A Review on Experimental Studies of Corrosion Inhibitor Adsorption on Copper Surface

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Abstract. The progresses of understanding of the corrosion inhibitor adsorption on copper surface from extensive experimental studies were reviewed here. In this respect the kinetic and equilibrium studies involve organic compounds, non-organic compounds and their derivatives on copper surface from the solution. Kinetics and equilibrium adsorption of corrosion inhibitors at the copper surface depend on the nature of compounds and the nature of the copper surface. Studies have been reported on the influence of corrosion inhibitors structure, concentration, media as well as temperature that inhibitor was used in on inhibition efficiency. Moreover, inhibition action mechanisms were also studied. Adsorption models of compounds on copper surface are built to predict of possibilities of newly synthesized compounds to act as corrosion inhibitors by combining theory and practical investigations of substances with similar structure.

1. INTRODUCTION

High frequency and high speed transmission of electric signal for copper is owing to its high strength, good toughness and high density. However, the surface oxidation and discoloration problem of copper cannot be effectively prevented during its soft state product storage period, even it accelerates the corrosion of products [1]. Using a suitable inhibitor in solution is one of the effective methods for protection against corrosion [2]. Therefore, corrosion of copper and its inhibition in air have attracted attention from a number of investigators [3].

Organic compounds containing polar groups including nitrogen, oxygen, and sulfur, and heterocyclic compounds with conjugated double bonds and polar functional groups as corrosion inhibitors have been reported in inhibit copper corrosion field. The inhibiting action of these organic compounds usually attributes to their interactions with the copper surface via their adsorption [4]. Polar functional groups are regarded as the reaction center that stabilizes the adsorption process [5]. Many heterocyclic compounds containing a mercapto group also have been used as copper corrosion inhibitors for different industrial applications [5]. Based on the results more and more compounds containing numerous heteroatoms and functional groups are developed synthesized since it is noticed they are responsible for good properties regarding corrosion inhibition because they enable chemisorption. In addition, molecular weight is larger due to its beneficial effect on physical adsorption. There are attempts to combine theory and practical experience from investigations of some substances having similar structure in order to find models those would enable prediction of possibilities of newly synthesized compounds to act as corrosion inhibitors.

2. INORGANIC COPPER CORROSION INHIBITORS
The use of inorganic inhibitors as an alternative to organic compounds is based on the possibility of degradation of organic compounds with time and temperature. Three different inorganic inhibitors are investigated: chromate \( \text{CrO}_4^{2-} \), molybdate \( \text{MoO}_4^{2-} \) and tetraborate \( \text{B}_4\text{O}_7^{2-} \) in concentration of 0.033M in solution containing 850g/l \( \text{LiBr} \) and has pH 6.9. Chromate is generally accepted as efficient corrosion inhibitor that can passivate metals by forming a monoatomic or polyatomic oxide film at the electrode surface, but it is also known that it can promote corrosion acting as a cathodic reactive. Possible process for chromates is the reduction or decomposition of the inhibitor on the copper surface, followed by precipitation. Chromates are reduced to \( \text{Cr(III)} \) hydroxide or oxyhydroxide on the copper surface that results in corrosion current density decrease. However, the main disadvantage is the toxicity of chromium (VI) oxidation state. This is the reason for search for less toxic alternatives. The logical alternative can be analogue of hexavalent chromium the molybdate species that is an environmentally friendly inhibitor. Nevertheless, molybdate and tetraborate showed no significant inhibition. The corrosion resistance is not improved because the film formation is not favorited in the electrolyte containing very aggressive anions such as bromides. Inhibin efficiency increases in the following order: molybdate (1.56%) < tetraborate (51.0%) < chromate (78.6%). [6]

3. THE ORGANIC COPPER CORROSION INHIBITORS

Azoles are organic compounds containing nitrogen atoms with free electron pairs that are potential sites for bonding with copper and that enable inhibiting action. In addition, there is a possibility of introduction of other heteroatoms and groups in molecules of these compounds so there is a wide range of derivatives that exhibit good inhibition characteristics.

