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FULL LENGTH ARTICLE

Corrosion protection of mild steel by a new phosphonate inhibitor system in aqueous solution

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Abstract A protective film has been developed on the surface of the mild steel in low chloride aqueous environment using a synergistic mixture of an eco friendly inhibitor, imino dimethyl phosphonic acid (IDMPA) and Zn^{2+}. The synergistic effect of IDMPA in controlling corrosion of the mild steel has been investigated by gravimetric and electrochemical studies in the presence of Zn^{2+}. The formulation consisting of IDMPA and Zn^{2+} has excellent inhibition efficiency. The mixed mode of inhibition studied by potentiodynamic polarization and electrochemical impedance spectroscopy has shown that the changes in the impedance parameters like charge transfer resistance (R_{ct}) and constant phase element (CPE) confirm the strong adsorption on the mild steel. Surface characterization inspection using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) is used to ascertain the nature of the protective film. The mechanistic aspects of corrosion inhibition are proposed.

1. Introduction

Mild steel is widely applied as a construction material in many chemical and petrochemical industries due to its excellent mechanical properties and low cost. Corrosion is the destruction or deterioration of metals. Corrosion in cooling water systems greatly affects the health of human beings and economic level of the world. One of the most practical methods for protection against excessive dissolution of metal by corrosion is the use of proper inhibitors [1]. Inhibitors are extremely effective even in very small concentrations and effectively reduce the corrosion rate. The technique of adding inhibitors to the environment of a metal is a well known method of controlling corrosion in many branches of technology. Among various inhibitors, phosphonates were considered as scale inhibitors at the beginning, later they were proved to be good corrosion inhibitors in nearly neutral aqueous media [2]. The inhibition of molecule depends on the nature of the charge distribution and the interaction between the metal surface and the inhibitor molecule and number of adsorption sites available.

Phosphonates have been extensively used as water treatment agents because of their low toxicity, high stability and corrosion inhibition activity in neutral aqueous media [3,4]. The reason for choosing phosphonate as an inhibitor is its property of adsorption on the metal surface, thereby forming

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poorly soluble compounds and thus decreases the area of active metal surface or by increase in the activation energy. Thus, the corrosion rate is decreased, which proves that corrosion in aqueous media is an electrochemical process.

Phosphonates have high hydrolysis stability and they cannot be easily degraded by microorganisms. In phosphonate based inhibitor system, the inhibition efficiency was increased by the addition of metal cations like Ca^{2+}, Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, Sn^{2+}, Cu^{2+}, Fe^{2+}, Ba^{2+}, Sr^{2+}, Al^{3+}, Cr^{3+} etc., in nearly neutral media. In the above series zinc was chosen as the good metal ion to enhance the inhibition property of phosphonates [5,6].

Donor–acceptor interaction between the metal and inhibitor forms a thin protective layer (chemisorption binding) on the metal surface that reduces the corrosion rate. Here the phosphonates act as the surfactant and are diprotic in nature, their properties are studied on the basis of polar head groups. Several corrosion inhibition studies have been carried out using phosphonic acids viz., aminotris (methylene phosphonic acid) (ATMP) [7], 1-hydroxyethane-1,1-diphosphonic acid (HEDP) [8], piperidin-1-yl-phosphonic acid (PPA) [9], 2-carboxy ethyl phosphonic acid (2-CEPA) [10], carboxy methyl phosphonic acid (CMPA) [11], propyl phosphonic acid [12], 2-chloroethyl phosphonic acid (2-ClEPA) [13], 4-phosphono-piperazin-1-yl-phosphonic acid (PPPA) [14], 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) [15], phosphonate anions [16] and so many other corrosion inhibitors that have been reported in the literature. Compounds with a phosphonic functional group are considered to be the most effective chemicals for inhibiting the corrosion process and it is well known that short-chain substituted phosphonic acids are good corrosion inhibitors for iron and low alloyed steels.

