copper alloy in NaCl; their results show that DDTC can restrain both the processes of anodic oxidation and cathodic reduction. However, literature available to date about DDTC as a corrosion inhibitor for steel in solution, especially in acid solution, is very scarce. It is well known that corrosion inhibitors are selective to prevent the corrosion of metals. So it is interesting in studying the corrosion of steel in acid solution in the presence of DDTC to find out whether it is effective to steel in corrosive media.

The objective of this investigation is to determine the effect of DDTC on the corrosion of cold rolled steel (CRS) in 0.5 M HCl solution. It is also aimed to predict the thermodynamic feasibility of adsorption of DDTC on CRS surface and study its adsorption behaviour. A probable inhibitive mechanism is presented to explain the experimental results.

## 2. Experimental method

### 2.1. Materials

The working electrodes were made of a sheet of cold rolled steel (CRS), which was of commercial specification with composition (wt.%): C ≤ 0.05, Si ≤ 0.02, Mn ≤ 0.28, S ≤ 0.023, P ≤ 0.019, Fe remainder.

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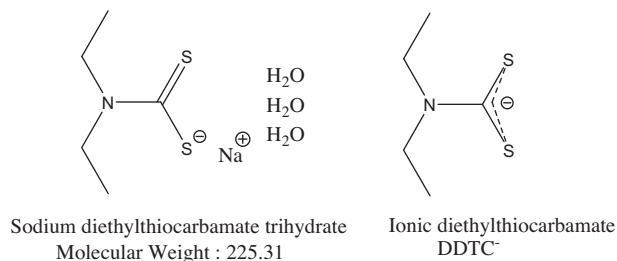


Fig. 1. Molecular structure of DDTC.

## 2.2. Solutions

DDTC and HCl were made of AR grade. The aggressive solution (0.5 M HCl) was prepared from distilled water.

## 2.3. Electrochemical measurements

A three-electrode system including a working electrode, an auxiliary electrode and a reference electrode was used for the electrochemical measurements in 250 mL solution. The working electrodes were made of CRS which were embedded in PVC holder using epoxy resin with a square surface of 1.0 cm<sup>2</sup>. The auxiliary electrode was a platinum foil. The reference electrode was a saturated calomel electrode (SCE) with a fine Luggin capillary positioned close to the working electrode surface in order to minimize ohmic potential drop. Each specimen was successively abraded by using SiC emery papers from 100 to 1000 grades on the test face. Before use, the abraded surface was thoroughly washed with distilled water and degreased in acetone then dried with a warm air stream. The working electrode was immersed in the test solution at open circuit potential for 2 h before measurement until a steady state appeared. Tafel polarization curves were determined by polarizing to  $\pm 250$  mV with respect to the free corrosion potential ( $E_{\text{corr}}$  vs. SCE) at a scan rate of 0.5 mV/s. A 10 mV peak to-peak sine wave over an ac frequency range extending from 0.1 Hz to 100 kHz was used for the impedance measurements. All electrochemical measurements were carried out at the open circuit potential using PARSTAT 2263 Potentiostat/Galvanostat (Princeton Applied Research). Each experiment was repeated at least three times to check the reproducibility. All tests have been performed in non-deaerated solutions under unstirred conditions at 10–40 °C.

## 2.4. SEM studies

Prior to monitoring the topographic changes of electrode surface, the CRS specimens were abraded with emery papers from 100 to 1000 grades, and then washed with distilled water and acetone. After immersion in 0.5 M HCl without and with addition of inhibitor at 30 °C for 4 h, the specimens were taken out and cleaned with distilled water and acetone, dried with a cold air blaster, and then used for Holland yielding XL30 ESEM-TMP scanning electron microscopy detection.

