



Synergistic interactions between tetra butyl phosphonium hydroxide and iodide ions on the mild steel surface for corrosion inhibition in acidic medium



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ABSTRACT

The corrosion inhibitive action of tetra butyl phosphonium hydroxide (TBPH) on mild steel was investigated in 0.5 M H₂SO₄. On adding the potassium iodide (KI) to the solution corrosion inhibition efficiency was significantly improved. The inhibitive action of TBPH was investigated at various inhibitor concentrations and at various temperatures; however, a synergistic improvement in the performance was seen when 10⁻³ M KI was added to TBPH solution. Potentiodynamic polarization studies at various concentrations of TBPH and (TBPH + KI) inhibitor revealed that TBPH is a mixed type of inhibitor for mild steel in 0.5 M H₂SO₄. Synergistic effect of TBPH and KI in corrosion inhibition of mild steel in 0.5 M H₂SO₄ containing a low concentration of iodide ions has been evaluated by potentiodynamic polarization and the results suggest that the iodide ions in solution stabilized the adsorption of TBPH molecule on the metal surface and improved the inhibition efficiency of TBPH. The corrosion behavior of steel in 0.5 M H₂SO₄ in the absence and with various concentrations of the inhibitor was studied from (298 to 328) K. It was found that the inhibition efficiency increases with inhibitor concentration and decreases with TBPH and (TBPH + KI) solution with an increase in temperature. Potentiostatic polarization study shows that TBPH and (TBPH + KI) are passivation type of inhibitor. The adsorption of TBPH is found to follow Frumkin adsorption isotherm whereas the adsorption of (TBPH + KI) follows the Temkin adsorption isotherm. Kinetic and thermodynamic parameters namely effective activation energy (E_a), and Gibbs free energy of adsorption (ΔG^o_{ads}) indicate that adsorption of TBPH and (TBPH + KI) on mild steel surface is primarily physical in nature. The results of scanning electron microscopy, atomic force microscopy, and quantum chemical analysis support the above inferences.

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1. Introduction

Mild steel is an extensively used metal in industries especially for structural applications, like fabrication of reaction vessels, store tanks, petroleum refineries, and so on [1,2]. Mild steel has a high rate of dissolution in the acid medium; it is the major obstacle for its use on large scale. Several methods are present for corrosion prevention in which one method used of an organic inhibitor [3]. Organic compounds which contain nitrogen, sulfur, oxygen, heterocyclic with a polar

functional group and a conjugated double bond have been reported to inhibit corrosion [4–10]. While the cationic organic inhibitors (e.g. ammonium salts) in the presence of the chloride ions show a synergistic effect in the inhibition of corrosion [11–13], these compounds are not good inhibitors in plain sulfuric acid media as a result of strong adsorption of sulfate ions on the metal surface [14]. Inhibitors protect the metals and alloys by effective adsorption and/or chemical bonding interactions through the hetero atoms with the corroding surface, thus giving a non-conducting protective layer on the surface. Inhibition of these organic compounds is attributed to the interactions between mild steel surface and inhibitor molecules via their adsorption. Two types of interactions are responsible for adsorption of the inhibitor on the metal surface. One is physical adsorption; electrostatic interactions can occur on a metal surface with inhibitor molecules. The other is chemical adsorption. This involves charge sharing or charge transfer

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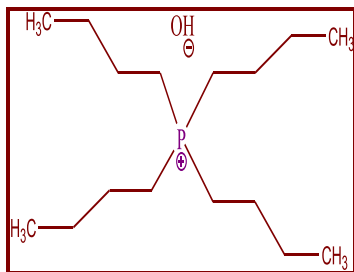
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from inhibitor molecules to the metal surface to form coordinate types of bond [15]. A large number of phosphonium compounds are known to be applicable as corrosion inhibitors for mild steel. They improve the corrosion resistance of metals and can be applied to the substrate by immersion or by incorporating in a polymer coating system. In this paper, synergistic inhibition of mild steel corrosion in 0.5 M H₂SO₄ and containing the desired amount of tetrabutylphosphonium hydroxide (TBPH) and KI has been studied at different temperatures by using electrochemical measurements (potentiodynamic polarization, potentiostatic polarization, and electrochemical impedance spectroscopy). Inhibiting effect of halide ions in strong acid depends on the electrostatic field set up by the charge of the ions on adsorption sites and the concentration of the halide ions. Indeed this effect on mild steel is due to the ability of halide ions to replace OH[−] adsorbed on the metal surface, thus reducing the catalytic effect of the hydroxyl ions. Tetrabutylphosphonium hydroxide is a phosphonium compound which has very high thermos ability. Therefore it is suitable when high-temperature reactions need to be carried out. Corrosion inhibition involves the use of any substance (called as an inhibitor), which retards the rate of corrosion when it is added to the reaction medium in small concentration. An efficient inhibitor is compatible with the environment, is economical for application, easily available, non-toxic and produces the desired effect when present in small concentration. Most of the effective inhibitors are organic compounds containing heteroatoms N, P, S and O in the structure since they are capable of forming a coordinate covalent bond with the metal owing to their free electron pairs. Compounds with aromatic character and with π bonds also generally exhibit good inhibitor properties due to the interaction of π orbital with the metal surface. Electron donating group attached to organic compounds also increases inhibition efficiency, that is, long alkyl chain organic compounds are good inhibitors.

