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Effect of hydrodynamic conditions on copper pitting corrosion inhibition in hydrocarbonate–chloride solutions by benzotriazole

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Abstract

It has been found that in hydrocarbonate–chloride solutions (pH = 8.4) benzotriazole inhibits copper pitting corrosion. Comparative results obtained on stationary and rotating disc electrode have shown that rotation stabilizes the metal / electrolyte systems. Under drastic hydrodynamic conditions, the benzotriazole concentration required for full suppression of copper pitting corrosion was reduced 10-fold on a rotating disc.

Keywords: *copper, pit corrosion, inhibition, benzotriazole.*

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Introduction

The inhibitive effect of azoles against general copper corrosion in neutral and acid media is widely covered in modern literature. Much less attention is paid to the analysis of their protective properties toward copper pitting corrosion (PC) that occurs in alkaline and weakly alkaline mediums in the presence of organic and inorganic activators.

In view of this, this study made an attempt to estimate the effect of benzotriazole (BTAH) on copper PC in hydrocarbonate–chloride solutions and to determine its efficiency depending on hydrodynamic conditions.

Experimental

Material and surface process

The experiments were carried out in a cell specially designed for this purpose, with a stationary disc electrode (SDE) and rotating disc electrode (RDE) (ω = 200 r.p.m.) made of copper (Cu 99.99%), at 0.1 M $NaHCO_3$ + 0.01 M NaCl background electrolyte (pH = 8.4) containing 10^{-6}–10^{-2} M BTAH. All solutions were prepared from analytical reagent grade chemicals using distilled water.

Electrochemical studies

A conventional electrolytic cell with three electrodes was used for electrochemical studies in naturally aerated solutions. A platinum gauze served as the counter electrode. The electrode potential was measured with reference to a silver/silver chloride electrode and

then recalculated *versus* normal hydrogen electrode (NHE). The experiments were performed under potentiodynamic control on a P-5827M potentiostat with a potential scan rate of 4 mV/s and with cathodic reductive pre-treatment (E = –1.000 V (NHE), τ = 10 min). The voltammetric pitting formation potentials thus obtained were checked by additional chronoamperometric studies in the region of PC potentials.

Microscopic observation

The copper electrode surface was analyzed in various solutions before and after experiments by the optical method (MBC-2 (×7) and MIM-7 (×100, ×500) microscopes).

Results and discussion

The results obtained show that a copper SDE undergoes PC in hydrocarbonate–chloride background electrolyte. This was supported by chronoamperometric and voltammetric data (Figure 1) and confirmed by microscopic observation results. According to the latter, copper surface was covered by shallow small pits after anodic polarization measurements.

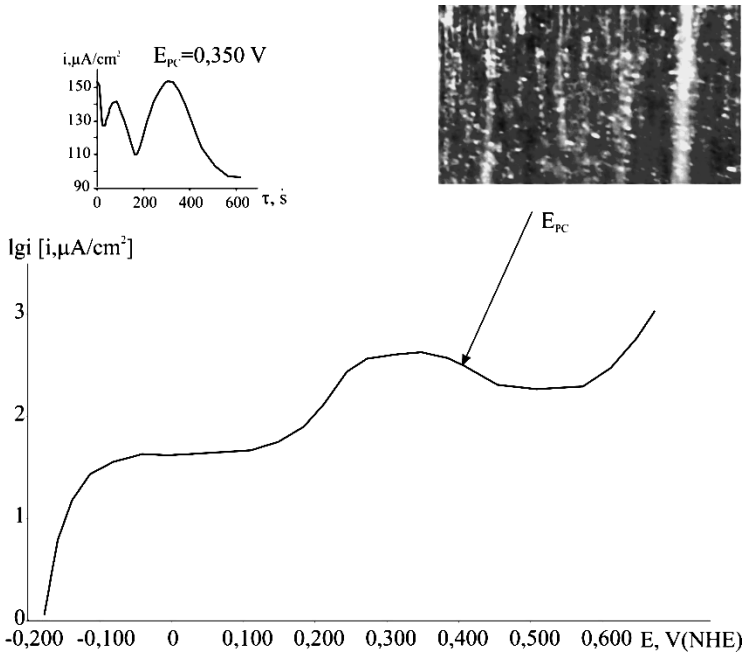

Figure 1. A voltammogram and chronoamperogram of Cu (SDE) in 0.1 M $NaHCO_3$ + 0.01 M NaCl and a micrograph of metal surface local destruction obtained using a MIM-7 microscope (×500).