## 2.5. FTIR studies

In order to confirm the corrosion products on CRS surface, after immersion in 0.5 M HCl containing 300 mg L<sup>-1</sup> DDTC for 4 h at 30 °C, the specimen was taken out and dried. The surface film was scratched carefully and the product obtained was thoroughly mixed so as to make it uniform. Model Magna-IR 560 FTIR was used to measure the spectra from the KBr wafer of the corrosion products, all the spectra in these experiments were obtained by adding 64 interferograms at a resolution of 8 cm<sup>-1</sup> in the region from 400 to 4000 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Tafel polarization curves

#### 3.1.1. Effect of DDTC concentration

Tafel Polarization curves of CRS in 0.5 M HCl in the absence and presence of different concentrations of DDTC at 30 °C were shown in Fig. 2. As it can be seen that, the corrosion potentials obviously shifts to more negative direction while the cathodic curves are shifted to lower current density region compared to that of the blank solution, which results in a notably decrease in  $i_{\text{corr}}$ . These phenomena clearly indicate that DDTC acts as a cathodic inhibitor for CRS in HCl solution, which is obviously different from the inhibitive mechanism of DDTC for copper alloy in NaCl as a mixed type inhibitor [27]. In addition, the anodic current densities increase obviously in the presence of DDTC comparing with the blank solution, suggesting that the anodic reaction may be accelerated by DDTC. Similar results were also observed in many other studies [28–32]. Kocojan et al. [33] and Capobianco et al. [34] validated that the anodic current densities increased in the presence of complexing agents due to the formation of metallo-organic complexes. In this study, the acceleration of the anodic reaction can be attributed to the formation of coordinated complex between Fe<sup>2+</sup> and DDTC. In factor, inhibitors of corrosion in acid solution can affect the corrosion reaction in a number of ways, some of which may occur simultaneously [35]. Thus, a conclusion can be drawn that DDTC can accelerate the anodic dissolution and retard the cathodic reaction simultaneously. But DDTC influences cathodic reaction more rather than anodic reaction, the predominant action of DDTC for CRS in HCl is to retard the cathodic reaction.

The corrosion rates ( $v$ ) of CRS were calculated from the corrosion current density ( $i_{\text{corr}}$ ) values in HCl solution with and without DDTC using the following equation [36,37]:

$$v(\text{ms}^{-1}) = k \times \frac{M \times i_{\text{corr}}}{\rho} \quad (1)$$

where  $k$  is a constant which is equal to  $3.454 \times 10^{-8} \text{ molA}^{-1}\text{s}^{-1}$  because the number of electrons involved in the oxidation reaction from Fe to Fe<sup>2+</sup> is 2,  $M$  is the molecular mass of iron in g mol<sup>-1</sup>,  $i_{\text{corr}}$  is the corrosion current density in A cm<sup>-2</sup>,  $\rho$  is the density of iron in g cm<sup>-3</sup>.

The inhibition efficiencies ( $\eta_p$ ) from Tafel polarization were obtained by the following relationship:

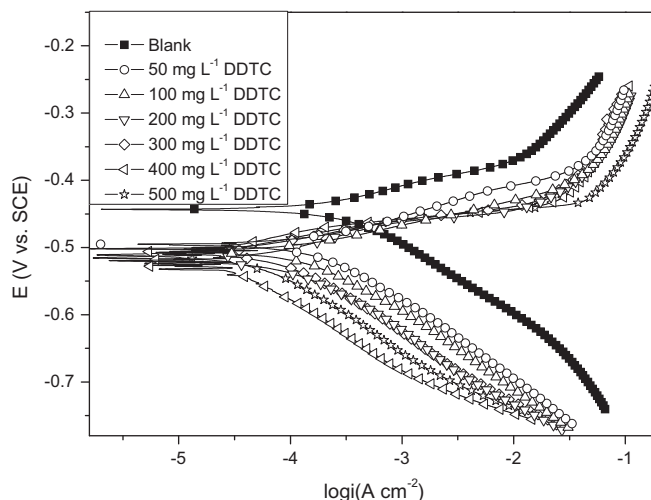


Fig. 2. Polarization curves for cold rolled steel in 0.5 M HCl with and without DDTC at 30 °C.

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