Journal of Environmental Chemical Engineering 3 (2015) 10–19

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Effect of benzotriazole on corrosion inhibition of copper under flow conditions

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ARTICLE INFO

Article history:
Received 1 September 2014
Accepted 3 November 2014
Available online 29 November 2014

Keywords:
Copper
Inhibitor
Benzotriazole
Rotating cage
Flow conditions

ABSTRACT

The corrosion inhibition of benzotriazole on the copper surface is often investigated in static environment. The evidence for the protection of copper in dynamic flowing environment is limited. Hence, we investigated the corrosion control of copper in 3.5% NaCl solution in the presence of benzotriazole by a rotating cage. The flow test was carried out at different velocities 0.5–3.0 m/s (100–700 rpm). Copper showed accelerated corrosion activity with respect to the increase in the velocity in 3.5% NaCl test solution. However, benzotriazole added to the test solution reduced the corrosion attack on the copper. This clearly shows the adsorption of inhibitor on copper surface resulted in decreasing the mass loss by 4–5 times. The surface property was examined by using a scanning electron microscopy, atomic force microscopy and contact angle measurements. Adsorption of benzotriazole on copper surface follows the Langmuir adsorption isotherm.

Introduction

Corrosion is one of the most serious engineering problems and of great economic concern. The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment and structures are often more serious in a corrosive environment. The understanding of corrosion mechanisms, prediction and controlling are the big challenges for safe operation of the components [1–6]. Copper in conjunction with inhibitor is widely used in preventing flow related corrosion for pipes, heat exchanger tubes handling waters or seawaters [7–10]. Thus, it is important to understand the interaction of inhibitors in flow environment to retard the corrosion.

Inhibition phenomena are an important subject of worldwide investigation due to the large economic losses caused by the corrosion [11,12]. The use of organic inhibitors adsorbed onto copper surface is one of the most practical approaches for the corrosion protection. During the past few decades, the chemistry of the carbon–nitrogen bond has been a hot research topic since this functional group has been shown to be one of the main building blocks of organic and material chemistry. The wide range of azole derivatives containing nitrogen are studied for inhibition of corrosion of copper in chloride media. Benzotriazole (1,2,3-benzotriazole, $C_6H_5N_3$), an aromatic five-member heterocyclic compound contains three nitrogen atoms (see Fig. 1) and its derivatives were studied extensively, and was proved to be a highly efficient inhibitor for preventing copper and copper-based alloys corrosion in neutral and alkaline media for a longer period [13–20]. Benzotriazole (BTAH) with a molar mass of 119.124 g/mol is sufficiently soluble in water (20 g/L) for use as a corrosion inhibitor. The benzotriazole can be either neutral, negatively charged (BTA^-) or protonated ($BTAH_2^+$) depending on the pH of the test solution. The various form of BTA arises in the solution.

$$BTAH^+_{2aq} \leftrightarrows AH_{aq} + H^+_{aq} pK_a = 1.0 \quad (1)$$

$$BTAH_{(aq)} \leftrightarrows A^-_{aq} + H^+_{aq}\, pK_a = 8.4 \quad (2)$$

The high pK_a (8.4) constant i.e., in acidic environment (at low pH), the molecule is predominantly in neutral or undissociated form (BTAH). As the pH increase towards alkalinity (low pK_a = 1), the deprotanation of molecule increases and is present in the BTA^- form . Benzotriazole has been extensively used for inhibition of copper corrosion which forms a *monolayer or multilayer* protective barrier layer in aqueous solutions. Various mechanisms, though

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http://dx.doi.org/10.1016/j.jece.2014.11.005

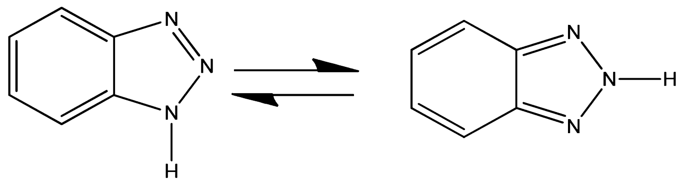

Fig. 1. Chemical structure of benzotriazole (BTAH) and its tautomeric forms.

some contradictory nature, has been proposed for benzotriazole molecules adsorption or film formation on copper surface. Cotton et al. proposed the formation of surface complex of Cu–BTAH during the immersion of copper in BTAH solution where soluble copper ion is formed [21]. Cotton and Scholes postulated a polymeric film of 50 Å thick BTA forms on copper covalently bonded by the replacement of the H atom from the N–H group and a coordination bonding involving a lone pair of electrons from one nitrogen atom [11]. The formation of linear polymeric Cu(I) BTAH structure was not limited to a monolayer but could grow up to several thousand Å thick due to transport of Cu(I) ions from the matrix of copper metal through the surface film [14]. Morito and Suetaka suggested Cu protection is based on the formation of Cu(I) BTAH complex aligned parallel to the Cu surface and not due to film of chemisorbed BTAH [22]. However Mansfield concluded BTAH chemisorbs only on a copper oxides surface which forms multilayer films [23]. The Cu_2O favours the adsorption process compared to CuO. Roberts suggested that for the first BTAH layer on the Cu_2O substrate, Cu(I) ions could be connected by two bonds to the two oxygen atoms in the Cu_2O lattice, and the remaining two to the deprotonated BTAH molecules [24]. Alternatively, it was suggested that BTAH may be sandwiched between the Cu_2O layers [25]. Clifton and Yoke proposed a structure with chlorine bridging the two coppers in the monovalent state i.e., the formation of the Cu_2Cl–BTAH surface complex related to the existence of the CuCl interlayer [26].

