Enhanced Copper Surface Protection in Aqueous Solutions Containing Short-Chain Alkanoic Acid Potassium Salts

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The ability of dissolved potassium monocarboxylate salts to produce surface passivation and to inhibit aqueous corrosion of copper was studied. The electrochemical measurements indicate that the inhibiting efficiency of these compounds, with a general formula \( \text{C}_n\text{H}_{2n+1}\text{COOK} \) or \( \text{C}_n\text{K} \) \((n = 3...12)\), is dependent on the hydrocarbon chain length. The inhibiting efficiency was higher for a longer hydrocarbon chain of \( \text{n-alkanoic acid} \). The degree of copper protection was found to increase with an increase in \( \text{n-alkanoic acid potassium salt} \) concentration; the optimum concentration of potassium dodecanoate \( (\text{C}_{12}\text{K}) \) in sulfate solutions was found to be 0.07 M. The protective layers formed at the copper surface subsequent to exposure in various \( \text{n-alkanoic acid potassium salt} \) solutions were characterized by contact angle measurements, electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy, and Fourier transform infrared reflection spectroscopy. Pronounced copper protection was attributed to the growth of a protective film on the copper surface, containing both copper oxides and copper carboxylate compounds. It is suggested that the organic molecules enhance copper protection by covering copper oxides with a thin and dense organic layer, which prevents water molecules or aggressive anions from interacting with the copper surface.

1. Introduction

Heterocyclic compounds such as benzimidazole, benzo triazole, 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, benzo triazole, one of the most widely studied compounds, has been suspected as a water bactericidal agent.9 For these reasons, researchers are searching for new copper corrosion inhibitors having all desired characteristics, such as being nontoxic, being easily biodegradable, and, above all, being environmentally friendly.

Our research group has recently described10–12 the versatile use of potassium sorbate (2,4-hexadienoic acid potassium salt, \( \text{CH}_3(\text{CH})_4\text{COOK} \)) as an efficient copper inhibitor. It was shown that potassium sorbate provides enhanced corrosion protection in sulfate solutions at various pH values (above 6). Moreover, enhanced copper protection was obtained in solutions containing chloride anions at a wide potential region with the presence of sorbate in the solution. Therefore, studying copper protection characteristics in basic electrolytes containing \( \text{n-alkanoic acid potassium salts} \) \( (\text{C}_n\text{H}_{2n+1}\text{COOK}, \text{C}_n\text{K}, n = 3...12) \) is highly appealing. These compounds \( (\text{C}_n\text{K}) \) have already been used as corrosion inhibitors of aluminum,13–15 mild steel,13–15 lead,16 and magnesium alloys17 in aqueous solutions. Here, we report for the first time on the capabilities of this group of materials to act as efficient copper corrosion inhibitors.

2. Experimental Section

Electrochemical characterization, namely, passivation currents \( (i_p) \) and breakdown potential \( (E_b) \) are evaluated by polarization measurements, while the physical properties of the protective layer formed at the copper surface in different \( \text{n-alkanoic acid potassium salts} \) are evaluated by electrochemical impedance spectroscopy (EIS). The hydrophobicity of a copper surface modified by a length of \( \text{n-alkanoic acid potassium salt} \) is determined by contact angle measurements using a droplet of water. Characterization of the copper surface subsequent to immersion in \( \text{n-alkanoic acid potassium salts} \) is obtained with the use of X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy.

2.1. Electrochemical Experiments, 2.1.1. Preparation of Solutions and Electrodes. \( \text{n-Alkanoic acid potassium salts} \) \( (\text{C}_n\text{H}_{2n+1}\text{COOK}, \text{C}_n\text{K}, n = 3...12) \), with aliphatic chain lengths of \( n = 3...12 \) carbon atoms, were prepared via the reaction of the corresponding \( \text{n-alkanoic acid} \) with potassium hydroxide, followed by neutralization. Electrolytes used in the electrochemical studies contained 1 g L \(^{-1}\) \( \text{K}_2\text{SO}_4 \) with the addition of different concentrations of \( \text{n-alkanoic acid potassium salts} \) (0.01 and 0.07 M). Solution pH values were adjusted to 10 by the addition of diluted potassium hydroxide. For \( n > 12 \), \( \text{n-alkanoic acid potassium salt} \) was immiscible, and thus, no experiments could be realized in these solutions.

