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Electrochemical studies on the inhibition behavior of copper corrosion in pickling acid using quaternary ammonium salts

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ABSTRACT

The inhibition effect of two quaternary ammonium salts namely: N^1,N^2-didodecyl-N^1,N^1,N^2,N^2-tetramethylethane-1,2-diaminium bromide (I) and N-(2-hydroxyethyl)-N,N-dimethyldodecan-1-aminium bromide (II) on the corrosion of copper in 1 M HNO_3 has been investigated by polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Polarization studies showed that these compounds are mixed-type inhibitors. The inhibition efficiency increases with increasing the inhibitor concentration and the maximum inhibition (93.9% and 90.8%) was obtained in the presence of 1×10^{-3} M of I and II, respectively. The adsorption of these inhibitors on the copper surface obeys Langmuir isotherm. The results obtained from the different electrochemical techniques were in good agreement.

1. Introduction

Copper is extensively used for industrial applications owing to its excellent electrical and thermal conductivities, good mechanical workability and resistance to atmospheric and chemical agents [1]. However, copper is susceptible to corrosion in acidic media which is used in dissolving encrustations and other corrosion products from the industrial equipment [2]. A variety of environmental factors can easily cause corrosion of copper. Scale and corrosion products have a negative effect on heat transfer, and they cause a decrease in heating efficiency of the equipment. That is why periodic descaling and cleaning in acidic pickling solutions are necessary. During the removal of corrosion products the acid comes into contact with copper metal and its dissolution occurs. One of the most important methods in the protection of copper against corrosion is the use of organic inhibitors. The organic inhibitors such as benzotriazole derivative [3], ortho-substituted anilines [4], 2-mercapto benzimidazole [5], bis-(1,10-benzotriazoly)-a,x-diamide [6], and Schiff bases [7] have been reported as corrosion inhibitors for copper in picking acids. There is unanimity that copper dissolution involves at first, single electron transfer process leading to oxidation thereby forming Cu(I) complex [3]. The action of inhibitors is electrochemical in nature and involves the discharge of positively charged particles at the cathodic area that form an adsorbed layer. The adsorption of inhibitors takes place by virtue of their physical and chemical properties and also depends on the nature of metal and the type of the electrolyte solution used [8].

In the present work, we focused on the development of selective surface active agent inhibitors. As part of our aimed program, we synthesized N^1,N^2-didodecyl-N^1,N^1,N^2,N^2-tetramethylethane-1,2-diaminium bromide and N-(2-hydroxyethyl)-N,N-dimethyldodecan-1-aminium bromide to be used as corrosion inhibitors for copper in 1 M HNO_3 solution. The corrosion inhibition studies of the synthesized quaternary ammonium salts were performed using potentiodynamic polarization, electrochemical impedance and electrochemical frequency modulation methods.

2. Materials and experimental methods

2.1. Synthesis of inhibitors

2.1.1. Synthesis of N^1,N^2-didodecyl-N^1,N^1,N^2,N^2-tetramethylethane-1,2-diaminium bromide

The inhibitor (I) was synthesized by the quaternization reaction of 2 mol of 1-bromododecane with 1 mol of tetramethyl ethylene diamine. The reactants were refluxed in ethanol at 70 °C for 48 h, and then the reaction mixture was left to cool at room temperature. The

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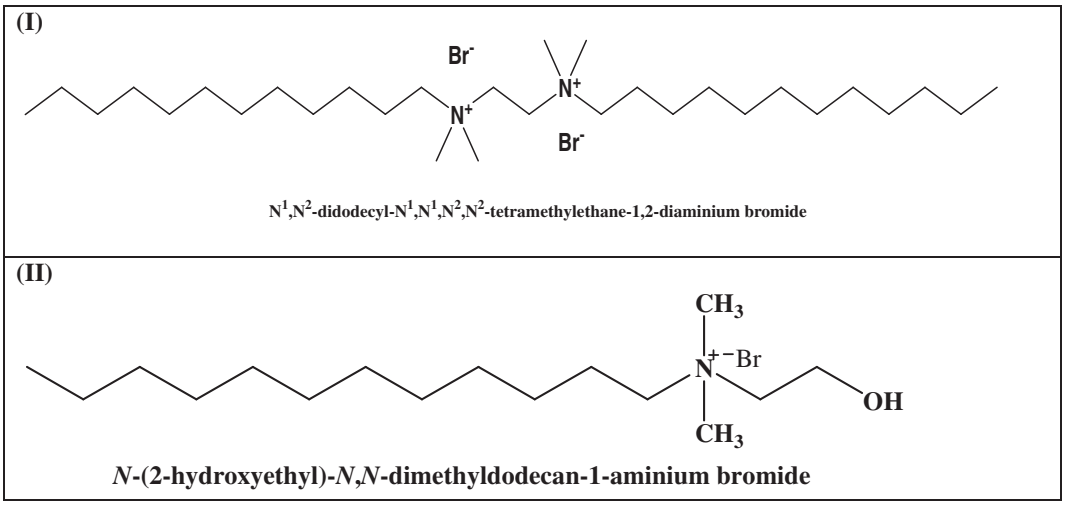