2. Experimental method

2.1 Material preparation

Mild steel rod of composition (Mn 1.02, C 0.15, P 0.025, Si 0.025, S 0.025 and balance Fe) was used in corrosion study. Tetrabutylphosphonium hydroxide (40 wt.% in H₂O), (TBPH) used as a corrosion inhibitor. The concentrations of TBPH (inhibitor) prepared and used for the study range from (10^{−2} to 10^{−3}) M, respectively. The concentration of 10^{−3} M KI was used for the synergistic studies. The aggressive solutions (test solutions) were made from AR grade H₂SO₄. 0.5 M concentration of acid was prepared by diluting AR acids with double distilled water. Each experiment was repeated and an average value was reported. The studies were carried out at (298 to 328) K. The molecular structure of TBPH is shown below:



Tetrabutylphosphonium hydroxide (40 wt.% in H₂O), (TBPH)

2.1. Electrochemical measurements

The working electrode (WE) for the potentiodynamic studies was cut from mild steel rod and was soldered on one end with an insulated copper wire and it was then embedded in chemical epoxy resin

(ARALDITE) leaving the exposed surface area of 1 cm² for the studies. The counter electrode was platinum and reference was saturated calomel electrode (SCE) coupled to luggin capillary. The potential of the metal electrode versus reference electrode was measured with the help of Galvanostat. A steady state potential was achieved in 4–5 h. The electrode system used for potentiostatic polarization studies and electrochemical impedance spectroscopy were same as the one used for potentiodynamic polarization studies. Potentiodynamic polarization and potentiostatic polarization measurements were performed using electrochemical analyzer CHI 6021B under aerated conditions. Potentiodynamic anodic and cathodic polarization curves were obtained with a scan rate of 0.001 V s^{−1} in the potential range from −1.0 V to 0 V relative to the corrosion potential (E_{corr}). Potentiostatic polarization curves were obtained with a scan rate of 0.01 V s^{−1} in the potential range from open circuit potential (OCP) to 2 V. Electrochemical impedance spectroscopy was performed using electrochemical analyzer CHI760C under aerated conditions. Impedance spectra were recorded at E_{corr} in the frequency range 10 kHz to 1 Hz. The AC voltage amplitude was 0.005 V. Equivalent circuit corresponding to impedance data was determined using *Z-simpwin* software version 3.20. Each experiment repeated three times to check the accuracy of experimental data and found to be 3% error in experimental data.

2.2. Surface morphological studies

Properly grinded and polished samples of mild steel (1 cm × 1 cm × 1 cm) were used for SEM and AFM. After being immersed in 0.5 M H₂SO₄, 10^{−2} M TBPH, 10^{−3} M TBPH and (10^{−2} M TBPH + 10^{−3} KI), (10^{−3} M TBPH + 10^{−3} KI) of the inhibitor in 0.5 M H₂SO₄ for 24 h at room temperature the sample was taken out of the solutions and dried in desiccator for 24 h and then these samples were used for SEM and AFM. SEM measurements were performed using Leo 435 VP in high vacuum mode and equipped with digital imaging and 35 mm photography system. SEM images were obtained by applying an operative voltage of 15–30 kV. AFM measurements were performed using VEECO CPII atomic force microscope model no. MPP-11123 using resonance frequency f₀ = 20–80 N/m and spring constant k = 20–80 N/m. The topographic images measured by AFM applying force in nano-Newton between the sample and Al-coated conductive tip.

2.3. Quantum chemical analysis

Quantum chemical analysis was performed using the PM3 method of the quantum chemical package MOPAC 6.0 of Hyperchem 7.5.

3. Results and discussion

3.1. Electrochemical studies

3.1.1. Potentiodynamic polarization studies

In order to study the effect of TBPH on the polarization behavior of mild steel, solutions of various concentrations of TBPH and (TBPH + 10^{−3} M KI) were prepared in 0.5 M H₂SO₄ such as 10^{−2} M, 7 × 10^{−3} M, 4 × 10^{−3} M and 10^{−3} M which were then used for the polarization studies. Potential values were plotted against the logarithm of current densities and various parameters were calculated which are given in Tables 1 and 2. Figs. 1 and 2 give the cathodic and anodic polarization curves for TBPH and (TBPH + KI) at 298 K. The inhibition efficiency was calculated using the following expression:

$$IE\% = \frac{I_{corr} - V_{corr}}{I_{corr}} \times 100 \quad (1)$$

where I_{corr} is the corrosion density current in the uninhibited solution and V_{corr} is the corrosion current in the inhibited solution. The corrosion current values are much lower in the presence of the TBPH than

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