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

2.1.2. Electrochemical Impedance Spectroscopy (EIS). EIS studies were carried out by using an EG&G Princeton Applied Research Model 273A potentiostat and an EG&G frequency response detector model 1025. A Cu (99.999 wt %) rod electrode (A = 0.2 cm\(^2\)) sealed in epoxy resin served as the working electrode, while round stainless steel (316) and saturated calomel electrode were used as the reference and counter electrode, respectively. A Luggin capillary having a porous tip was employed for minimizing the contamination and preventing potential variation of the reference electrode. All experiments were conducted at room temperature. Impedance spectra were measured at the corresponding open circuit potential (OCP) and at 0.2 V SCE. A sinusoidal potential perturbation of 5 mV amplitude, at the examined potential, was used for excitation of the system in the frequency range between 100 kHz to 0.01 Hz. Nyquist and Bode plots were analyzed and simulated with the proposed equivalent circuit by Zview software. Polarization resistance, double layer capacitance, and inhibition efficiencies were also calculated.

2.2. Surface Characterization. 2.2.1. Sample Preparation. 2.2.1.1. Copper XPS Samples. XPS studies were performed on a copper (99.999 wt %) disc electrode, 2 cm in diameter and 1–2 mm thick. Electrodes were mechanically polished up to 1 μm SiC and then washed in ethanol and DI water. Prior to immersion of the copper electrode into the examined solution, it was immersed in diluted H\(_2\)SO\(_4\) solution to remove air formed copper oxides. Afterward, the Cu electrode was washed and rinsed with DI water once again and was immersed in the examined solution. Subsequent to exposure in the examined solution, the copper electrode was taken out, rinsed with DI water, and dried over a nitrogen flow and then it was directly put in the XPS chamber.

2.2.1.2. Reference Sample. The copper (99.999 wt %) disc electrode was mechanically polished up to 1 μm SiC, washed in ethanol and DI water, immersed in diluted H\(_2\)SO\(_4\) to reduce air formed copper oxides, and then carefully washed with DI water and dried under nitrogen flow.

2.2.1.3. Copper Dodecanoate. Solid copper(II) dodecanoate, Cu\(_2\) (RCO\(_2\))\(_4\) [noted Cu\(_2\)(C\(_{12}\))\(_4\)], where R is C\(_{11}\)H\(_{23}\), was synthesized in our laboratory to identify the high-resolution XPS spectra for C 1s, O 1s, and Cu 2p core levels of a copper-oxygen bond. Copper dodecanoate was synthesized by mixing a copper(II) sulfate (0.01 M) aqueous solution with a potassium dodecanoate (0.02 M) solution. The blue solid precipitates were filtered, rinsed with distilled water, and dried in desiccators.

2.2.2. Contact Angle Measurements. The wetting characteristics of the copper modified surfaces were evaluated via measurement of the contact angle, using the captive bubble method. In this method, a droplet of water formed by manipulation of a micrometer syringe is placed in contact with a solid surface, and the contact angle is measured via scanning the drop profile with a camera.

2.2.3. X-ray Photoelectron Spectroscopy (XPS). XPS spectra were collected using a VG Scientific Microlab III and a Thermo VG Scientific Sigma Probe spectrometer with monochromated Al K\(_\alpha\) radiation (h = 1486.8 eV). Emitted photoelectrons were detected by using a hemispherical analyzer providing both high sensitivity and high resolution. The operating pressure in the sampling chamber was below 1 × 10\(^{-6}\) Pa. 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 radial lens is θ = 53 ± 30°. Spectra were acquired and processed by XPS Peak Fit software and referenced to the C 1s peak at 285.0 eV. Peak area intensity data were obtained after Shirley-type background subtraction. Peak decomposition of the complex lines was performed by the peak synthesis method using a mixed Gaussian–Lorentzian peak shape while minimizing the error between the actual data and the sum of the deconvoluted peaks.