The following values directly related to the pit formation process were used for full characterization of the copper PC process: the PC potential (E_{PC} = 0.350 V) and the PC induction period (τ_{ind} = 10 s) [1, 2].

Transition to a copper RDE (Figure 2) did not prevent electrode local attack. After an electrochemical experiment, copper surface was covered by a gray film with many small pits underneath. The E_{PC} and τ_{ind} values were 0.300 V and 50 s, respectively.

Addition of $1 \cdot 10^{-6}$ M BTAH to the system with a stationary electrode (Figure 3) did not affect E_{PC}, but the induction period abruptly increased to 100 s. However, in this case the pattern of copper surface destruction differed: small shallow pits changed to shallow but more uniform conglomerates.

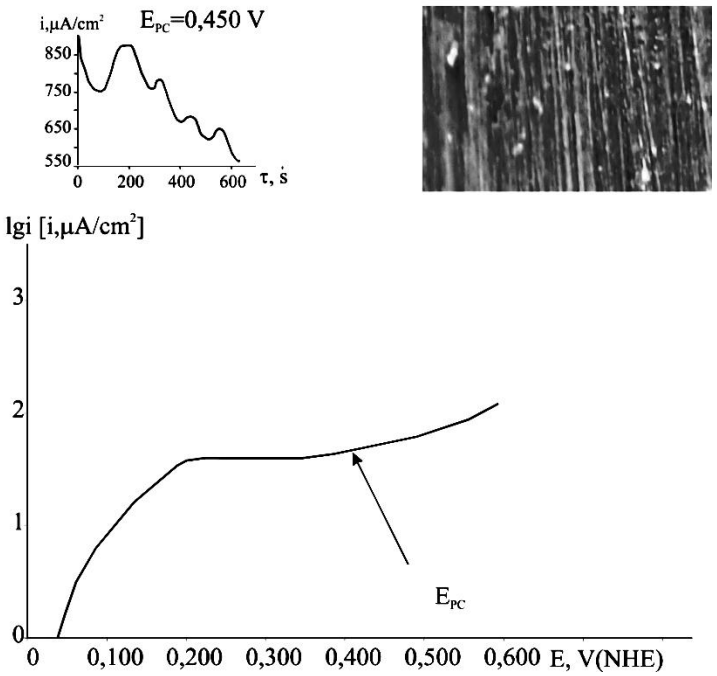

Figure 2. A voltammogram and chronoamperogram of Cu (RDE) in 0.1 M $NaHCO_3$ + 0.01 M NaCl and a micrograph of metal surface local destruction obtained using a MIM-7 microscope (×500).

The efficiency of BTAH as an inhibitor of local corrosion was determined using coefficient *Z* [1] which, in the system being studied (where the PC rate characteristic was determined as $1/\tau_{ind}$), was determined as [2]:

$$Z = (1 - \tau_{ind,0}/\tau_{ind}) \cdot 100\%,$$

where $1/\tau_{ind,0}$ and $1/\tau_{ind}$ are the PC rates in the background solution and in the solution with the inhibitor, respectively. The value obtained was ~90%.

A further inhibitor concentration increase up to $C_{BTAH} = 1 \cdot 10^{-5}$ M totally protected copper against PC, as confirmed by the results of voltammetric and chronoamperometric studies (Figure 4) and microscopic observation data.

It is interesting to note that the smallest inhibitor concentration, $C_{BTAH} = 1 \cdot 10^{-6}$ M, in the system with copper RDE (ω = 200 r.p.m.) totally suppressed PC on copper surface (Figure 5). It was also confirmed by the results of microscopic observations and the shape of the voltammogram and chronoamperogram, *i.e.*, full protection of RDE took place at a BTAH concentration that was 10 times smaller than in the case of SDE. It may be due to the fact that rotation stabilized the system and thus copper achieved a stable passive state at a smaller inhibitor concentration.

