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Novel cationic surfactant based on triazole as a corrosion inhibitor for carbon steel in phosphoric acid produced by dihydrate wet process

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ABSTRACT

The corrosion inhibition effect of novel cationic surfactant based on tolyltriazole on carbon steel in 7 M H_3PO_4 solution has been evaluated by weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods. The inhibition efficiency increases with increasing inhibitor concentration, but it decreases with increasing the temperature. The adsorption of inhibitor is mixed physical and chemical adsorption and found to obey the Langmuir adsorption isotherm. Data obtained from EIS studies were analyzed to model inhibition process through appropriate equivalent circuit model. Potentiodynamic polarization studies have shown that the inhibitor acts as a mixed type of inhibitor. Scanning Electron Microscopy (SEM) study also confirmed the protection of the metal surface by the used cationic surfactant.

1. Introduction

Phosphoric acid (H_3PO_4) is widely used in the production of fertilizers and surface treatment of steel such as chemical and electrolytic polishing or etching, chemical coloring, removal of oxide film, phosphating, passivating, and surface cleaning. Most of the acid is produced from phosphate rocks by the so-called dihydrate wet process, equivalent to 7.0 M H_3PO_4 (about 35% H_3PO_4) [1]. There is a great need to protect steel materials used in the phosphoric acid industry produced by dihydrate wet method process. However, little work appears to have been done on the corrosion inhibition of steel in 7.0 M H_3PO_4 (35% H_3PO_4). The use of corrosion inhibitors is an important method to protect metallic materials against corrosion in acidic medium. Organic compounds containing N, O and S atoms are considered to be effective corrosion inhibitors. The effectiveness of organic inhibitors depends on the nature and the condition of the metallic surface, the chemical composition and structure of the inhibitor. The inhibitors which have N and S simultaneously provide a better inhibition performance [2]. The inhibitory action of the hetero compounds is usually attributed to their adsorptive interaction with the metal surface [3–5]. A bond may be formed between electron lone pairs and/or electron cloud of the donor atoms of the inhibitor and the metal surface, thereby reducing the corrosive attack in an acid medium [6]. The stability of the adsorbed inhibitor film on the metal surface depends on some physicochemical properties of the molecule related to their functional groups, aromaticity, the possible steric effects, electronic density of donor atoms, type of corrosive environment and the nature of the interaction between the p orbital of the inhibitors and the d orbitals of iron [7]. It has been proposed that n-alkyl-quaternary ammonium salts act as corrosion inhibitor by adsorption on the metal surface, and the adsorption takes place through electrostatic attraction between positively charged N^+ ion and the induced negative charges on the metal surface. Study of the inhibition actions of n-alkyl-quaternary ammonium compounds on the corrosion of steel is of considerable interest due to its academic and industrial importance. 1-Dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide is a new class of n-alkyl-quaternary ammonium salt. However, to the best of our knowledge, 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide has not been used as a corrosion inhibitor in 7 M H_3PO_4. However, no substantial information is available on the corrosion inhibition of quaternary ammonium salts in H_3PO_4 solution.

In the present work, we are developing n-alkyl-quaternary ammonium salt based on triazole derivatives as corrosion inhibitors in 7 M H_3PO_4 produced by dihydrate wet process. The inhibition effect of novel cationic surfactant, namely, 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide, on the corrosion of carbon steel in 7 M H_3PO_4 was studied using weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. Also, the effect of inhibitor concentration and temperature on

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the corrosion inhibition was discussed. Adsorption thermodynamic parameters are calculated and discussed in detail. The protective film formed on the metal surface was characterized by Scanning Electron Microscopy (SEM).

2. Materials and experimental techniques

2.1. Inhibitor

A novel cationic surfactant used in this study was synthesized from the reaction of one mol 5-methyl-1H-benzo[d][1,2,3]triazole with one mol 1-bromododecane in ethanol at 70 °C for 24 h [8]. The mixture was allowed to cool-down. The obtained pale brown precipitate product was further purified by diethyl ether then recrystallized from ethanol to form a white precipitate called 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide.

Chemical structure of the synthesized inhibitor (Fig. 1) was confirmed by FTIR and ^{1}HNMR spectroscopy. FTIR analysis was carried out using ATI Mattson infinity series TM, Bench top 961 controlled by Win First TM V2.01 software. ^{1}H NMR analysis was measured in DMSO-d_6 using a Joel ECA 500 MHZ NMR spectrometer.

2.2. Steel specimen

Tests were performed on a carbon steel of the following chemical composition (wt.%): 0.28% C, 0.06% Ti, 1.40% Mn, 0.03% P, 0.03% S and the remainder is Fe.

2.3. Electrochemical measurements

The electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a silver/silver chloride (RE) as a reference electrode. The working electrode (WE) was a rod of carbon steel embedded in PVC holder using epoxy resin so that the flat surface was the only exposed surface in the electrode. The area of the working exposure surface was 0.42 cm^2. This area was abraded with emery paper (grade 320-400-600-800-1000-1200) on the test face, rinsed with distilled water, degreased with acetone and dried. Before measurement, the electrode was immersed in a test solution at open circuit potential (OCP) for 30 min until a steady state was reached. All electrochemical measurements were carried out using a VoltaLab 40 (PGZ301 & VoltaMaster 4)-(Radiometer Analytical-FRANCE) at 20 °C.