2.2.4. Fourier Transform Infrared Spectroscopy (FTIR). FTIR analysis is recognized as a useful analytical tool for tracking chemical changes occurring in polymeric films. In this work, reflection–absorption infrared spectroscopy (RAIRS) was used to characterize the orientation of the molecules within the surface film. Reflection–absorption infrared spectra were obtained using a Bruker Equinox 55 FTIR instrument equipped with a Tech model FT-80 fixed grazing angle specular reflectance sample apparatus at an incident angle of 80° and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. IR spectra were collected at a resolution of 2 cm\(^{-1}\) using 512 interferometer scans in the wavenumber range of 400–4000 cm\(^{-1}\) and reported in absorbance units, A = −log R/R\(_0\), where R is the reflectivity of the substrate with the protective layer and R\(_0\) is the reflectivity of the reference. Spectra were obtained by subtracting the spectra of bare copper substrate from the spectra of copper modified substrates.

3. Results and Discussion

3.1. Electrochemical Behavior of Copper in n-Alkanoic Acid Potassium Salt Based Solutions. Potentiodynamic curves shown in Figure 1 demonstrate the electrochemical behavior of copper in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) containing different concentrations of potassium dodecanoate (C\(_{10}\)K) at a pH value of 10.

![Figure 1](image-url) -- Polarization curves obtained from copper immersed in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solutions containing different concentrations of potassium dodecanoate (C\(_{10}\)K) at a pH value of 10.

A step size of 0.05 eV. The standard mode of operation for the radian lens is θ = 53 ± 30°. Spectra were acquired and processed by XPS Peak Fit software and referenced to the C 1s peak at 285.0 eV. Peak area intensity data were obtained after Shirley-type background subtraction. Peak decomposition of the complex lines was performed by the peak synthesis method using a mixed Gaussian–Lorentzian peak shape while minimizing the error between the actual data and the sum of the deconvoluted peaks.


indicating the formation of a protective film on the copper surface. At a potential of 0.15 V_SCE, a breakdown of the protective film was detected and anodic currents increased markedly, indicating passive film deterioration. Reverse potential scanning, conducted in solutions containing 0.01 M C10K, revealed a marked hysteresis, indicating that the copper electrode surface suffers from localized corrosion attacks. At higher concentrations of C10K (0.05 and 0.07 M), no breakdown of copper passivity was detected up to a potential of 1 V_SCE. Current density values measured in the 0.07 M C10K solution were extensively lower in comparison with those in the 0.05 M solution. It should be noted that current density values measured during positive potentiodynamic sweeps in 0.07 M C10K were in the region of copper passive current densities and lesser degrees of order, as reported elsewhere. 20

The impact of n-alkanoic acid chain length is shown in Figure 2, which presents anodic potentiodynamic curves obtained from copper polarization in 1 g L⁻¹ K₂SO₄ solutions containing 0.07 M n-alkanoic acid potassium salts (CₙK, n = 3...12) at pH 10. Solid line represents anodic polarization curves obtained from copper immersed in 1 g L⁻¹ K₂SO₄ solutions adjusted to pH 10.

![Figure 2](image)

Figure 2. Anodic polarization curves obtained from copper immersed in 1 g L⁻¹ K₂SO₄ solutions containing 0.07 M n-alkanoic acid potassium salts (CₙK, n = 3...12) at pH 10. Solid line represents anodic polarization curves obtained from copper immersed in 1 g L⁻¹ K₂SO₄ solutions adjusted to pH 10.

3.2. Contact Angle Measurements. Hydrophobic characteristics of copper surfaces, subsequent to 24 h immersion in a solution of 1 g L⁻¹ K₂SO₄ containing 0.07 M n-alkanoic acid potassium salts with different hydrocarbon chain lengths, were visualized using contact angle measurements of water droplets. Figure 3 presents recorded images of a water droplet on copper surfaces prior (a) and subsequent to copper surface modification for 24 h in C6K (b), C8K (c), and C12K (d). The contact angle of the fresh copper surface is estimated to be 50° (Figure 3a). The contact angle did not change significantly subsequent to treatment for 24 h in C6K solution (Figure 3b). However, a further increase in chain length from six to eight dramatically modified the surface wettability. As one can see, remarkable hydrophobic properties were obtained subsequent to copper electrode immersion in 24 h in C8K solution. The contact angle was measured to be 110° subsequent to treatment in C12K solution (Figure 3c), indicating a water repellent surface. Furthermore, the contact angle measured from a copper electrode immersed for 24 h in C12K solution was estimated to be 115° (Figure 3d). The increase in the contact angle values for n = 8 to n = 12 indicates the formation of water repellent surfaces composed of CₙA⁻ on the copper substrate. The reduced wettability can be attributed to the close packed and regularly arranged alkyl tails of CₙA⁻ ions. These results clearly demonstrated that a higher degree of hydrophobicity was provided by the use of longer hydrocarbon chains of n-alkanoic acid potassium salts may be explained by longer hydrophobic tails having formed at the copper surface, which prevents the penetration of water and aggressive anions, such as SO₄²⁻ or Cl⁻.