El-Sayed M.Sherif[7] investigated the influence of 2-amino-5-ethylthio-1,3,4-thiadiazole (AETD) on copper corrosion in aerated \( \text{HCl} \) solution as well as the influence of 2-amino-5-ethylthio-1,3,4-thiadiazole (AETD) \[8\], 2-amino-5-ethyl-1,3,4-thiadiazole (AETDA) \[9\] and 5-(phenyl)-4H-1,2,4-triazole-3-thiole (PTAT) \[10\] in \( \text{NaCl} \) solution. It is expected that these compounds show high inhibition efficiency since they are heterocyclic compounds containing more donor atoms, besides that they are non-toxic and cheap. AETD, AETDA and PTAT proved to be good mixed type copper corrosion inhibitors and the inhibition efficiency increased with concentration \[8-10\], exposure period \[7,9,10\] and oxygen content \[9,10\]. AETD, AETDA and PTAT molecules strongly adsorb on copper forming complexes with copper ions and prevent forming of Cu chloride and oxychloride complexes. In his work Gy.Vastag \[11\] investigated thiazole derivatives: 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (BDT); 5-(‘-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (IPBDT); 5-(‘-thenylidene)-2,4-dioxotetrahydro-1,3-thiazole (TD) and 5-(‘,‘-dimethoxybenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (MBDT) as copper corrosion inhibitors in 0.1M sodium sulphate solution, pH=2.94. The best protection is achieved by IPBDT as expected based on the structural analyses i.e. the presence of isopropyl group. It is shown that the investigated thiazole derivatives (especially IPBDT) have potential to replace toxic inhibitors such as triazoles) that are used in closed systems.

The influence of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) on the corrosion resistance of Cu in 0.1M \( \text{HNO}_3 \) is also studied[12]. The action effect of PMT is compared with the influence action of other organic compounds of this type the same family such as 1,2,3,4-tetrazole (TTZ), 5-amino-1,2,3,4-tetrazole (AT) and 1-phenyl-1,2,3,4-tetrazole (PT). They behave as mixed type inhibitors. The mechanism of action is chemisorption on the copper surface that follows Langmuir isotherm. Inhibition efficiency increases in the following order: TTZ<ZT<PT<PMT. Inhibition efficiency increases with increasing concentration and decreases with increasing temperature from 25 to 50°C. It also depends on the time of immersion. The inhibition efficiency increases with time and reaches a maximum value after 48h, and afterwards decreases. [13]

E.Sz cs[14] in his research investigated the inhibitor 5-mercapto-1phenyl-tetrazole (5-MPhTT) in 1mM \( \text{H}_2\text{SO}_4 \) solution. The results show reveal that the anodic current density and mass loss are two times twice less lower in the presence of 5-MPhTT. The investigated concentration is 0.5mM. Measurements are conducted in three intervals where the first is in blank solution, the second in the solution containing inhibitor while the third is again in the blank solution. The mass change is
observed in the first interval while in the second and third didn’t change. The inhibition efficiencies for the second and the third interval are 99.93% and 99.8% respectively. It is concluded that inhibitor forms a protective film chemisorbed on the surface. The structure of the protective film is further investigated by X.R.Ye [15] and the following conclusion is reached. The film contains a layer of inert, insoluble and long-lasting polymeric Cu(I) complex. These films are probably built over Cu2O layer through surface reaction of PMT and Cu(I) ions. The copper surface treated with PMTA can be described as composite structure Cu-PMTA/Cu2O/Cu. Each molecule of PMTA bridges two or more Cu(I) ions via N and S atoms. The hydrophobic backbone on PMTA ligand in Cu-PMTA prevents contact between hydrated corrosive ions and the copper surface and thus inhibit substrate corrosion. The optimum conditions for PMTA treatment are: 0.005mol/l PMTA solution, pH=3, temperature 20-50℃ and 30min of treatment time. It is noticed that the films of coordination compounds formed by reaction of PMTA with copper surface are more efficient in corrosion inhibition (under the influence of atmosphere, sulphide and chloride media) than those formed with TTA (tetrazole), BTA (benzotriazole), HBTA (hydroxybenzotriazole), MBT (2-mercaptobenzothiazole), MBI (2- mercaptobenzoimidazole), 2-AP (2-aminopyrimidine), IBM (imidazole) and chromates. Adsorption models of compounds on copper surface is built to predict of possibilities of newly synthesized compounds to act as corrosion inhibitors by combining theory and practical investigations of substances with similar structure.

J.C.Marconato [16] investigated the effect of 2-mercaptobenzothiazole in the ethanol solution. The solution contains 10-2M HClO4 in ethanol. When MBT is added the inhibition of anodic copper dissolution and cathodic reaction of hydrogen evolution is observed. The concentration of MBT of 0.001M lead to reduction of current density 4 times that is associated with formation of complex between metal ions and inhibitor. MBT is oxidized to 2,2’-dithiobis(benzothiazole) and/or 2,2’-thiobis(benzothiazole) and forms a complex involving its ionized thiol form and Cu(II) ions. The characteristics of adsorption and the influence of MBT and tetrazole (TTA) on the growth of oxide film on copper in 0.1M NaOH are also investigated [17]. The inhibition efficiency is strongly dependent on the structure and chemical properties of the species formed under the specific experimental conditions. MBT contains three atoms available for coordination i.e. N and S atoms in the ring and S atom of the thiocarbonyl group. The S atom of the thiocarbonyl group (C=S) that is ionized in alkaline medium can react with Cu and form thick polymeric film. The surface coverage is 0.89 which is the highest value recorded among all the investigated compounds. TTA does not act as a copper corrosion inhibitor in 0.1M NaOH.