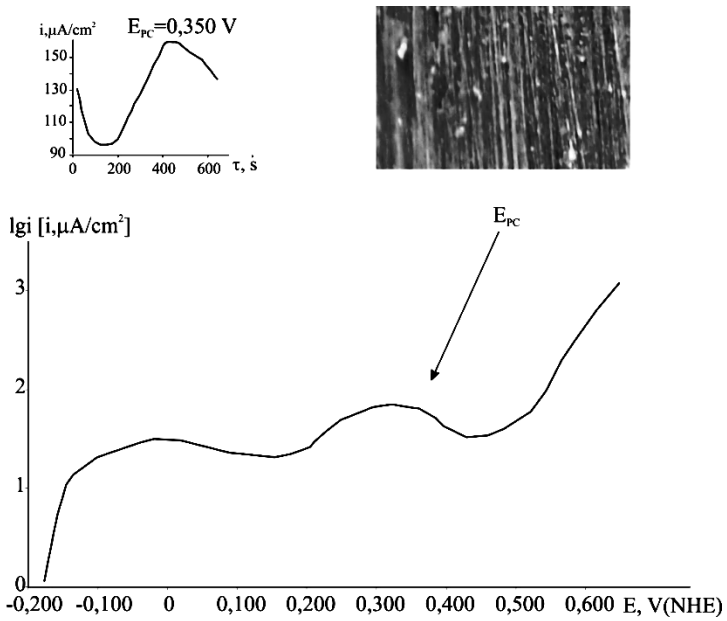

Figure 3. A voltammogram and chronoamperogram of Cu (SDE) in 0.1 M $NaHCO_3$ + 0.01 M NaCl + $1 \cdot 10^{-6}$ M BTAH and a micrograph of metal surface local destruction obtained using a MIM-7 microscope (×500).

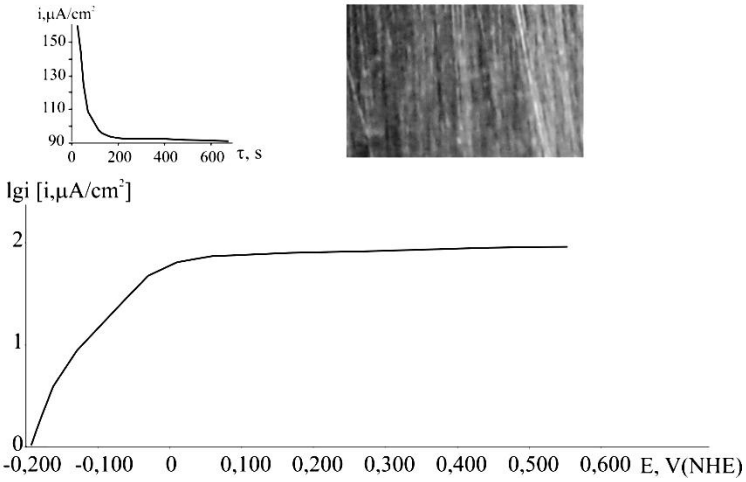

Figure 4. A voltammogram and chronoamperogram of Cu (SDE) in 0.1 M $NaHCO_3$ + 0.01 M NaCl+$1 \cdot 10^{-5}$ M BTAH and a micrograph of metal surface local destruction obtained using a MIM-7 microscope (×500).

As shown previously [3], copper PC in background solution (0.1 M $NaHCO_3$ + 0.01 M NaCl) occurs by an adsorption–penetration mechanism (with participation of an insoluble CuCl particle as an activator), corresponding to T. Okada's theory [4].

