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Electrochemical Approaches of Evaluating Galvanic Corrosion Kinetics of Copper Alloy – Steel Alloy Couple in Inhibited Cooling Water System

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Abstract

The purpose of this paper is to evaluate the electrochemical kinetics parameters of galvanic corrosion inhibition of the copper alloy- steel alloy couple, exposed to cooling tower water. Polyvinyl alcohol was utilized to evaluate the inhibition behaviour under galvanic couple conditions. Polarization technique was used to evaluate the corrosion rate data. Barnartt`s three point method and McLaughlin method were used to evaluate the kinetics parameters. The results were compared with the results of conventional Tafel extrapolation method.

Keywords: Regression, Galvanic corrosion, Electrochemical calculation, Kinetic parameters.

1. Introduction

Tafel equation and Tafel extrapolation technique are a conventional method in electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential and used widely everywhere [1 – 4].This technique uses data obtained from cathodic and anodic polarization measurements. Many attempted were proposed to evaluate the corrosion parameters [5, 6]. Barnartt`s three point [7] and McLaughlin method [8] were one of these methods. Barnartt`s three point method was used to calculate corrosion current and Tafel slopes from polarization curves. This method was based on the basis that a polarization curve can be represented by the equation [7]:

$$i = i_{corr1}\left(10^{\frac{x}{ba_1}} - 10^{\frac{-x}{bc_1}}\right) \qquad 1$$

i is applied current density, i_{corr1} is the corrosion current, b_{a1} and b_{c1} are the Tafel slopes for the anodic and cathodic process respectively, and x = E – E_{corr}, where E_{corr} is the corrosion potential and E is the electrode potential corresponding to the applied current. On the other hand, McLaughlin method was based on the following equation [8]:

$$i = \frac{i_{\lim,a}\ i_{corr2}}{i_{corr2} + (i_{\lim,a} - i_{corr2})\, 10^{\frac{-x}{ba2}}} - \frac{i_{\lim,c}\ i_{corr2}}{i_{corr2} + (i_{\lim,c} - i_{corr2})\, 10^{\frac{x}{bc2}}} \qquad 2$$

$i_{\lim,a}$and $i_{\lim,c}$ are diffusion currents for anodic and cathodic processes respectively. The symbols i_{corr2}, b_{a2} and b_{c2} have been used instead of i_{corr1}, b_{a1}, and b_{c1} in order to avoid confusion when comparing the results obtained by equation1 and equation 2. The total derivation of equation 1 and 2 were given in the literature[8]. The aim of the present work is to evaluate the electrochemical behaviour of corrosion inhibition of the Copper alloy/ steel alloy galvanic couple expose to simulated cooling water. Polyvinyl alcohol (PVA) was utilized to evaluate the inhibition behaviour 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.Galvanic corrosion kinetics parameters were evaluated using Barnartt method (BM) and McLaughlin method (MM). The results were compared with Tafel method (TM).

2. 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, and the distance between Copper alloy as cathode and mild steel as anode of 3 at room temperature were carried out. Two alloys were used in present work as a couple. Mild steel (SA515GR6) with two sizes (4.9×3×0.3 cm and 2.83×3×0.3 cm) supplied by the Ministry of Oil – Al-Dura Refinery (Iraq) having the following chemical compositions (% wt): C 0.24, Mn 0.9, P 0.035, S 0.035, Si 0.15 – 0.4, Fe is balance. The second electrode was a copper alloy type ASTM B-111-443 with one size (3.5 ×4.43 ×0.2 cm) having the chemical compositions (wt%) of: Cu 70 – 73, Pb 0.07, Fe 0.06, As 0.02 – 0.06 and the remainder is Zn. The corrosion environment was industrial water used in the cooling system of Al-Dura Refinery (Iraq)with chemical compositions and specifications listed in Table 1. The specimens were first degreased with analar benzene and acetone, and then annealed in a vacuum at 600 ^{o}C for 1 hour, 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. Polarization 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 in 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 1: Specifications of water cooling tower.

