Potassium sorbate—A new aqueous copper corrosion inhibitor
Electrochemical and spectroscopic studies

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Abstract

This work presents the novel nature of 2,4-hexadienoic acid potassium salt (potassium sorbate (KCH₃CH=CHCH=CHCO₂)) as an effective copper aqueous corrosion inhibitor. The influence of pH and potassium sorbate concentration on copper corrosion in aerated sulfate and chloride solutions is reported. Degree of copper protection was found to increase with an increase in potassium sorbate concentration; an optimum concentration of this inhibitor in sulfate solutions was found to be 10 g/L. Copper is highly resistant to corrosion attacks by chloride ions in the presence of potassium sorbate. X-ray photoelectron spectroscopy (XPS) studies suggest that copper protection is achieved via the formation of a mixed layer of cuprous oxide, cupric hydroxide and copper(II)-sorbate at the metal surface.

Keywords: Copper; Corrosion; Inhibitor; Potassium sorbate

1. Introduction

Heterocyclic compounds such as benzimidazole, benzotriazole, benzothiazole, triazole, tetrazole and their derivatives are the most common inhibitors used in the battle against copper corrosion and its alloys in aqueous solutions [1–8]. The effectiveness of these heterocyclic molecules is based on their ability to form a polymer like film, which prevents copper corrosion. A major limitation using these copper corrosion inhibitors originates from their aromaticity, which limits their current and future use, since they are being suspected as carcinogenic materials. Moreover, benzotriazole, one of the most widely studied compounds, has the disadvantage of reacting with chlorine, which is normally used as a bactericidal agent [9]. For these reasons, researchers are in alert to seek and find new copper corrosion inhibitors having all desired characteristics, such as being non-toxic, easily biodegradable and above all, being environmentally friendly.

Research of substitute compounds, more acceptable from an environmental point of view, has led to the study of the protection characteristics of copper in basic electrolytes without [10,11] and with the addition of fatty acid salts, and especially, saturated linear carbon chain carboxylates of sodium (CH₃(CH₂)ₙ–₂COONa) [12]. These compounds, which do not contain nitrogen, sulfur or aromatic rings, have already been used as corrosion inhibitors of aluminum [14–16], mild steel [14–16], lead [18], magnesium alloys [19] and copper [12–17] aqueous corrosion.

Our research group has recently described, in a short communication, the versatile use of potassium sorbate (often being used in the food industry as a preservative agent), as non-selective metals inhibitor [20]. The current paper presents a comprehensive study of the electrochemical characteristics of copper in 2,4-hexadienoic acid potassium salt (potassium sorbate (CH₃(CH₄)COOK)) medium. Evaluation of inhibition efficiency has been studied with the use of electrochemical methods. XPS analyses have been carried out in order to provide more information on the identity and structure of the passivation layers.

2. Experimental

2.1. Electrochemical experiments

A pencil-type electrode made of 5 mm diameter copper rod (99.9995 wt.%) mounted in a room temperature-curing-epoxy
was used at electrochemical measurements. Subsequent to polishing with 1200 grit SiC paper, the samples were carefully degreased with acetone and rinsed with double-distilled water. The electrochemical measurements were conducted with 273A EG&G Potentiostat (Princeton Applied Research) in 500 mL three electrodes electrochemical cell equipped with calomel reference electrode (SCE) and Pt counter electrode. The reference electrode was installed into the solution through a Luggin–Haber capillary tip assembly. All the potentiodynamic experiments and cyclic voltammetry were performed at a scan rate of 1 mV/s.

2.2. Chemicals

Solutions were prepared with deionizer water (DI, 18 MΩ cm, Millipore System) with the addition of analytical grade chemicals, such as 2,4-hexadienoic acid potassium salt (potassium sorbate, KCH3CH=CHCH=CHCO2), K2SO4 and KCl. Potassium sorbate was purchased from Centrum Ltd., while potassium chloride and potassium sulfate were purchased from Aldrich Chemicals. All chemicals were used without any further purification. The study was performed in both neutral (pH 7) and slightly basic solutions (pH 9) containing potassium sulfate as supporting electrolyte. Potassium sulfate was added to the K-sorbate solutions since copper is inactive in neutral solutions containing this salt. The durability of K-sorbate was studied in solutions containing also chloride ions, as copper is highly sensitive to pitting corrosion in the presence of this aggressive anion.