EIS measurements were carried out as described elsewhere [9,10]. A small alternating voltage perturbation (5 mV) was imposed on the cell over the frequency range from 100 kHz to 30 mHz at open circuit potential at 20 °C. Simulation of Nyquist diagrams with the suggested model was done by ZSimpWin program.

The potentiodynamic polarization measurements were obtained by changing the electrode potential automatically from −800 to −300 mV vs. Ag/AgCl with scan rate 0.2 mV s^{-1} at 20 °C.

2.4. Weight loss measurements

The carbon steel pipeline sheets of 6 cm × 3 cm × 0.4 cm were abraded with a series of emery paper (grade 320-400-600-800-1000-1200) and then cleaned successively with distilled water, ethanol, and acetone, and finally dried in dry air. A&D analytical balance, (Model: HR 200, readability: 0.1 mg and standard deviation: ±0.2 mg), was used for the gravimetric analysis. After accurately weighting, the samples were immersed in 100 ml of 1 M HCl solution with and without the addition of different concentrations of cationic surfactant at various temperatures. The temperature for weight loss measurements was controlled by water bath provided with thermostat control ±0.5 °C. The carbon steel specimens were taken out after 24 h and then rinsed with distilled water twice and degreased with acetone, and finally dried in dry air and accurately weighted. The experiments were carried out in triplicates in order to give a good reproducibility and the average weight loss of three parallel carbon steel pipeline sheets was obtained. All tests in this paper were done under aerated conditions.

2.5. Surface characterization

The surface morphology of the carbon steel and protective film were investigated by a Jeol 5400 (made in Japan) Scanning Electron Microscope (SEM). The specimen, after immersion in 7 M H_3PO_4 solution for 24 h at 25 °C, was thoroughly washed with double distilled water and dried with a cold air blaster before being put on the slide. A SEM photograph was taken for the polished carbon steel specimen before and after immersed in 7 M H_3PO_4 solution in the absence and presence of 5×10^{-3} M of the synthesized cationic surfactant.

3. Results and discussion

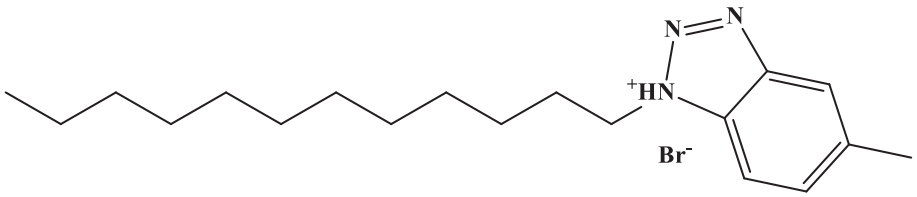
3.1. Structure confirmation of the synthesized inhibitor

3.1.1. FTIR spectroscopy

FTIR spectrum of the synthesized cationic surfactant showed the following absorption bands at 716.86 cm^{-1} ($(CH_2)_n$ rocking), 1249.31 cm^{-1} (CH_3 symmetric bending), 1461.31 cm^{-1} (CH_2 asymmetric bending), 2851.50 cm^{-1} (CH symmetric stretching), 2919.50 cm^{-1} (CH asymmetric stretching) and 1035.63 cm^{-1} (R_4N^+), 1506.34 and 1610.04 cm^{-1} (CH stretching of aromatic ring), 1361.40 cm^{-1} (CH_3 rocking of benzene) and 3418.19 cm^{-1} (NH stretching). The data of FTIR spectrum confirmed the expected functional groups in the synthesized cationic surfactant.

3.1.2. ^{1}H NMR spectroscopy

^{1}HNMR (DMSO-d_6) spectrum of the synthesized cationic surfactant (Fig. 2) showed different bands at δ = 0.8448 ppm (t, 3H, ($C\underline{H}_3(CH_2)_9CH_2CH_2N^+$); δ = 1.2160 ppm (m, 18H, $CH_3(C\underline{H}_2)_9CH_2CH_2N^+$); δ = 1.6351 ppm (m, 2H, $CH_3(CH_2)_9C\underline{H}_2CH_2N^+$); δ = 2.0090 ppm (t, 2H, $CH_3(CH_2)_9CH_2C\underline{H}_2N^+$); δ = 3.3528 ppm (s, 3H, $C\underline{H}_3$-toluidene nucleus); δ = 7.8638 ppm (d, 1H, 4-benzene nucleus); δ = 8.3404 ppm (s, 1H, 6-benzene nucleus); δ = 8.3626 ppm (d, 1H, 3-benzene nucleus). The



1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide

Fig. 1. Chemical structure of the synthesized 1-dodecyl-5-methyl-1H-benzo[d][1,2,3]triazol-1-ium bromide.