Na^+	441 ppm
Cl^-	303 ppm
SO_4^{-2}	352 ppm
HCO_3^-	123 ppm
CO_3^{-2}	37ppm
pH	7.5
Conductivity	2500 µS.cm^{-1}

3. Results and discussion

3.1 Corrosion kinetics parameters via Tafel method

Fig. 1 shows the polarization curves for Cu alloy in simulated cooling water solution in the presence and absence of different concentrations of PVA. Similar figures were obtained for steel alloy at different conditions. The polarization parameters were (i_{corr}, b_a, b_c) obtained via Tafel extrapolation method i.e. extrapolating both cathodic and anodic linear regions back to the corrosion potential.

The presence of inhibitor shifts the polarization curves to lower values of current densities. In other words, the copper alloy and mild steel corrosion are retarded by PVA addition. From polarization curves, the lines shift to positive potentials compared with the blank. The positive shift of E_{corr} values indicates that inhibitor is adsorbed on anodic sites and, consequently, affects mainly the anodic dissolution of mild steel.

The inhibitor can be classified as an anodic or cathodic type when the change in E_{corr} value is larger than 85 mV [9]. Since the largest displacement exhibited by inhibitor is 3 mV in the case of Cu alloy, and 200 mV in case of mild steel, then these molecules can be considered as mixed-type inhibitor of Cu alloy and anodic – type inhibitor of steel alloy. Apparently, i_{corr} decreases in the presence of PVA, and decreases with increasing the inhibitor concentration. In addition, there are no significant changes in Tafel slopes of $b_a$and b_c, which indicates that the presence of inhibitor does not change the mild steel corrosion mechanism [10].

3.2 Galvanic corrosion kinetics parameters via Tafel method (TM)

Polarization curves of copper alloy and mild steel are obtained in the absence and presence of difference inhibitor concentration. Mild steel is the anodic element of the pair under all test conditions because its corrosion potential is less noble than that of copper alloy. Corrosion resistance of mild steel decreases due to the galvanic effect produced by coupling with copper alloy, while the latter remain protected. The predicted coupled potential (E_{corr}^{coup}) and the galvanic current density (i_{corr}^{coup}) values of the pair were estimated at different inhibitor concentrations from the polarization curves by superimposing the anodic branch of the less noble material (mild steel) to the cathodic branch of the most noble material (copper alloy). The experimental values of galvanic parameters are shown in Table 2.

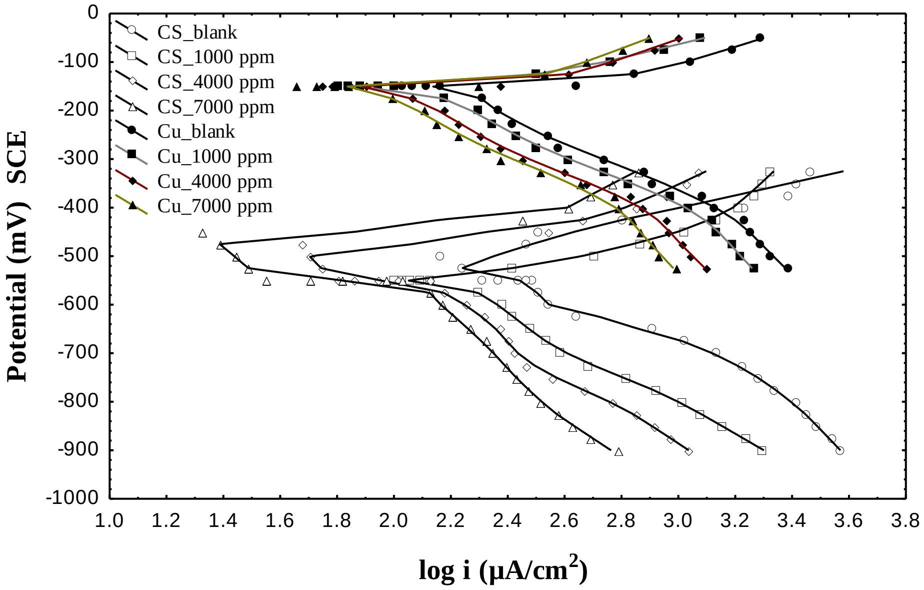

Fig. 1 Polarization curves of Cu and CS alloy in simulated cooling water in absence and presence of PVA.