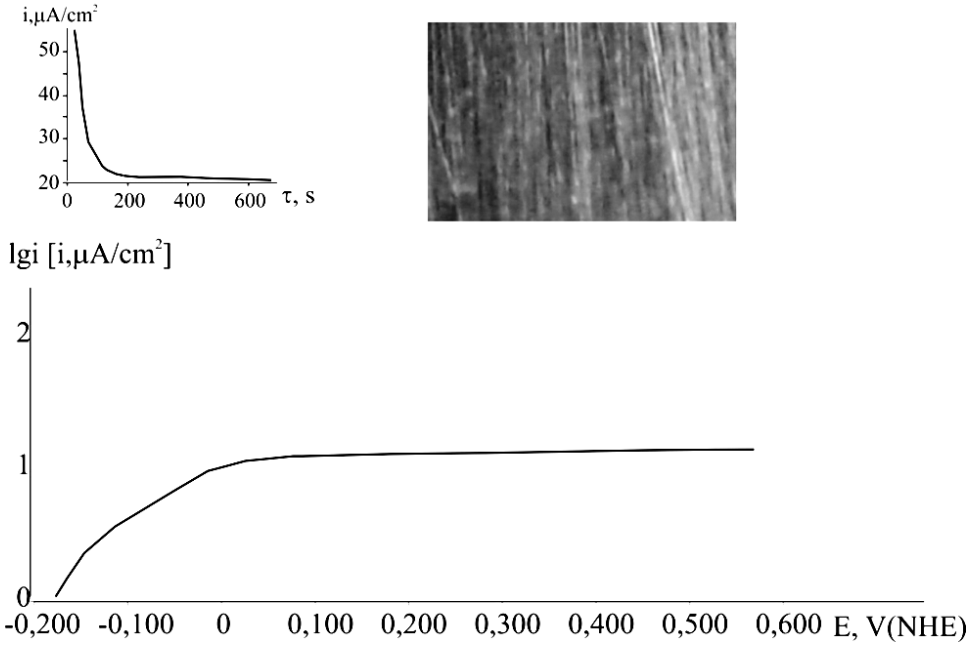

Figure 5. A voltammogram and chronoamperogram of Cu (RDE) in 0.1 M $NaHCO_3$ + 0.01 M NaCl+$1\cdot10^{-6}$ M BTAH and a micrograph of metal surface local destruction obtained using a MIM-7 microscope (×500).

The protective action of BTAH is due to its high adsorption ability and formation of a dense insoluble copper benzotriazolate film on the metal surface [5]. On the one hand, this film [Cu(I)–BTA] is a physical barrier to corrosive ions, and on the other hand, it inhibits copper anodic dissolution sites. It is known that in alkaline solutions, BTAH is predominantly in the anionic form and can exist as mono- and poly-adsorption $(Cu–BTA)_{ads}$ layers on copper surface at the free corrosion potential [6].

$$Cu + BTA^- \rightarrow (Cu–BTA)_{ads} \quad (1)$$

$$nCu^+ + nBTA^- \rightarrow (CuBTA)_n \quad (2)$$

$$(Cu–BTA)_{ads} + (CuBTA)_n \rightarrow [(Cu–BTA)–(CuBTA)_n] \quad (3)$$

The protective film can be additionally stabilized by incorporation of halide ions (Figure 6), moreover the film thickness increases in this case [7].

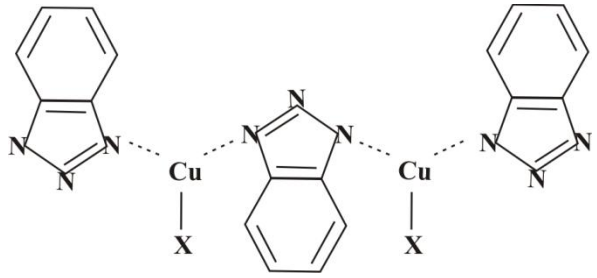

Figure 6. Structure of a complex polymer, where X is a halide anion.

In alkaline medium, the copper surface contains oxide–hydroxide compounds (the fraction of which increases with temperature), and BTA^- adsorption on oxide-coated metal surface is preferred and occurs sufficiently fast [8], probably due to the ability of oxygen atoms in the oxide (Cu–O–Cu) to form hydrogen bonds with hydrogen atoms of the benzotriazole anion (C–H). The increase in inhibitor efficiency with temperature is probably due to an increase in the fraction of oxygen compounds on the metal surface and an increase in the polymerization degree of the protective film [9], indicating the increase in the protective complex stability.

Thus, experiments demonstrate that in background electrolytes BTAH forms surface copper complexes [(Cu–BTA)–$(CuBTA)_n$], decreasing its susceptibility to nucleophilic attack by Cl^- ions and making it possible to screen the metal surface.

The effect that electrode rotation causes stabilization of copper passive state is due to inflow of OH^- ions and O_2, as well as malachite formation (in the absence of BTAH) and increase in inhibitor protection due to BTAH inflow.

This fact showed that rotation stabilized the system, increased the thickness of the passive oxide–hydroxide layer and reduced the concentration of the CuCl activator in the reaction zone because of friction between the RDE and the corrosive medium. In view of this, the BTAH concentration necessary for full PC suppression decreased 10-fold in comparison with SDE.

The difference between the BTAH concentrations required for full PC suppression on a copper SDE and RDE was probably due to the fact that a protective polymeric layer $[Cu(I)–BTA]_n$ was formed more readily on an RDE because of a significantly higher O_2 concentration [10, 11] in the reaction zone compared to SDE.

Conclusions

The results obtained show that BTAH inhibits copper PC in the hydrocarbonate–chloride solution studied. BTAH prevents the surface complex [(Cu–BTAN)–$(CuBTA)_n$] decomposition and decreases the sensitivity to nucleophilic attack by Cl^- ions. This effect can be due to the low solubility and high stability of the complex that screens the metal surface and inhibits the process of its dissolution. Simultaneously it was found that full suppression of copper PC caused by Cl^- ions takes place at $C_{BTAH} = 1 \cdot 10^{-5}$ M in case of the stationary electrode and at $C_{BTAH} = 1 \cdot 10^{-6}$ M in case of the rotating disc copper electrode.

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