2.3. X-ray photoelectron spectroscopy (XPS) measurements and data processing

Characterization of the surface was conducted by X-ray photoelectron spectroscopy. XPS was performed using a VG Scientific Microlab III with Al Kα radiation (hν 1486.6 eV; spot size = 400 μm) and a Thermo VG Scientific Sigma Probe spectrometer with mono-chromated Al Kα radiation. Ejected photoelectrons were detected by a hemispherical analyzer that provided high sensitivity and resolution. Operating pressure in the sampling chamber was below 5 × 10−9 Torr. The detailed spectra of Cu 2p, O 1s and C 1s photoelectron lines were measured with a pass-energy of 20 eV and a step size of 0.05 eV. The standard mode of operation for the Radian lens was θ = 53 ± 30°. All spectra were acquired and processed by the XPS Peak Fit software and referenced to the C 1s peak at 285.0 eV. Peak area intensity data were obtained after subtraction of Shirley type background. Peak decomposition of the complex lines was performed by the peak synthesis method using mixed Gaussian–Lorenzian peak shape.

3. Results and discussion

3.1. Effect of potassium sorbate concentration on copper corrosion behavior

The potentiodynamic curves presented in Fig. 1 demonstrate the electrochemical behavior of copper in 1 g/L K2SO4 with different concentrations of potassium sorbate (this material will be termed as “K-sorbate” from here on) at two pH values of 7 and 9. Both cathodic and anodic polarization curves were obtained individually by shifting the potential in negative and positive directions, respectively. In both Fig. 1a and b, the electrochemical behavior of copper in sorbate-free solution containing 1 g/L K2SO4 (pH value of 9 was adjusted by KOH addition) is also being presented (bold black line), for comparison. As can be seen from Fig. 1a, the onset of anodic current in a basic (pH 9) solution containing 1 g/L K2SO4 was obtained at a potential of −0.10 V_SCE. Further positive potential shift reveals a narrow region of copper passivity with anodic currents of few (3–6) mA/cm², while at potentials above 0.025 V_SCE the anodic currents gradually increased, indicating an active copper dissolution. The observed passivity region is well corresponded with the formation of cuprous oxide (Cu2O) at the copper surface. The addition of K-sorbate to the sulfate solution, significantly affects the electrochemical behavior of copper. As can be seen, the onset of anodic currents, in all of the studied solutions at pH 9 (see Fig. 1a) was near the potential of
−0.10 V_{SCE}. For example, with the addition of 4 g/L K-sorbate to the sulfate solution the onset of anodic currents was observed at a potential of −0.09 V_{SCE}. Further positive potential shift reveals a wide range of copper passivity. The recorded anodic currents were lower than a few micro-amps, indicating copper passivity. Only at a potential of 0.4 V a breakdown of copper passivity was detected and anodic current rapidly increased during further positive potential shift. Thus, with the addition of 4 g/L K-sorbate the region of copper passivity was extended up to a potential of 0.4 V_{SCE}. It should be noted that as the solution pH values increases due to the increase in sorbate concentration, not only that copper passivity region was expanded (from 0.4 V to more than 1 V), but also the recorded anodic current peak was narrower, while its potential was shifted to slightly lower potentials (for example, at pH 7 peak position was recorded to be 150 mV and at pH 9 the peak position was recorded at 1 mV). The formation of anodic current peak was obtained at potential of 0.2 V_{SCE} and peak current was recorded to be 40 μA/cm². The anodic current peak associated with Cu₂O formation was also obtained at 0.18 V_{SCE} (30 μA/cm²) and 0.15 V_{SCE} (50 μA/cm²), respectively, for 10 and 50 g/L K-sorbate concentrations.

