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Influence of the N-3 alkyl chain length on improving inhibition properties of imidazolium-based ionic liquids on copper corrosion

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ABSTRACT

1-butyl-3-ethylimidazolium bromide ionic liquid, [beim]Br, was studied experimentally and theoretically as a potential inhibitor of copper corrosion in acidic media (pH = 3) by *dc* polarization, quartz crystal microbalance (QCM), scanning electron microscopy (SEM) and density functional theory (DFT). This ionic liquid is selected to study an effect of the alkyl chain length at the position N-3, since so far only ionic liquids with different alkyl substituents at the position N-1 are investigated. Improved inhibitory properties of the investigated ionic liquid against corrosion of copper in acidic solution at the given conditions are confirmed comparing to corresponding 1-butyl-3-methylimidazolium bromide ionic liquid. It is found that [beim]Br acts as a cathodic corrosion inhibitor, whereby its effectiveness depends on the applied concentration. The inhibitory effect of the studied ionic liquid (IL) was achieved through quick and spontaneous adsorption on the copper surface following the Langmuir's adsorption isotherm. Results obtained by SEM showed that copper protection is achieved through the less damaged copper surface in the presence of inhibitor. Applying DFT calculations, it is found that interactions with the metal surface occur by donating electron from the Br^- anion to the copper. Based on the obtained Fukui functions influence of the inductive effect of ethyl/methyl group on the inhibitory activity is also discussed.

1. Introduction

A variety of the methods were developed worldwide to overcome one of the most serious technological problems such as metal corrosion, which results in huge economic losses, especially in the aerospace, automotive and petroleum industries. One of the possibilities to protect metal against corrosion is to introduce corrosion inhibitor. Copper and its alloys in modern industries are extensively used in various chemical processes and equipments. Despite excellent corrosive resistance, copper corrosion can take place at lower pH especially in the presence of oxygen which is essential for its dissolution [1,2].

The corrosion processes of copper in aerated sulfuric acid involve the cathodic reduction of oxygen and anodic dissolution of copper as described by the following two continuous steps:

$$Cu \rightarrow Cu^{+}{}_{ads} + e^{-} \tag{1}$$

$$Cu^{+}{}_{ads} \rightarrow Cu^{2+} + e^{-} \tag{2}$$

where $Cu^{+}{}_{ads}$ is an adsorbed species at the copper surface and does not diffuse into the bulk solution [3–6].

Reduction of oxygen can be expressed either by a direct $4e^-$ transfer as shown by the equation:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{3}$$

or by two consecutive $2e^-$ steps involving an oxygen reduction to hydrogen peroxide first:

$$O_2 + 2H^+ + 2e^- \rightarrow 2H_2O_2 \tag{4}$$

followed by a further reduction [7,8]:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{5}$$

The transfer of oxygen from the bulk solution to the Cu-solution interface will strongly affect the reaction rate of oxygen reduction despite how oxygen reduction takes place, either in $4e^-$ transfer or two consecutive $2e^-$ transfer steps [7].

$Cu^{+}{}_{ads}$ is a very important for copper corrosion process since copper (I) ion can form film on the copper surface, such as Cu_2O layer which represents an additional barrier for copper corrosion. In acidic solution Cu_2O cannot exist [4], which leads to a significant increase of copper corrosion.

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Several compounds have been investigated as potential copper corrosion inhibitors and in the most cases these molecules are organic heterocyclic compounds with nitrogen, sulfur or oxygen as the hetero atom [9–12]. These organic molecules can reduce corrosivity of the metal due to electrostatic or covalent bonding between the adsorbed molecules and the metal surface [13–16]. Unfortunately, most of them achieve good inhibitory efficiency only in neutral media while the number of molecules with good inhibition properties in the acidic medium are rather limited [17–26].

Recently, the attention of the scientific communities has been paid to growing environmental problems and pollution. Accordingly, toxic inhibitors [9,26] that were widely used in many industrial processes have to be replaced with new environmentally friendly inhibitors. The research in the field of green corrosion inhibitors has been addressed towards the cheap and effective molecules with negligible or zero environmental impact [19,21,24,27–30].

In the past two decades a new class of the chemistries, namely ionic liquids (IL), have been considered as the green chemicals, due to their biodegradability, non-toxicity, tunable and designable physicochemical properties, such as good electrical conductivity, thermal stability, excellent solvent properties and a relatively wide electrochemical window [31–34]. Usually, ionic liquids have cations with nitrogen, sulfur or phosphorus as the heteroatoms, and an amphiphilic group with a long chain, hydrophobic tail and a hydrophilic polar head, which make them potentially good corrosion inhibitors. Imidazolium based ionic liquids are reported to show corrosion inhibitor property on the steel [35], copper [36,37] and aluminum [38].

In this work the possibility of copper protection against corrosion using 1-butyl-3-ethylimidazolium bromide ionic liquid as potential new inhibitor in acidic 0.1 mol·dm^{-3} Na_2SO_4 solution was studied. Bromide based ionic liquids are, in the most cases, room temperature ionic liquids. It was confirmed that selected [beim]Br with the ethyl group in the position N-3 of the imidazolium cation shows lower viscosity and higher conductivity compared to corresponding methyl substituted ionic liquid [39]. Also, these ionic liquids comparing to corresponding chloride based ILs can be prepared easily applying one-step synthesis. Obtained ionic liquids with bromide anion show weaker ion-dipole interactions and they are electrochemically and hydrolytically stable in the acidic solutions. In the same time, the solubility of many substances in bromide based ionic liquids is high, allowing application of these liquids in many technological areas. Thus, it was interesting to investigate inhibitor activity of [beim]Br ionic liquid in the acidic medium for copper protection against corrosion process.

