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Galvanic corrosion inhibition behavior of coupled copper—Steel alloys in cooling water system

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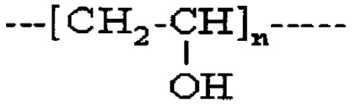
ABSTRACT

The purpose of this paper is to evaluate the electrochemical galvanic behavior of corrosion inhibition of the copper alloy–mild steel couple which exposed to cooling water. Polyvinyl alcohol inhibition behavior has been evaluated under different operating conditions. Weight loss and polarization techniques have been used to evaluate the corrosion rate kinetics. The inhibition efficiency increases with increasing concentration of inhibitor. Maximum inhibitor efficiency was 86% at 7000 ppm inhibitor concentration and 1:1 anode to cathode ration. The experimental data fit Langmuir isotherm. Mathematical analyses were used to correlate the variables. Quantum chemical parameters were calculated using the PM3-SCF method.

Introduction

The design of many industrial units and equipment is directly or indirectly determined by considering corrosion or corrosion control problems. The increasing demands being placed on structures and equipment have led to the requirement of using a combination of materials to obtain the desired performance. Galvanic corrosion is often the unfortunate result. In such cases, the corrosion is stimulated by the potential difference that exists between the two metals, the more noble material acting as a cathode where some oxidizing species is reduced, the more active metal, which corrodes, acting as the anode. The galvanic corrosion rates and the potential distribution over a galvanic couple, in general, depend upon the electrochemical properties of the metals, on environmental variables such as temperature, salinity, oxygen content, and solution flow, as well as the geometry of the corroding system. The severity of an attack depends on the conditions [1]. Cooling water system is one of the most important industrial units. The aim of this work is to evaluate the electrochemical behavior of corrosion inhibition of the copper alloy/mild steel galvanic couple expose to simulated cooling water. Polyvinyl alcohol (PVA) was utilized to evaluate the inhibition behavior under galvanic conditions. Inhibitor concentration, the cathode/anode (C/A) area ratios, and distance between anodic and cathodic elements in galvanic system were the variables of research. Polyvinyl alcohol (PVA), a colorless, water-soluble synthetic resin employed principally in the treating of textiles, paper and as a corrosion inhibitor [2,3]. PVA has a relatively simple chemical structure with a pendant hydroxyl group. The chemical structure of the polyvinyl alcohol is



Experimental work

Materials and methods

Corrosion rate of copper alloy/mild steel couple in the absence and presence 1000, 4000, and 7000 ppm of polyvinyl alcohol (PVA) as corrosion inhibitor, area ratios (C\\A) of 1:1 and 2.4:1, the distance between copper alloy as cathode and mild steel as anode was 3 and 7 cm at room temperature and at static conditions were carried out. Two alloys were used in present work as a couple. Mild steel (SA515GR6) with two sizes ($4.9 \times 3 \times 0.3$ cm and $2.83 \times 3 \times 0.3$ cm) supplied by the Ministry of Oil – Al-Dura Refinery. The second electrode was a copper alloy type ASTM B-111-443 with one size ($3.5 \times 4.43 \times 0.2$ cm). The chemical compositions of both alloys are listed in Table 1. The corrosion environment was industrial water used in the cooling system of Al-Dura Refinery with specifications listed in Table 2. The specimens were first

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Table 1
Chemical composition of working electrode.

Alloy	Chemical composition (% wt)
Steel alloy	C = 0.24, Mn 0.9, P = 0.035, S 0.035, Si 0.15–0.4, Fe is balance
Copper alloy	Cu 70–73, Pb 0.07, Fe 0.06, As 0.02–0.06, Zn is balance

degreased with analar benzene and acetone, and then annealed in a vacuum at 600 °C for 1 h, and cooled to room temperature. Samples were abraded in sequence under running tap water using emery paper of grad number 220, 320, 400, and 600 then washed with running tap water followed by distilled water, dried with a clean tissue, immersed in acetone and benzene, kept in desiccators over silica gel bed until use.