4. CONCLUSIONS
Corrosion inhibitors effectively eliminate the undesirable destructive effect and prevent metal dissolution due to adsorption of the inhibitor molecules on the copper surface and blocking its active sites. The inhibition efficiencies obtained by weight-loss, dynamic polarization, and theoretical calculations are in reasonably good agreement with each other. The inhibition of the compound inhibitor is better due to their synergistic interaction than single system. Media that inhibitor is used in is very important for selection. The presence of aggressive ions and pH are among the most important parameters. Action mechanisms are different. Inorganic compounds act through oxide films formation. Organic compounds mostly act via adsorption on copper surface and complex formation. Higher inhibitor concentration and longer exposure of copper in inhibitor solution lead to inhibition efficiency increase.

References
[1] Colley A L, Macpherson J V, Unwin P R. Effect of high rates of mass transport on oxygen reduction at copper electrodes: Implications for aluminium corrosion[J]. Electrochemistry Communications, 2008, 10(9): 1334-1336.
[2] Harvey T G, Hardin S G, Hughes A E, et al. The effect of inhibitor structure on the corrosion of AA2024 and AA7075[J]. Corrosion Science, 2011, 53(6): 2184-2190.
[3] Cao Z, Bian J, Xue R, et al. Electrochemical corrosion behavior of Cu-40Ni-20Cr alloys with different grain sizes in solutions containing chloride ions[J]. Transactions of Nonferrous Metals Society of China, 2007, 17(6): 1236-1241.

[4] Zhu L, Lou B, Yang K, et al. Effects of ionizable organic compounds in different species on the sorption of p-nitroaniline to sediment[J]. Water Research, 2005, 39(2–3): 281-288.

[5] Brunel S, Brumas V, Fiallo M M L. Potentiometric and spectroscopic studies on the solution molecular structures of copper(II)-[S]-2-[N-(2′-hydroxybenzyl)aminomethyl]pyrrolidine complexes, potential non-steroidal anti-inflammatory agents (NSAIDs)[J]. Inorganica Chimica Acta, 2009, 362(11): 4043-4052.

[6] özcan M, Dehri İ, Erbil M. Organic sulphur-containing compounds as corrosion inhibitors for mild steel in acidic media: correlation between inhibition efficiency and chemical structure[J]. Applied Surface Science, 2004, 236(1–4): 155-164.

[7] Gece G. The use of quantum chemical methods in corrosion inhibitor studies[J]. Corrosion Science, 2008, 50(11): 2981-2992.

[8] Larabi L, Benali O, Mekelleche S M, et al. 2-Mercapto-1-methylimidazole as corrosion inhibitor for copper in hydrochloric acid[J]. Applied Surface Science, 2006, 253(3): 1371-1378.

[9] Sherif E M, Erasmus R M, Comins J D. Corrosion of copper in aerated acidic pickling solutions and its inhibition by 3-amino-1,2,4-triazole-5-thiol[J]. Journal of Colloid and Interface Science, 2007, 306(1): 96-104.

[10] Sherif E M, Park S. Inhibition of copper corrosion in acidic pickling solutions by N-phenyl-1,4-phenylenediamine[J]. Electrochimica Acta, 2006, 51(22): 4665-4673.

[11] Fallavena T, Antonow M, Gonçalves R S. Caffeine as non-toxic corrosion inhibitor for copper in aqueous solutions of potassium nitrate[J]. Applied Surface Science, 2006, 253(2): 566-571.

[12] Müller B, Schubert M. Corrosion inhibition of copper and brass pigments in aqueous alkaline media by copolymers[J]. Progress in Organic Coatings, 1999, 37(3–4): 193-197.

[13] Norkus E, Vaiciunien J, Vuorinen T, et al. Cu(II) complex formation with xylitol in alkaline solutions[J]. Carbohydrate Research, 2004, 339(3): 599-605.

[14] Fujita W, Awaga K, Yokoyama T. Controllable magnetic properties of layered copper hydroxides, Cu2(OH)3X (X=carboxylates)[J]. Applied Clay Science, 1999, 15(1–2): 281-303.

[15] Yang F, Boero M, Rabu P, et al. First principles investigation of the atomic structure and magnetic properties of copper hydroxide acetate[J]. Comptes Rendus Chimie, 2012, 15(2–3): 202-208.

[16] Norkus E, Vaškelis A, Zakaitė I. Influence of ionic strength and OH−ion concentration on the Cu(II) complex formation with EDTA in alkaline solutions[J]. Talanta, 1996, 43(3): 465-470.

[17] Mishra A, Loo Y, Deng R, et al. Ultrasmall natural peptides self-assemble to strong temperature-resistant helical fibers in scaffolds suitable for tissue engineering[J]. Nano Today, 2011, 6(3): 232-239.