Benzotriazole is effective in preventing copper corrosion under stationary condition. However, under dynamic conditions or flow environment, very few studies has been carried out on benzotriazole in chloride environment [27]. A limited number of studies such as BTAH action on copper in flowing H_2SO_4 media [9] or in dynamic acetate-buffered solution [28] has been carried out.

The mechanism by which metals dissolve during corrosion process is complex, particularly in the presence of inhibitors which promote formation of surface films by adsorption. Flow causes the mass transfer of species to and from the surface i.e., dissolved oxygen or the dissolved metal ions to diffuse from the solution to the metal or from the metal to the solution respectively [29]. Depending on the system, the nature of adsorbed film may vary from physical and/or chemical adsorption to precipitation of a separate phase from the solution. Such adsorbed layer can either act as physical barriers to the metal ion diffusion through the film promoting dissolution or serve to affect the kinetics of cathodic reactions. The effect of fluid flow is important since flow may disrupt and/or affect the thickness and protective efficiency of adsorbed benzotriazole film. The issues such as the effectiveness of inhibitor in high velocity and high shear flow are a main consideration for their function. The hydrodynamic nature of the flowing fluids can affect inhibitor efficiency by either slowing the rate of formation of the inhibitive layer or causing degradation of well-formed inhibitive layers or a combined effect may also be active [5].

Copper possess good resistance to static seawater corrosion by virtue of a stable and strongly adherent oxide film [30]. However, flow induced localized corrosion (FILC) is likely to occur only above critical flow velocities which are high enough to break down protective scales, layers or films on the metal surface [31,32]. The copper was mostly preferred for piping material to avoid corrosion–erosion in a limited flow velocity such as 1.2 m/s in seawater [30]. However exposure to high flowing corrosive media could prevent the protective surface film from forming or could erode the film locally, thereby exposing the unprotected parent substrate. The mass transport enhanced corrosion due to flow is studied by various hydrodynamic systems which uses the convection to enhance the rate of mass transfer over a stagnant system. Various hydrodynamic devices have been used to study such effects, namely jet impingement rig (JIR), rotating disc electrodes (RDE) and rotating cylinder electrodes (RCE) and rotating cage (RC). The RC is employed here to investigate the corrosion inhibition of benzotriazole on copper surface. The RC has been widely used for evaluating corrosion inhibitors in oil field and refinery applications [33]. The rotating cage is frequently used to screen the susceptibility of materials to flow induced localized corrosion [34–36]. Thus, the current aim of the project is to investigate the role of benzotriazole inhibitor on the copper surface to control its corrosion. The influence of benzotriazole at a different concentration (1–10 mM) and at various velocities (0.5–3 m/s) in 3.5% NaCl is carried out on copper in RC. The gravimetric measurements were used to quantify the corrosion process as a function of velocities and inhibitor concentration in a rotating cage. The Langmuir adsorption model is verified for the benzotriazole at different velocity.

Experimental details

Materials

Copper (99.99% purity) metal for the corrosion inhibition study was supplied by Alfa Aesar, United Kingdom. Benzotriazole (BTA) as inhibitor and sodium chloride for the electrolyte was supplied by Sigma–Aldrich, Bangalore, India. Ultrapure distilled water was used for making the electrolytes/test solutions of 3.5% NaCl. The copper samples were mechanically polished to mirror finish, degreased with acetone, rinsed in distilled water and then dried in desiccators.

Rotating cage (RC)

A purpose made rotating cage (RC), see Fig. 2, was used to investigate the flow effect on the corrosion inhibitions of benzotriazole on copper surface. The rotating cage design has been already reported by several authors [36,37]. The sample holder consists of four copper coupons (8.0 cm × 2.0 cm × 0.127 cm) held by two pieces of Teflon disks (80 mm diameter and 6 mm thickness) cut from teflon solid rod. The Teflon disks were mounted on rotating shafts (75 mm apart) which reach at the bottom of the Perspex acrylic vessel and keep the coupons away from wobbling. The holes (10-mm diameter) about 15 mm away from the centre are drilled in the top and bottom PTFE plates of the cage to increase the flow of electrolyte on the inside surface of the coupon. The Perspex acrylic vessel had capacity for the 8 L of the test solutions. The flow experiments were carried out in 3.5% NaCl solutions with and without benzotriazole inhibitor, see Table 1. The concentrations of benzotriazole tested are 1, 5 and 10 mM. The duration of the experiments are 3 h, see Table 1. The study was carried out at mean linear flow velocities between 0.5 and 3 m/s (100–700 rpm) which represent Reynolds number between $40{,}000 < Re < 260{,}000$. This flow behaviour is homogenous in nature without any vortex on the coupons [33].

The Reynolds numbers Re were calculated according to the following relationships:

$$Re = \frac{\omega r^2}{\nu} \tag{3}$$

r is the radius of the rotating cage (m), ω is the rotational speed (s^{-1}) and ν is the kinematic viscosity (m^2/s). The approximation of