In the present work, the inhibitive effect of using a new organic inhibitor viz., imino dimethyl phosphonic acid (IDMPA) and Zn^{2+} ions in controlling the corrosion of the mild steel in neutral aqueous environment containing low chloride has been studied by non electrochemical and electrochemical studies such as: potentiodynamic polarization and impedance spectroscopy. Surface analytical techniques, viz., Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX) were used to investigate the nature of protective film formed on the metal surface. A plausible mechanism of inhibition of corrosion is proposed. For all these studies, aqueous solution of 60 ppm chloride has been chosen as control because the water used in cooling water systems is generally either demineralized water or unpolluted surface water.

2. Experimental

2.1. Materials

The molecular structure of the IDMPA is shown in Fig. 1. The tested compound namely imino dimethyl phosphonic acid (IDMPA) obtained from Sigma-Aldrich was used without further purification. Zinc sulfate ($ZnSO_4{\cdot}7H_2O$), sodium chloride and other reagents were analytical grade chemicals. All the solutions were prepared using triple distilled non-deaerated water.

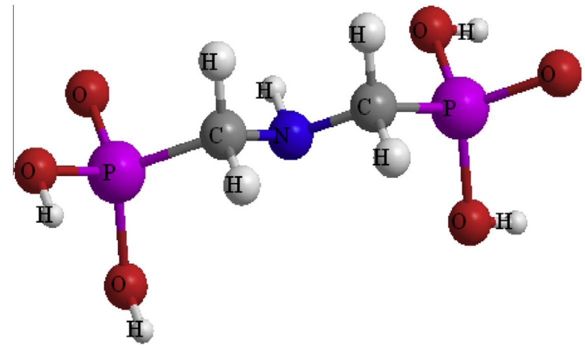

Figure 1 Molecular structure of imino dimethyl phosphonic acid (IDMPA).

2.2. Preparation of specimens

Mild steel specimens (0.026% S, 0.035% P, 0.58% Mn, 0.104% C and the rest iron) of dimensions 3.5 cm × 1.5 cm × 0.2 cm, were polished to a mirror finish with 1/0, 2/0, 3/0, 4/0, 5/0, and 6/0 emery polishing papers respectively, degreased with acetone, dried and used for gravimetric measurements, FTIR and SEM for surface studies. The dimensions of the specimens with 1.0 cm × 1.0 cm and 0.2 cm thickness of the electrode were encapsulated by araldite paste and the effective exposed surface area of 1 cm^2 was used for electrochemical studies

2.3. Gravimetric studies

Gravimetric experiments are the classical way to find the corrosion rate (CR) and inhibition efficiency (IE). In all gravimetric experiments, the polished specimens were weighed and immersed in duplicate, in 100 ml in the absence (control solution) and presence of inhibitor formulations of different concentrations, for a period of 7 days and pH 7.0 was maintained for all test solutions. Then, the specimens were reweighed after washing and drying. The weights of the specimens before and after immersion were determined with Mettler electronic balance AE 240 model with a readability of 0.1 mg. Accuracy in weighing up to 0.0001 g and its surface area measurement up to 0.1 cm^2, as recommended by ASTM, was followed. Corrosion rates of the mild steel in the absence and presence of various inhibitor formulations are expressed in milligram per dm^2 per day (mdd). The corrosion rate was calculated according to the following equation:

$$\mathrm{CR}\ (\mathrm{mdd}) = \left[\frac{\Delta W}{St}\right] \times 100 \tag{1}$$

where ΔW (mg) is the weight loss, S (dm^2) is the surface area and t (days) is the immersion period. Inhibition efficiencies (IE) of the inhibitor were calculated by using the formula

$$\mathrm{IE}_g\ (\%) = \left[\frac{\mathrm{CR}_0 - \mathrm{CR}_I}{\mathrm{CR}_0}\right] \times 100 \tag{2}$$

where CR_0 and CR_I are the corrosion rates in the absence and presence of inhibitor, respectively.