Reverse scanning conducted in a solution containing 4 g/L K-sorbate reveals a marked hysteresis, indicating that the copper electrode surface suffers from localized corrosion attacks. At higher concentration of K-sorbate (10 g/L and above) no breakdown of copper passivity was detected, up to a potential of 1 V_{SCE}. It should be noted that current density values measured in the region of copper passivity during positive potentiodynamic sweeps in solutions containing K-sorbate are in the order of one-tenth of μA/cm², indicating an enhanced copper passivity. The cathodic branch of the polarization curves reveals that addition of K-sorbate to the sulfate solution at pH 9 does not cause any change or modification in the cathodic currents. Thus, it can be concluded that at a slightly basic pH (9) K-sorbate is acting as anodic inhibitor.

Fig. 1b presents the impact of K-sorbate concentration on copper electrochemical behavior in solutions containing sulfate solutions at neutral pH of 7. Similarly to the results obtained from copper polarization in basic solutions, the anodic branch of the polarization curves reviles that in solutions containing K-sorbate concentrations of 10 g/L and above, copper was protected in a wide potential range (from OCP to 1 V_{SCE}). The introduction of only 4 g/L is proven to be insufficient, capable of protecting the copper surface up to a potential of 0.4 V_{SCE} only. Again, evaluation of the cathodic polarization curves reveals that addition of K-sorbate to the sulfate solution at a pH 7 did not cause any significant changes in the cathodic current profile. Therefore, we can conclude that K-sorbate is acting as copper anodic inhibitor in neutral and basic sulfate based solutions.

Fig. 2 presents an anodic profile obtained from copper electrode during positive potential scans and back-scans at different reverse potentials in a solutions containing 1 g/L K₂SO₄ and 10 g/L K-sorbate. The potential sweep was reversed immediately once a specific reverse potential value was achieved at the positive potential sweep. Reverse scans were applied at potentials of 0.20, 0.50, 1.00 and 1.50 V_{SCE}. Reversing the scan at potentials of 0.20, 0.50 and 1.00 V_{SCE} results in a decrease in the anodic currents, compared with values obtained during positive potential scans. Breakdown potential was obtained at 1.50 V_{SCE}, while, reversing the scan reveals a marked hysteresis. This indicates that copper surface in 10 g/L K-sorbate based solutions was covered with a stable protective film at a potential ranging between OCP (−0.09 V_{SCE}) and up to a potential of 1 V_{SCE}.

3.2. Effect of pH on copper passivity in K-sorbate based solutions

The inhibition characteristics of copper in 10 g/L K-sorbate solutions as a function of pH was investigated. Fig. 3 presents potentiodynamic scans of copper obtained in 10 g/L K-sorbate solutions containing 1 g/L K₂SO₄ at different pH values. The solutions were adjusted to a desired acidic pH value by addition of a diluted H₂SO₄ solution. The electrochemical behavior of copper was investigated at pH values ranging from 9 (original pH of solution) to 5. At lower pH values we observe in immiscible sorbic acid (pK₅ = 5) precipitations being formed. Copper maintained its passivity up to potential of 0.4 V_{SCE} in a K-sorbate solution having a pH value of 5. Further positive shift in the potential reveals a rapid increase in the recorded anodic currents, indicating a breakdown of copper passivity. At higher pH values of 6 and 7 a breakdown of copper passivity was not detected up to a potential of 1 V_{SCE}. In solutions containing K-sorbate with pH values of 6 and 7 an anodic current peak was obtained at a potential of 0.1 V_{SCE}. In a solution with a higher pH value of 9.5, this anodic current peak was shifted to more negative potential of 0.025 V_{SCE}. One can suggest that this anodic current peak is associated with the formation of cuprous oxide (Cu₂O) at the surface. Results concerning this subject are extensively discussed in the last section of this report. It can be concluded that an enhanced copper passivity can be achieved in sulfate solutions containing K-sorbate at pH values above 5.
3.3. Effect of sulfate and chloride anions on copper corrosion behavior in the presence of K-sorbate

