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Some aspects of the role of inhibitors in the corrosion of copper in tap water as observed by cyclic voltammetry

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ABSTRACT

Cyclic voltammetric examination of the corrosion and inhibition of copper in hard and soft tap-waters in the presence of a commercial inhibitor containing benzotriazole (BTA) and triethanolamine (TEA), or its separate components, is presented. The anodic and cathodic reactions are both strongly inhibited, although the anodic reaction more so. BTA is by far the dominant inhibiting component. The inhibitor forms a polymerized reactive adsorbed surface film. Inhibition of the cathodic reaction (oxygen reduction) is not due to electron resistivity of the inhibitor, but rather, by heavily reduced surface coverage of adsorbed oxygen over a wide range of oxygen reduction overpotential.

1. Introduction

Copper is widely used for domestic water systems—it is easy to install, abundant in nature and low in cost [1–4]. Severe corrosion of copper plumbing can result from pitting corrosion, which is a non-uniform localised attack of the wall of the copper tube initiated most likely from the waterside surface in the water distribution system. Pitting can lead to pipe failure in the form of pinhole leaks only a few months after the installation of copper plumbing [5–7].

Inhibitors are used extensively to protect copper from corrosion. Fernox® Alphi 11, which is a complex blend of chemicals, is one of the most extensively used commercial corrosion inhibitors for copper plumbing. Benzotriazole (BTA, $C_6H_4N_3H$), which is a heterocyclic organic compound, is one of the main components of Fernox® and known as an effective inhibitor for copper and copper based alloys in aqueous solutions. Its inhibiting effect has been studied for decades [8–16]. There are two main mechanisms proposed for the inhibitory action of BTA on copper corrosion. One is that the inhibitory action of BTA is due to chemisorption of BTA on the copper surface which acts as the protective barrier layer [8,11]. The other mechanism is that the inhibition of BTA could arise from the formation of a polymeric film (Cu-BTA complex) on the Cu surface [16]. A combination of these mechanisms [12,17–19] with the formation of the first chemisorbed layer composed of BTA in molecular form and subsequent layer of Cu-BTA complex on top is also proposed. Although there is abundant literature concerning the mechanism of the inhibition effect caused by BTA for copper corrosion in various solutions [11,17–27], there is no unified agreement about the nature of the protection offered by the inhibitor, and the literature concerning the electrochemical behaviour of copper in tap water in the presence of inhibitor is limited [28]. The true nature of the BTA protective action on copper remains to be determined. It is nevertheless important to be able to assess the long-term performance of an inhibitor within a reasonable period of time and this requires an understanding of the mechanisms of inhibition.

In the present study, cyclic voltammetry was employed to examine the action of the inhibitors. These are a commercial inhibitor—Fernox® Alphi 11 and its main components: benzotriazole (BTA), triethanolamine (TEA) and their mixture. The role of these in retarding copper corrosion in tap water is presented.

2. Experimental

2.1. Materials

Experiments were run with a three-electrode electrochemical cell in a volume of 160 mL. Both hard and soft tap-waters were used: the former originated from Cambridge (England) and the latter from Livingston (Scotland). The water compositions are listed in Table 1. The ionic conductivity was measured using a Jenway-4310 conductivity meter and calibrated Pt-black electrodes. Both tap-waters were inhibited with a concentration of 25% by volume

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Table 1
Analysis data of hard and soft tap water (data supplied by Mitsubishi Electric, UK).

	Hard tap water (Cambridge)	Soft tap water (Livingston)
K^+/mg L^{-1}	0.3	0.2
Mg^{2+}/mg L^{-1}	2.4	1.0
Ca^{2+}/mg L^{-1}	121.0	8.3
Cl^-/mg L^{-1}	26.5	6.4
$NO_3{}^-$/mg L^{-1}	0.1	0.6
$PO_4{}^{3-}$/mg L^{-1}	39.4	1.0
$SO_4{}^{2-}$/mg L^{-1}	3.0	5.3
Alkalinity/mg L^{-1}	206	44
pH	7.56[a]	6.98[a]
Conductivity/μS cm^{-1}	652[a]	79.4[a]

[a] Measured by the authors in the Cambridge laboratory.

Table 2
Analysis data of Fernox® Alphi 11 (data supplied by Mitsubishi Electric, UK).

Fernox® Alphi 11	(mg kg^{-1})
Cl^-	20
$SO_4{}^{2-}$	<2
Triethanolamine	4300
Benzotriazole	540
PO_3	<2
P_{total}	<10
Propylene glycol	99 wt%
pH	7.8
Conductivity/μS cm^{-1}	33