Fig. 1. The chemical structure of the synthesized quaternary ammonium salts.

obtained white precipitate was further purified by diethyl ether then recrystallized from ethanol [9].

2.1.2. Synthesis of N-(2-hydroxyethyl)-N,N-dimethyldodecan-1-aminium bromide

The inhibitor (II) was synthesized by the quaternization reaction of 1 mol 2-(dimethylamino)ethanol and 1-bromododecane. The reactants were refluxed in ethanol at 70 °C for 48 h, and then the reaction mixture was left to cool at room temperature. The obtained white precipitate was further purified by diethyl ether then recrystallized from ethanol [10]. The chemical structure of the synthesized quaternary ammonium salts (Fig. 1) was confirmed by FTIR and ^{1}H NMR 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 Jeol ECA 500 MHz NMR spectrometer.

2.2. Solutions

The aggressive solution, 1 M HNO_3, was prepared by dilution of analytical grade 37% HNO_3 with distilled water. The concentration range of the prepared quaternary ammonium salts was varied from 1×10^{-5} to 1×10^{-3} M for corrosion measurements. All solutions were prepared using double distilled water.

2.3. Copper specimen preparation

The copper specimens of the following chemical composition (wt.%) were used in the experiments: 0.001 Ni, 0.019 Al, 0.004 Mn, 0.116 Si and Cu-balance. A pre-treatment was carried out prior to each experiment, in which specimen surface was mechanically grinded with 340, 400, 600, 800, 1000 and 1200 grades of emery papers, rinsed with bidistilled water, degreased in ethanol and dried at room temperature before use.

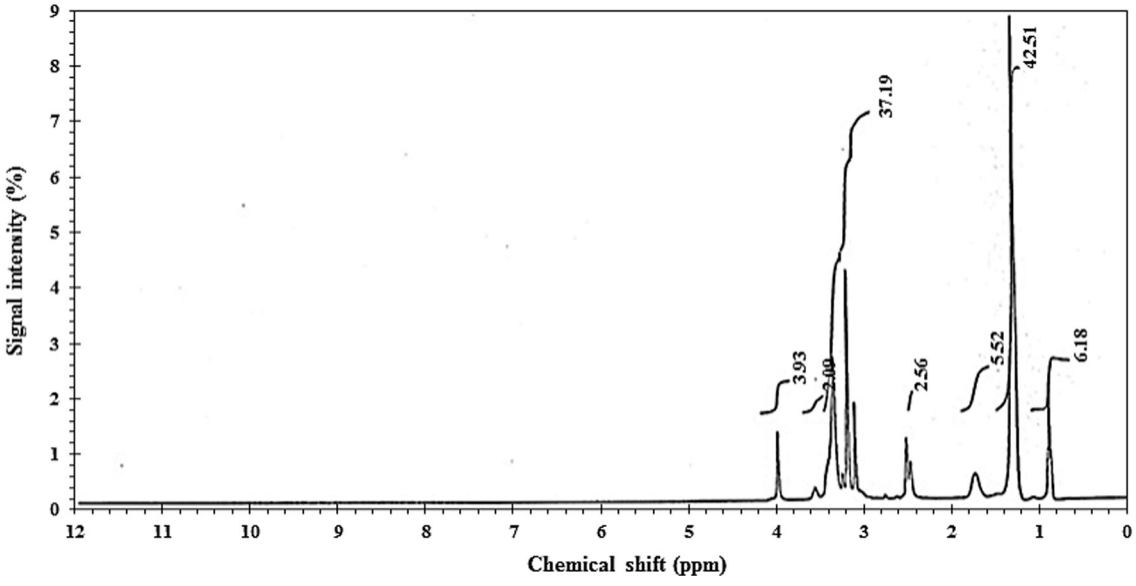

Fig. 2. ^{1}H NMR spectrum of the synthesized quaternary ammonium salt (I).