Fig. 4a presents potentiodynamic curves of copper in 10 g/L K-sorbate solutions containing different concentration of potassium sulfate. Wide range of copper passivity (up to 1 V\text{SCE}) was obtained in 10 g/L K-sorbate solution with the addition of 1 and 5 g/L \text{K}_2\text{SO}_4, while at higher sulfate concentration (10 g/L), breakdown of the passivity was detected at a potential of 0.37 V\text{SCE}. The marked hysteresis between current values measured at positive potential scan and back-scan was detected once the potential was reverse at 1 V\text{SCE}, indicating that a
Fig. 5. Anodic potentiodynamic curves of copper in 1 g/L KCl K-sorbate-free solution and 10 g/L K-sorbate solution containing 0.1 g/L (●) and 1 g/L KCl (○). (Inserted graph) anodic potentiodynamic curves obtained from copper polarized in solutions containing 1 g/L KCl at pH values of 7 and 9.5. pH value was adjusted by KOH addition.

Concentration of 10 g/L K-sorbate was not sufficient to protect copper surface in 10 g/L K₂SO₄ solution. We realized that in order to prevent breakdown of copper passivity in 10 g/L K₂SO₄ solution, a higher concentration of K-sorbate should be introduced (see Fig. 4b). Addition of 25 g/L K-sorbate to the 10 g/L K₂SO₄ solution noticeably extended copper passivity region (up to a potential of 1 V SCE).

The preservative characteristics of K-sorbate capable of protecting copper surface against breakdown of the passive film were also studied in solutions containing different content of potassium chloride (KCl). In order to clarify the role of chloride concentration on copper electrochemical behavior, potentiodynamic experiments were conducted in 10 g/L K-sorbate solutions containing different concentrations of KCl. Fig. 5 presents potentiodynamic curves obtained from polarizing copper in 10 g/L K-sorbate solutions containing 0.1 and 1 g/L KCl. For comparison, electrochemical behavior of copper in K-sorbate free solution containing 1 g/L KCl is presented in Fig. 5, as well. It should be noted that the addition of K-sorbate to the KCl solutions strongly influenced the alkalinity of the solution, for example, 1 g/L KCl solution posses a pH of 7, while the addition of 10 g/L K-sorbate, increases the pH value up to 9.5. Thus, we present in the inserted graph (in Fig. 5) potentiodynamic curves obtained from polarizing copper in solutions containing 1 g/L KCl both at pH 7 and 9.5 (pH was adjusted with the addition of diluted KOH). As can be seen, the onset of anodic currents in a solution containing 1 g/L KCl (pH 7; bold, solid line) was slightly below the potential of 0.0 V SCE (−0.03 V SCE). The anodic current gradually increased with a positive shift in the potential, indicating an active copper dissolution. Increase in solution alkalinity to 9.5 only slightly affected the electrochemical behavior of copper (Fig. 5, inserted graph). The onset of the anodic current was shifted to more negative potentials of −0.1 V SCE. Further positive potential shift resulted in low anodic currents; at a potential of 0.065 V SCE a breakdown of passivity was detected. The narrow region of copper passivity is attributed to the formation of copper oxide at the copper surface. With the addition of 10 g/L K-sorbate to the 0.1 g/L KCl solution (Fig. 5, ●), wide range of copper passivity was obtained and no breakdown of the protective film was detected up to a potential of 1 V SCE. It should be noted that current density values measured from polarizing copper in the K-sorbate containing solutions in the potential region from OCP (−0.09 V SCE) up to a potential of 1 V SCE were below 10 µA/cm², indicating copper passivity. In addition, formation of an anodic current peak was observed at a potential of 0.1 V SCE. As previously mentioned, this anodic current peak is attributed to the formation of the cuprous oxide (Cu₂O) on the copper surface. Copper was highly resistant to corrosion attacks by chloride ions in the presence of K-sorbate and it is shown that one cannot relate the extended and impressive copper passivity in K-sorbate solutions only to the impact of solution alkalinity.