Fernox® Alphi 11, for which analysis data are shown in Table 2. This dilution of Fernox® gives a concentration of 4.7 mM benzotriazole and 30 mM triethanolamine. The main components of Fernox® were also examined (for the hard-water system only) using 4.7 mM benzotriazole (BTA), 30 mM triethanolamine (TEA) and a combination of 4.7 mM BTA and 30 mM TEA. Fernox® was provided by Mitsubishi Electric, UK. BTA and TEA (analytical grade) were from Sigma–Aldrich. A ϕ 6.35 mm Cu rod (Advent, Oxford, UK, purity 99.99+%) mounted in epoxy resin functioned as the working electrode (WE). A Ag/AgCl electrode equilibrated with test solution, or a saturated calomel electrode (SCE) was used as the reference electrode (RE) and a graphite rod as the auxiliary electrode (AE). The cell was equipped with a Luggin capillary-tipped tube by which the reference electrode was separated from the working cell. This minimises the transport of Ag^+ and Cl^- from the reference electrode into the working cell. The connecting tube was filled with the same solution as the working cell. The Cu electrodes were ground to 2400 grit silicon carbide surface finish followed by ultrasonic cleaning with twice-distilled water. The finished Cu electrodes were left exposed to air at room temperature for 1 h before testing.

The Ag/AgCl reference electrode was calibrated against a saturated calomel electrode (SCE) regularly. All the potential values presented in this work refer to the SCE scale.

2.2. Cyclic voltammetry

Cyclic voltammetry was performed in hard tap water (Cambridge, England) and soft tap water (Livingston, Scotland) in the absence and in the presence of inhibitor, with the potential (E) swept linearly from −0.8 V(SCE) to +0.4 V(SCE) at a sweep rate of 1 mV s^{-1}. All the tests were controlled thermostatically at 25 ± 0.1 °C in stirred solutions without deaeration. The polarization curves presented here have not been corrected for the ohmic drop in the electrolyte between the WE and the Luggin probe tip. The ohmic drop is discussed below.

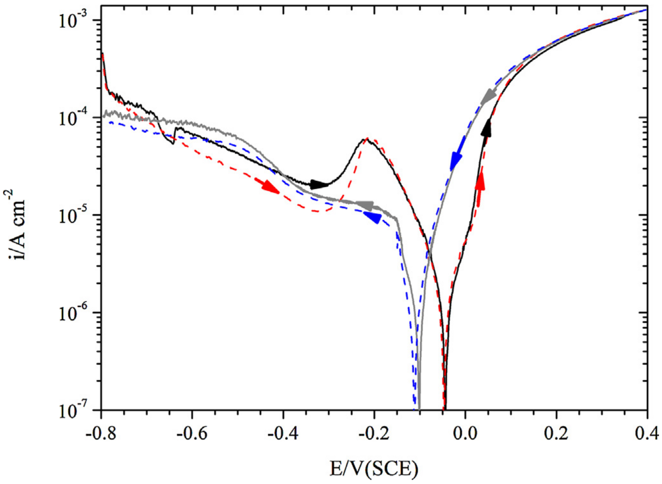

Fig. 1. Polarisation curves, showing positive and negative sweeps, of ϕ 6.35 mm Cu electrode in hard tap water (Cambridge) at 25 ± 0.1 °C. Repeated results are shown here, as 1st run (solid line) and 2nd run (dashed line): these are completely independent surfaces and show the reproducibility.

3. Results

3.1. Cyclic voltammetry in uninhibited Cambridge tap water

Fig. 1 gives the two independent cyclic polarisation curves of Cu in inhibitor-free Cambridge tap water at 25 ± 0.1 °C between the limits of −0.8 V(SCE) and +0.4 V(SCE). The two measurements of this electrochemical behaviour show good reproducibility in both positive and negative sweeps. There is a cathodic peak in the current density at about −0.22 V(SCE) in the positive sweep which was formed before any corrosion occurred. The origin of this peak is not yet known, but is reproducible. This cathodic current peak cannot be due to reduction of corroded Cu, since it is observed on the data in Fig. 1 in the first positive sweep, before the potential had been swept into the anodic region. There is also a sharp current increase in the potential range between −0.78 V(SCE) and −0.8 V(SCE). The equilibrium potential for the H_2/H_2O reaction at pH 7.56 is −0.691 V(SCE). The cathodic reaction negative of this potential therefore involves some H_2 evolution. The cathodic reaction positive of this potential cannot involve hydrogen. In the absence of dissolved Cu ions, the cathodic current can be only the reduction of dissolved oxygen.

Fig. 1 also shows that there is no clear sign of passivation in the anodic region and beyond the corrosion potential (−0.05 V(SCE)), the current increases continuously until the reversal of the direction of the sweep. There is in fact a small inflection at about +0.02 V(SCE) on the positive sweep. At potentials higher than this on the positive sweep, pitting corrosion occurs, as suggested by the sharper increase in the anodic current. It also shows that the current density of the negative sweep is greater than that of the positive sweep in the anodic region. This is due to the continuous growth of pits on copper when exposed in uninhibited tap water: pit growth raises the active area of the electrode giving higher current density on the negative sweep.

3.2. Role of Fernox® Alphi 11

Fig. 2 presents the polarisation curves for copper in Cambridge tap water in the absence and in the presence of 25% (by volume) Fernox® at 25 ± 0.1 °C. It shows that both anodic and cathodic reactions are heavily suppressed by the presence of Fernox®, with the anodic reaction more heavily suppressed, by up to 4 orders of magnitude. The rise in anodic current with the increase in potential is