3.3. Surface Characterization. Characterization of the copper passive layer formed in potassium dodecanoate (C₁₂K) solution was performed with means of XPS and FTIR spectroscopy. FTIR studies provide detailed information on the structure of the organic layer formed at the copper surface subsequent to exposure in potassium dodecanoate solution.

![Figure 3](image)

Figure 3. Water droplet contact angles on copper electrode interfaces which were previously immersed for 24 h in 1 g L⁻¹ K₂SO₄ solutions containing n-alkanoic acid potassium salts with different hydrocarbon chain lengths: (a) reference, (b) C6K, (c) C8K, and (d) C12K.

Figure 4. XPS spectra of C 1s, O 1s, and Cu 2p\(3/2\) core levels obtained from (a) a copper surface subsequent to 1 h exposure at 0.2 V\(_{\text{SCE}}\) in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solution containing 0.07 M potassium dodecanoate, (b) synthesized copper dodecanoate, and (c) a reference copper electrode.

Figure 4 presents high-resolution XPS spectra of C 1s, O 1s, and Cu 2p\(3/2\) core levels obtained from copper samples. The data in Figure 4a were obtained from a copper surface subsequent to 1 h exposure at 0.2 V\(_{\text{SCE}}\) in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solution containing 0.07 M potassium dodecanoate followed by XPS characterization. The C 1s spectrum depicts three components: at 285 eV, attributed to a C–C or C–H binding; at 286.2 eV, attributed to C–O binding; and at 288.6 eV, assigned to COO\(^-\) binding, originating from the carboxylate species on the surface.\(^\text{(21,22,28–31)}\) The ratio between the C–C and COO\(^-\) peaks is close to that of the theoretical value of potassium dodecanoate 11:1 (based on a ratio in dodecanoic acid). For comparison, copper reference spectra are present in Figure 4c. The C 1s spectrum reveals only one peak, obtained at 284.9 eV, indicating the existence of some organic contaminations at the surface. Therefore, it is concluded that the uptake of C\(_{11}\)COO\(^-\) molecules occurred at the copper surface subsequent to 0.2 V\(_{\text{SCE}}\) exposure for 1 h in a solution containing C\(_{12}\)K. In addition, the presence of copper dodecanoate on the copper surface can be realized from the Cu 2p\(3/2\) and O 1s lines. The O 1s spectrum (Figure 4a) obtained from the copper electrode was resolved into two components; the main peak was located at 530.6 eV (peak 1) and attributed to Cu\(_2\)O, and the second peak was located at a higher binding energy, 532.1 eV (peak 2). These two components were resolved in the Cu 2p\(3/2\) spectrum. The main peak in the Cu 2p\(3/2\) spectrum was located at a binding energy of 932.7 eV (peak 1), which is assigned to either Cu(I) in the form of Cu\(_2\)O (cuprous oxide), metallic copper (Cu\(^0\)), or both species.\(^\text{(23–25)}\) The second peak (peak 2) in the Cu 2p\(3/2\) spectra was depicted at a higher binding energy, 935 eV. We relate peak 2, in the Cu 2p\(3/2\) and O 1s spectra, to the formation of copper(II) species bonded with a dodecanoate chain through a carboxylate group at the copper surface.\(^\text{(33,35)}\) Mukhedkar et al.\(^\text{(26)}\) observed the O 1s line at 532.8 eV in the XPS spectra of Cu(2,4-pentanedione), in which the oxygen atoms are present only in the Cu(II)–O–C bond. An additional example of a metal–O–C bond studied with XPS was found in a study performed by Dicke et al.\(^\text{(27)}\) in which the O 1s line at 532.0 ± 0.2 eV was assigned to oxygen in the Zr–O–C bond of bis(acetylacetonate) zirconium.