In acidic 0.1 mol·dm^{-3} Na_2SO_4 solution, the sulfate and bromide ions can be absorbed on the metal surface and form an interconnecting bridge between the metal atoms and imidazole cations [40–42]. Due to a high concentration of the sulphate ions in the solution, their pronounced absorption can be expected. However, poor solubility of CuBr in water and also in H_2SO_4 leaves possibility of film formation on a copper surface with both anions [43], since Cu^+ as a soft acid highly attracts softer Br^- base in comparison to harder SO_4^{2-} anion.

$$Cu^+{}_{ads} + SO_4{}^{2-} \rightarrow CuSO_4{}^-{}_{ads} \tag{6}$$

$$Cu^+{}_{ads} + Br^- \rightarrow CuBr_{ads} \tag{7}$$

As a result, between the Cu^+ and SO_4^{2-} ions occur Coulomb interactions, while the bond between Cu^+ and Br^- has a higher content of covalent character. The adsorbed anions can achieve interactions with IL cations through free electron pairs in the electron-deficient π-orbital delocalized between the two N atoms of the imidazolium cation (see Fig. 1) or forming hydrogen bonds, whereas in the case of $CuSO_4{}^-{}_{ads}$ occur Coulomb interactions. In this way, cations from the ionic liquid form a protective film layer which practically make impossible further oxidation of Cu^+ via the reaction (2). Inhibitory efficiency of imidazolium ions depends on the strength of their interactions with the adsorbed anions, and if the anions adsorbed on the metal surface form strong hydrogen bonds with imidazolium cations, IL cation inhibitory activity will be greater [44].

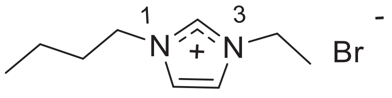

Fig. 1. Chemical structure of [beim]Br.

On the other hand, considerable research has shown that inhibitory activity strongly depends on the N-substituted alkyl chain length of the cation. In general, the imidazolium cation with a longer alkyl chain should demonstrate better inhibitory properties, because the metal surface would be better covered and protected from contact with the corrosive environment [45–48]. However, several studies have shown that simply increasing the length of the alkyl chain on one N atom does not necessarily lead to a consequent increase in inhibitory activity [40,44]. For example, Murulana et al. [49] have been experimentally and applying computer simulations shown that an imidazolium based cations with a methyl group at the position C-2 and a shorter alkyl chains show better inhibition effect comparing to ILs with a H atom at the position C-2 and longer side chains. Electron push and pull inductive effect of substituents on the imidazolium cation have great influence on the strength of interaction with the adsorbed anions and its inhibitory activity, but the effect is much less studied in relation to the effect of the alkyl chain length. Also, the effect of increasing the alkyl chain length was observed so far only in the 1-alkyl-3-methylimdazolium ionic liquids [40,44–49]. As our previous research shows [39], increasing the alkyl chain length at the N-3 position for only one C atom significantly changes the physical and chemical properties of designed ionic liquids, it is interesting and justified to examine this effect on the inhibitory activity of [beim]Br. Thus, the aim of this work is experimentally and theoretical study and the possible application of 1-butyl-3-ethylimidazolium bromide as potential inhibitor against copper corrosion in acidic 0.1 mol·dm^{-3} Na_2SO_4 solution.

2. Experimental

The inhibitor property of 1-butyl-3-ethylimidazolium bromide (Fig. 1) was investigated against copper corrosion in 0.1 mol·dm^{-3} Na_2SO_4 solution at pH = 3. The investigated ionic liquid was synthesized as described in our previous paper [39].

All necessary solutions were prepared from the stock inhibitor solution ($c = 0.05$ mol·dm^{-3}) to obtain diluted working inhibitor solutions with desired concentrations in the range from ($1 \cdot 10^{-3}$ to $1 \cdot 10^{-5}$) mol·dm^{-3} in 0.1 mol·dm^{-3} Na_2SO_4. The pH = 3 was adjusted using diluted sulfuric acid. All experiments were done in the open atmosphere and at the room temperature.

For the electrochemical measurements three-electrode cell was used, with copper as the working electrode, the saturated calomel electrode (SCE) as the reference electrode and the platinum as the counter electrode. The working electrode was constructed from copper rods of high purity (99.99% Cu) with an exposed area of 0.7 cm^2 embedded in an epoxy resin. Before each measurement, the electrode was wet-polished applying SiC papers (grit sizes of 800 and 1200), rinsed with acetone and double distilled water, and then immersed into investigated solution. A PC controlled VoltaLab PGZ 301 was applied for the electrochemical measurements. The potential was scanned between open circle potential (OCP) and 300 mV in the cathodic and OCP and 300 mV in the anodic directions at the scan rate of 10 mV·min^{-1}. The polarization measurements were performed in the blank solution (0.1 mol·dm^{-3} Na_2SO_4) at five different inhibitor concentrations in the range from ($1 \cdot 10^{-3}$ to $1 \cdot 10^{-5}$) mol·dm^{-3}.

An electrochemical quartz crystal nanobalance EQCN-700 Elchema with a 10 MHz AT-cut quartz resonator was used for QCM study. For this purpose freshly galvanostatically deposited copper layer (onto