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Mass transfer effect on corrosion inhibition process (D CrossMark of copper–nickel alloy in hydrochloric acid by Benzotriazole

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Abstract The corrosion inhibition of copper–nickel alloy by Benzotriazole (BTA) in 1.5 M HCl has been investigated by weight loss and polarization techniques at different temperatures. Maximum value of inhibitor efficiency was 99.8% for BTA at 35 °C and 0.1 M inhibitor concentration, while the lower value was 86.8% at 55 °C and 0.02 M inhibitor concentration. The non-linear region of the polarization curve near the corrosion potential can be discussed depending on data of over potential as a function of current densities. These data can be analyzed by suggestion of a mathematical model to take into account the effect of mass transfer on activation process.

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1. Introduction

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Copper and its alloys have an excellent thermal conductivity, good corrosion resistance and mechanical workability and are widely used in heating and cooling systems. It is wellknown that corrosion products have a negative effect on heat transfer on the copper based heat exchanger, which can be re-

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duced by periodic cleaning in hydrochloric acid pickling solutions. Corrosion inhibitors could effectively eliminate some of the undesirable reactions connected with destructive effects of hydrochloric acid pickling solutions on the copper surface and prevent its dissolution ([Sherif et al., 2008](#page--1-0)). Corrosion inhibitors are chemical substances, when added in small concentrations to environment, effectively checks, decreases or prevents the reaction of metal with the environment ([Da-Quan](#page--1-0) [et al., 2008](#page--1-0)). It must be clearly understood that no universal corrosion inhibitor exists. Each inhibitor must be tailored to the specific corrosion problem that needs solution. While the use of inhibitors for some types of corrosion can be similar to others, this similarity must be treated as coincidence. Most inhibitors have been developed by empirical experimentation. Amines and triazoles derivatives have been reported to be very effective inhibitors for copper in acidic solutions [\(Sherif et al.,](#page--1-0) [2007; Sherif and Park, 2006](#page--1-0)). The present work is an attempt to study the corrosion inhibition of Benzotriazole for copper–nickel alloy in 1.5 M HCl at different temperatures. The

 b_a and b_c anodic Tafel slopes.

- C_i^s concentration of species j at the electrode surface $\text{(mol cm}^{-3})$.
- i_{corr} and i_1 corrosion and limiting currents, respectively.
- i_0^s exchange current density referring to surface concentrations $(A \text{ cm}^{-2})$.
- k^0 rate constant (cm s⁻¹).
- n number of electron transferred in electrochemical reaction.

effect of mass transfer on corrosion rates were studied by application of some basic theoretical models. Kinetics and electrochemical parameters were also obtained.

2. Experimental work

The electrochemical behavior of copper–nickel alloys, which are used widely in many industrial equipments, was studied using polarization technique in the absence and presence of Benzotriazole (BTA) in 1.5 M HCl solution at different temperatures (35, 45, and 55 $^{\circ}$ C), and different inhibitor concentrations $(0.02, 0.04, 0.08, 0.1 M)$. Ring shape specimen of Cu–Ni alloy with dimension (2.22 cm) outside diameter, (1.5 cm) width, and (0.13 cm) thickness. Specimens were washed by the detergent and flushed by tap water followed by distilled water, degreased by analar benzene and acetone, then annealed in vacuums to $600\,^{\circ}\text{C}$ for one hour and cooled under vacuum to room temperature. Before each run, specimens of Cu–Ni were abraded in sequence using emery paper of grade number 220, 320, 400 and 600, then washed by running tap water followed by distilled water then dried by clean tissue, degreased with benzene, dried, degreased with acetone, dried, and finally left in desicater over silica gel. The chemical compositions of Cu–Ni alloy were $(0.148\%$ Sn, 0.2% Fe, 0.134% Zn, 0.015% Al, 0.0003% P, 0.5% Sb, 0.0583% Pb, 0.0202% Si, 0.017% S, 0.0056% As, 10% Ni, and the remainder is Cu). Tests were carried out using a standard cell of 2.5 l. The cell was equipped with six necks, five of them are used. One was for the working electrode (Cu–Ni ring). One had a spherical joint for mounting the lugging capillary prob., one for thermometer, and two for the two counter gold electrodes. All potential values were measured in reference to saturated calomel electrode (SCE). The lugging capillary probe was adjusted such that it was at a distance of not more than (2 mm) from the working electrode. The working electrode was copper–nickel alloy ring; this ring was fixed on brass zone on the shaft. Gold electrodes were used as a counter electrode. Saturated calomel electrode (SCE) was used as reference electrode. After preparation of the working electrode, the corrosion cell parts were joined to each other, and then connected to the power supply (Type 6236B, Hewlett Packard, USA). The cathodic polarization was carried out beginning from low potential of (-450 mV) until reaching the corrosion potential. The potential was changed to (10–15 mV) for each step after a one-minute period, then, the current was recorded by inverting the connection of the power supply after polarization

- α_+ and α_- transfer coefficients of anodic and cathodic partial reactions, respectively.
- η^{ct} charge-transfer over potential of an electrochemical reaction (V).
- η^{mt} mass-transport over potential of an electrochemical reaction (V).
- λ the mass transfer correction factor.

readings had been taken. The anodic polarization readings started at a potential resulting in zero current density and was increased in a step of $(10-15 \text{ mV})$ with the current recorded at each step and with one minute interval until a potential of about (-50 mV) .

3. Theoretical background and mathematical model derivation

The general used methods for calculation of corrosion rates from polarization measurements are based on the assumption that the process is controlled by the rate of anodic and cathodic partial reactions and supply of reactants is unlimited, and the mixed-control case, when the rate of the process is jointly controlled by the surface reaction and the transport of material to and from the surface has been much less investigated, even thought this case may quite frequently reflect practical situations. So, it is very important to study the effect of neglecting the mass transfer on corrosion parameters. The basic electrode kinetic equation, which is derived in many references for general redox reaction, $O + ne = R$, is usually written as [\(Bockris](#page--1-0) [and Reddy, 1973; Kreyszig, 1999\)](#page--1-0):

$$
i = i_0^s \left\{ \exp\left(\frac{\alpha^+ F \eta^{\text{ct}}}{RT}\right) - \exp\left(\frac{\alpha^- F \eta^{\text{ct}}}{RT}\right) \right\} \tag{1}
$$

where

$$
t_0^s = nFk^0 (C_0^s)^{\frac{\alpha^+}{n}} (C_R^s)^{\frac{\alpha^-}{n}}
$$
 (2)

$$
\alpha^+ + \alpha^- = n \tag{3}
$$

Eq. (1) is useful for conditions when mass-transport effect is negligible, that is, the surface concentrations are equal to the bulk concentrations and the measured over potential is equal to the charge-transfer over potential. If mass-transport effect is not negligible, Eq. (1) has to be modified. Two modifications are needed: (1) the measured over potential must be corrected for the mass-transport over potential, and, (2) the exchange current density has to be expressed as a function of bulk concentrations. After taking into account this two-assumption, Eq. (1) can be re-derived to yield ([Kreyszig, 1999\)](#page--1-0),

$$
i = i_{\text{corr}} \left[\exp \left(\frac{2.3 \Delta E}{b_a} \right) - \lambda \exp \left(-\frac{2.3 \Delta E}{b_c} \right) \right]
$$
 (4)

$$
\lambda = \frac{1}{1 - \frac{i_{\text{corr}}}{i_l} + \frac{i_{\text{corr}}}{i_l} \exp\left(-\frac{2.3\Delta E}{b_c}\right)}\tag{5}
$$

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