Fig. 6. Current transient obtained from copper in 10 g/L K-sorbate solution containing 1 g/L KCl during exposure at: (a) 0.1 V SCE, (b) 0.2 V SCE and (c) 0.3 V SCE. Copper electrode surface was repeatedly scratched by a glass microneedle. Inserted graphs display expanded view of a single current transient (●).
3.4. Copper repassivation in K-sorbate solutions

In order to evaluate the repassivation rate of copper in chloride solutions containing K-sorbate, copper electrode was scratched a few times with the use of a glass microneedle. A copper electrode was polarized potentiostatically to selected potentials \(\text{V}_{\text{constant}} = 0.1 \text{--} 0.3\) V versus SCE reference electrode. Throughout the experiment period, copper electrode was held potentiostatically at a predetermined constant potential. Scratching of copper surface was performed using a glass microneedle. Fig. 6 presents an abrupt peaks of anodic current observed in the current–time profile obtained from such study at different applied potentials of: (a) 0.1 V\(_{\text{SCE}}\), (b) 0.2 V\(_{\text{SCE}}\) and (c) 0.3 V\(_{\text{SCE}}\). Inserted graphs in Fig. 6a–c presents only a single current decay, observed in the transient, resulting from a single scratch (●) at the copper electrode surface in 10 g/L K-sorbate solution containing 1 g/L KCl at the different applied potentials. Time axis in the inserted graphs was normalized to the time of peak current \(t_0\) (\(t_0 = 0\) s). Observed acceleration in electrochemical reaction rate produced by scratching glass microneedle at the copper electrode is a direct consequence of the damage caused to the existing protecting surface films. The recorded current rise time subsequent to the impact was a few seconds, before the current reaches its maximum value. The current then decreases to its initial background level within approximated time of 20 s. The transient shows an exponential decay, typical for a self-inhibiting process, such as repassivation. Therefore, the addition of K-sorbate to chloride containing solutions can significantly decrease copper corrosion attacks and provide superior protection of the surface.

3.5. X-ray photoelectron spectroscopy study of copper surface

XPS analysis has been used to determine the chemical nature of copper surface subsequent to an exposure in K-sorbate solution. High resolution C 1s, O 1s and Cu 2p photoelectron spectra and Cu LMM Auger lines of copper sample subsequent to 0.2 V\(_{\text{SCE}}\) exposures for 5 min in 1 g/L \(\text{K}_2\text{SO}_4\) solution containing 10 g/L K-sorbate are presented in Fig. 7. The C 1s spectrum

![Fig. 7. XPS spectrum of: (a) C 1s, (b) O 1s, (c) Cu 2p\(_{3/2}\) core level and (d) Cu LMM Auger line obtained from copper surface subsequent to 0.2 V\(_{\text{SCE}}\) exposure for 5 min in a 10 g/L K-sorbate solution.](image-url)
The C I peak is attributed to alkyl chain (C−C/CH) at binding energy of 285 eV. The high binding energy C 1s peaks (II and III in Fig. 7a) are due to C−O and C=O bonds originated from the sorbate chain [21–24]. Therefore, uptake of sorbate occurs at the copper surface subsequent to the 0.2 V_SCE exposure for 5 min in K-sorbate solution. In addition, the presence of sorbate at the copper surface can be concluded from O 1s and Cu 2p lines.

The O 1s (Fig. 6b) spectrum of the copper electrode is resolved into three components, centered at 530.5, 531.2 and 532.25 eV, which are attributed to Cu2O [22–29], Cu(OH)2 [24–28] and copper(II)-sorbate species, respectively. In the Cu 2p3/2 line a main peak is located at the binding energy of 932.8 eV, which is assigned to either Cu(I) in the form of Cu2O (cuprous oxide), metallic copper (Cu0) or both species [27–28]. The high binding energy peaks at 934.6 and 935.9 eV, corresponding to Cu(II) species; Cu(OH)2 [24–28] and copper-sorbate, respectively. Fig. 7d presents Cu LMM Auger spectra of copper surface. The peak at a kinetic energy of 916 eV, corresponds to Cu(I), while the second peak at 918 eV can be attributed to Cu(II) species. It is important to note that according to Auger parameter (α) the peak with B.E. = 935.9 eV and K.E._LMM = 918 eV is attributed to Cu(II) compound formation [29]. These XPS results suggest that the protective layer formed on copper surface subsequent to anodic polarization in K-sorbate solution consists of Cu2O, Cu(OH)2 and copper(II)-sorbate. Angular resolved XPS confirms the presence of organic layer on top of an oxide layer [30].