Table 2: Galvanic parameters of the Cu/CS in simulated cooling water in absence and presence PVA concentrations.

C (ppm)	Area ratio	TM				BM			MM			IE%*
		E_{corr}^{coup} (mV,SCE)	i_{corr}^{coup} (μA/cm^2)	b_c	b_a	$i_{corr,1}$ (μA/cm^2)	$b_{c,1}$	$b_{a,1}$	$i_{corr,2}$ (μA/cm^2)	$b_{c,2}$	$b_{a,2}$	
Blank	1:1	-400	393.04	81.1	117.7	377.11	66.4	122.3	388.11	76.3	120.7	0
1000		-350	174.28	96.4	111.1	165.22	78.7	99.3	170.27	94.3	113.6	56
4000		-300	50.57	78.7	126.3	40.91	55.5	111.1	54.71	79.1	127.7	87
7000		-275	12.32	109.2	117.2	09.12	97.2	99.9	11.12	103.4	118.9	97
Blank	2.4:1	-450	538.61	99.8	117.7	455.66	89.1	125.1	541.62	100.2	119.3	0
1000		-375	224.85	100.6	111.1	200.85	92.5	93.4	222.95	99.8	116.8	58
4000		-350	70.15	107.7	126.3	55.17	100.1	122.2	69.13	103.2	125.4	88
7000		-325	17.598	116.4	117.2	12.43	100.6	88.8	16.12	106.9	119.2	96
*average inhibitor efficiency												

Corrosion potentials shift to more noble values as the inhibitor concentration increases. Therefore the predicted coupled potential values follow the same tendency observed at all corrosion potential of mild steel, E_{corr}^{coup} values are closer to the mild steel corrosion potential than copper corrosion potential at all inhibitor concentrations. On the other hand, galvanic current density decreases with increasing the inhibitor concentration.

3.3 Galvanic corrosion kinetics parameters via Barnartt method (BM) and McLaughlin method (MM)

Potential against current density data can be used as input and output of equation 1 and 2. Nonlinear regression of equation 1 and 2 was used in order to obtain the parameters of these equations. The regression method based on *Levenberg-Marquardt* estimation method was used. Table 1 gives values of i_{corr}, b_a, and $b_c$corresponding to various values of x. For x>20 mV, there is little variation in these parameters; for x < 20 mV there is large variation. This variation at low values of x may be attributed to the nonlinearity of potential – current curve near the corrosion potential. Khadom*et. al.*[6] and Yaro and Khadom[11] discussed this behavior in detailed. They concluded that the shape of both anodic and cathodic curves, in turn, depends on the respective kinetic parameters of their reaction. The current-potential curve of corroding metal is rather complex non-linear equation; hence a general analytical solution is equally complex. Also they concluded [6] that the deviation from linearity may be attributed to effect of mass transfer or concentration polarization on activation process. Therefore, the accurate values of corrosion parameters will be above 20 mV. The average values above 20 mV (i.e. at 30, 40, 50 mV) of corrosion kinetic parameters were obtained. For application of equation 2, values of $i_{lim,a}$and $i_{lim,c}$were set as large as enough for polarization curves . Value of $i_{lim,a}$=5000 µA.cm^{-2} for steel alloy and $i_{lim,c}$=-5000 µA.cm^{-2} for copper alloy. Both equations 1 and 2 give comparable results. The results are more accurate with application of equation 2; the corrosion parameters are closer to TM results than data of equation 1. This may be attributed to that equation 2 applicable with systems contains concentration polarization more than the system with activation process only.

Conclusion

Barnartt`s three point method (BM) and McLaughlin method (MM) can be applied to determine the corrosion kinetic parameters with high correlation coefficients. McLaughlin method was better than Barnartt`s three point method in mixed control systems (i.e. both activation and concentration polarization).These methods can be used to take in to account the effects of mass transfer on activation corrosion process. The results were comparable with traditional Tafel methods. Nonlinear mathematical regression was powerful methods for evaluation of kinetics parameters.

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