In our laboratory (the reader is directed to section 2.2.1 for more details). High-resolution XPS C 1s, O 1s, and Cu 2p3/2 spectra of copper dodecanoate are presented in Figure 4b, while the reference electrode spectrum is presented in Figure 4c for comparison. The C 1s spectrum depicts three components: at 285 eV, attributed to a C–C or C–H binding; at 286.2 eV, attributed to C–O binding; and at 288.6 eV, assigned to a C≡O binding, originating from the carboxylate.\textsuperscript{21} The reference sample spectrum revels some organic contaminations (peak at 285 eV); however, the peak at 288.6 eV is not shown, indicating that no carboxylic groups are present.

The O 1s spectra (Figure 4b) is resolved into two components; the main peak was located at 532.1 eV and attributed to oxygen in carboxylate group, while the second peak at 533.8 eV can be attributed to the adsorbed water. In the Cu 2p3/2 spectra, the main peak at 934.9 eV (peak 2) is attributed to the Cu\textsuperscript{2+} bonded to the carboxylate species. The peak at 932.7 eV is attributed to Cu\textsubscript{2}O, which could be formed during the synthesis of the copper dodecanoate compound or after exposure of the compound to air.

The data from the copper surface modified by exposure in potassium dodecanoate provide strong indication for the establishment of a Cu(II)–O–C bond. Moreover, the peaks 2 energies, in both the O 1s and Cu 2p3/2 spectra (Figure 4a), corresponded well with the peaks obtained from the synthesized copper dodecanoate compound (Figure 4b). Therefore, the XPS results suggest that the protective layer formed at the copper surface subsequent to 0.2 V\textsubscript{SC} polarization in potassium dodecanoate solution mainly consists of Cu\textsubscript{2}O and copper dodecanoate on the surface.

Moreover, studying the bonding in copper dodecanoate was demonstrated using AR-FTIR characterization. Figure 5a presents an infrared spectrum with an inset scanning electron microscopy (SEM) micrograph of copper dodecanoate crystals. Long (> 20 μm) needle shaped crystals were observed in the SEM micrograph obtained from the synthesized copper dodecanoate. The bands at 2956 and 2871.5 cm\textsuperscript{-1} are assigned to the asymmetric ν\textsubscript{as} (CH\textsubscript{3}) and symmetric ν\textsubscript{s} (CH\textsubscript{3}) modes, respectively; the bands at 2921.6 and 2850 cm\textsuperscript{-1} are assigned to the asymmetric ν\textsubscript{as} (CH\textsubscript{2}) and symmetric ν\textsubscript{s} (CH\textsubscript{2}) modes, respectively.\textsuperscript{32–38} The bands at 1590 and 1418 cm\textsuperscript{-1} are associated with the asymmetric ν\textsubscript{as} (COO\textsuperscript{-}) and symmetric ν\textsubscript{s} (COO\textsuperscript{-}) carboxylate stretches, respectively, while the bands at 1467 and 1435 cm\textsuperscript{-1} are attributed to the δ(CH\textsubscript{2}) scissoring and δ\textsubscript{as}(CH\textsubscript{3}) antisymmetric bending modes, respectively.\textsuperscript{32–38}

The infrared spectra of carboxylic acids or their salts are characterized by the generally strong absorption at 1750–1700 and 1300–1200 cm\textsuperscript{-1}, associated with C=O and C–O bonds of the carboxylic group, whereas the carboxylate ion has strong antisymmetric (ν\textsubscript{as}) and relatively strong symmetric (ν\textsubscript{s}) COO\textsuperscript{-} stretch absorptions at 1650–1510 and 1450–1280 cm\textsuperscript{-1}, respectively.\textsuperscript{36} It has been proposed\textsuperscript{37} that the relative positions of the asymmetric [ν\textsubscript{as}(COO\textsuperscript{-})] and symmetric [ν\textsubscript{s}(COO\textsuperscript{-})] carboxylic bands [Δν(COO\textsuperscript{-}) = ν\textsubscript{as}(COO\textsuperscript{-}) - ν\textsubscript{s}(COO\textsuperscript{-})] can be used to shed light on the type of carboxylate-to-metal complexation structure in a given metal carboxylate.\textsuperscript{34,37–39} Three common coordination modes for metal carboxylates are described and illustrated in Scheme 1: monodentate (structure I), bridging bidentate (structure II), and chelating bidentate (structure III).\textsuperscript{37} Band separations are generally 350–500 cm\textsuperscript{-1} for monodentate