Angle resolved XPS confirms X-ray photoelectron spectra of copper surface treated in K-sorbate solutions implies that an organic layer (C6H7O2) is formed on an oxide film (Cu2O/Cu(OH)2). It was reported that compounds, such as carboxylic acid C_n−1H_2n−1CO2H and theirs anions, can strongly chemisorbed on oxidized metal surfaces by the formation of stable hard acid−hard base interaction with multivalent cations on the surfaces of metals such as aluminum and iron [31,32]. Therefore, it is realized that the densely packed alkyl tails on the film act as a barrier layer to Cl− and other aggressive anions diffusion, leading to suppression of Cl− incorporation into the film. Thus, elimination of Cl− accumulation at film defects, resulting in prevention of passive film breakdown on copper in K-sorbate solution containing Cl− can be realized.

4. Conclusion

The electrochemical behavior of copper in potassium sorbate based solutions was presented in this study. The presence of potassium sorbate in sulfate based solutions significantly decreased copper corrosion. The optimal concentration of potassium sorbate was found to be 10 g/L in 1 g/L K2SO4 solution. At these conditions, copper was found to be protective in the potential range between OCP (−0.1 V_SCE) and 1 V_SCE. Enhanced copper passivity was obtained in sulfate solutions containing K-sorbate at pH values above 6. Increasing the sulfate concentration may lead to localized corrosion attacks that can be further avoided if K-sorbate concentration would be adjusted, as well. The effectiveness of protective layer formed at the copper surface in chloride based solutions containing K-sorbate was demonstrated by various electrochemical means. It was shown that the impressive copper passivity could not be related to the impact of the solution alkalinity, but rather to the presence of K-sorbate in the solution. Passivation and repassivation characteristics of the protective layers formed at the copper surface in chloride solutions containing K-sorbate in a potential region, from OCP up to a potential of 0.3 V_SCE were studied by mechanical scratching of the copper surface with the use of a glass microneedle. It was shown that copper repassivation rate was in order of one-tenth of seconds, indicating high rate of repassivation.

XPS spectroscopy demonstrated that copper surface at a potential of 0.2 V_SCE imposed subsequent to immersion in K-sorbate solution was covered with a protective layer consisting of cuprous oxide, cupric hydroxide and copper(II)-sorbate. It is assumed that potassium sorbate inhibits copper corrosion by the formation of a thin coating on the metal surface, which restricts aggressive anions (chlorides and sulfates) access to the metal surface. The carboxylate end group of sorbate molecule is being attached to the metal surface through an oxide/hydroxide “binder” and the hydrophobic nature of the sorbate moiety is capable of eliminating the action of the aggressive anions dissolved in the solution.

K-sorbate is found to be, in addition to its frequent use in the food industry as a preservative material, a superior advanced material, serving as copper anodic corrosion inhibitor. The thin copper soap-like film has impressive protection capabilities. Impressive stability of copper/protective film interfaces in aggressive media, containing chloride and sulfate ions, was found to be in a wide range of potentials, up to more than 1 V (versus SCE reference electrode). Hence, a possibly versatile and advanced new family of inhibitors based on short chain fatty acid salts should be considered. The use of short chain fatty acids, capable of protecting metals is most appealing. The use and applications of such advanced materials can range from an additive in cooling system utilizing metals such as aluminum and copper, through the application of such a protective material as a robust copper passivator in the ultra large system integrated (ULSI) microelectronic industry. Therefore, in addition to K-sorbate, other short chain fatty acid with different molecular weights and structures should be evaluated and studied, as well.

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