Weight loss technique

For weight loss tests, the dimensions of each sample were measured with a vernier to 2nd decimal of millimeter and accurately weighted to the 4th decimal of a gram. The metal samples were completely immersed each in 1000 cm^3 solution of the corrodant contained in a conical flask. They were exposed to a period of 24 h at the desired inhibitor concentration. Then, the metal samples were cleaned, washed with running tap water followed by distilled water dried with clean tissue then immersed in acetone and benzene and dried again. Weight losses in g m^{-2}/day (g m d) were determined in presence and absence of inhibitor at different operating conditions using the following formula:

$$W = \frac{\text{weightloss(g)}}{\text{area}(m^2) \times \text{time(day)}} \quad (1)$$

From the corrosion rate, the percentage inhibition efficiency was calculated using the following equation:

$$IE\% = \frac{W_{\text{uninibit}} - W_{\text{inhibit}}}{W_{\text{uninhibit}}} \times 100 \quad (2)$$

where $W_{\text{uninhibit}}$ and W_{inhibit} are the corrosion rates in the absence and presence of inhibitor, respectively.

Polarization technique

For polarization tests, corrosion cell has four necks was used, one was fitted with working electrode, one for immersing a thermometer in order to observe the test temperature and the other one had a spherical joint for manipulating the lugging capillary probe. The probe was adjusted to be at a distance not more than 2 mm from the working electrode. The fourth necks input platinum electrode. All potential values were measured with reference to a saturated calomel electrode (SCE). Polarization was carried out by using potentiostat (type PRT 10-0.5). The potentiostat was connected to voltmeter and ammeter to read the applied voltage and current density, respectively.

Table 2
Specifications of water cooling tower.

Na^+	441 ppm
Cl^-	303 ppm
SO_4^{-2}	352 ppm
HCO_3^-	123 ppm
CO_3^{-2}	37 ppm
pH	7.5
Conductivity	2500 μS/cm

Results and discussion

Weight loss measurements

The weight loss of the Cu alloy/mild steel couple in the absence and presence of PVC was determined after 24 h period of immersion at room temperature. The corrosion rates (W) and percentage inhibition efficiency (IE%) were collected in Table 3. The corrosion rate decreases with distance between Cu alloy/mild steel couple and increases with area ratio. Addition of PVC reduces the corrosion rate value with a maximum inhibition of 86% at 1:1 area ration and 7 cm distance. Fig. 1 shows the graphical behavior of corrosion rate and inhibitor efficiency.

Adsorption studies

The inhibition action of many organic compounds is assumed to be assigned to their adsorption on metal surface. Therefore, investigation of adsorption isotherms can provide important information on the adsorption of PVA on couple surface in corrosive solution. In an attempt to find the most suitable adsorption, the surface coverage Θ (Θ = IE%/100) was subjected to different adsorption isotherms, such as, Langmuir, Frendlich, Temkin, Frumkin, and Flory–Huggins. It is found that the corrosion data fit well to Langmuir adsorption isotherm and kinetic–thermodynamic model isotherms. The Langmuir adsorption isotherm [4] is given by:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (3)$$

where C is the inhibitor concentration, K adsorptive equilibrium constant, representing the degree of adsorption (i.e., the higher the value of K indicates that the inhibitor is strongly adsorbed on the metal surface). The plot of C/Θ against inhibitor concentration (C) displayed a straight line for tested inhibitor (Fig. 2). The average value of K was 0.00115 ppm^{-1} which obtained from the reciprocal of the intercept of a Langmuir plot line, and the slope of this line is near unity meaning that each inhibitor molecules occupies one active site on the metal surface. The kinetic–thermodynamic model isotherm [5] is given by:

$$\log\frac{\theta}{1-\theta} = \log K' + y\log C \quad (4)$$

where K' is a constant, and y is the number of inhibitor molecules occupying one active site. A plot of $\ln(\theta/1-\theta)$ vs. $\log C$ gives a straight line of slop y and intercept of $\log K'$, as shown in Fig. 3. Equilibrium constant corresponding to adsorption isotherm is given by, $K = K'^{\frac{1}{y}}$. Values of $y > 1$ implie the formation of multilayer of inhibitor on the surface of metal. Values of $y < 1$ mean a given inhibitor molecules will occupy more than one active site. As shown in Table 4, the kinetic–thermodynamic model data were in a good agreement with that obtained by Langmuir adsorption isotherm model. The values of y were lower than unity indicating the formation of monolayer on the metal surface, and the values of K was comparable. The standard adsorption free energy (ΔG^o_{ads}) was calculated using the following equation [6]:

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^o_{ads}}{RT}\right) \quad (5)$$

where 55.5 is the concentration of water in solution expressed in molar, R is gas constant, and T is absolute temperature. The average value of standard adsorption free energy (ΔG^o_{ads}) was −16.8 kJ/mol. The negative value of ΔG^o_{ads} ensures the spontaneity of the