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Infrared absorption spectra for (a) synthetically produced copper dodecanoate (inset graph presents a SEM micrograph of synthesized copper dodecanoate crystals) and (b) a copper surface subsequent to 1 h exposure at 0.2 V\textsubscript{SC} in 1 g L\textsuperscript{-1} K\textsubscript{2}SO\textsubscript{4} solution containing 0.07 M potassium dodecanoate.

**Scheme 1.** Schematic Representation of Carboxylate–Metal (I) Monodentate, (II) Bridging, and (III) Chelating Types of Coordination

![Scheme 1](https://example.com/scheme1.png)

**Scheme 2.** Carboxylate–Metal Coordination Structure of Copper(II) Carboxylates in the Crystalline (Bridging Bidentate Coordination)

![Scheme 2](https://example.com/scheme2.png)

To fully understand the nature of peak 2 (Figure 4a) in the Cu 2p3/2 and O 1s XPS spectrum, we synthesized copper dodecanoate in our laboratory (the reader is directed to section 2.2.1 for more details).
1995

The peak positioned at 1588 cm\(^{-1}\) of water and/or hydroxyl groups incorporated or adsorbed at the surface film. Peaks positioned at 2960 and 2916 cm\(^{-1}\) to the symmetric stretching vibrations of CH\(_3\) groups and CH\(_2\) groups, respectively. The peaks positioned at 3265 cm\(^{-1}\) were assigned to the asymmetric stretching of these groups. 32 The presence of both peaks in substantial intensity suggests that the carboxylate group binds to the surface at an angle so that both transition dipoles have a significant component along the surface normal. The \(\Delta\nu(COO^-)\) of 142 cm\(^{-1}\) can be attributed to a copper binuclear complex with symmetrically bound carboxylate groups via a bridging bidentate divalent structure.34,40–42

The results obtained with the use of XPS and FTIR spectroscopy from copper samples treated in a potassium dodecanoate solution indicate that the surface film formed on the copper surface consists mainly of cuprous oxide (Cu\(_2\)O) and copper dodecanoate species. Thus, the copper surface is being covered with cuprous oxide (Cu\(_2\)O) with an organic layer on top of it. This layer excludes water and ionic species by hydrophobic group orientation toward the bulk solution.

**3.4. Impedance Measurements.** Electrochemical impedance spectroscopy (EIS) provided an effective method for measuring the resistance against the transfer of ionic species to the underlying metal surface, and it has been widely used to evaluate the barrier properties of inhibitors. Figure 6 presents a set of Nyquist (a) and Bode (b) impedance diagrams measured at 0.2 V\text{SCE}\) subsequent to 1 h exposure of the copper electrode in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solutions containing 0.07 M potassium dodecanoate salts (\(n = 4...12\)) at pH 10. Impedance plots were obtained subsequent to 1 h exposure at 0.2 V\text{SCE}\).

**Figure 6.** (a) Nyquist and (b) Bode plots with corresponding (c) capacitance and (d) resistance curves of the passive layer of the copper electrode in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solutions containing 0.07 M different chain length \(n\)-alkanoic acid potassium salts (\(n = 4...12\)) at pH 10. The peaks positioned at 2874 and 2848 cm\(^{-1}\) of water and/or hydroxyl groups incorporated or adsorbed at the surface film. Peaks positioned at 2960 and 2916 cm\(^{-1}\) to the symmetric stretching vibrations of CH\(_3\) groups and CH\(_2\) groups, respectively. The peaks positioned at 3265 cm\(^{-1}\) were assigned to the asymmetric stretching of these groups. 32–38,43

The peak positioned at 1588 cm\(^{-1}\) was assigned to the asymmetric stretch of \(\nu_{as}(\text{COO}^-)\), and the peak at 1447 cm\(^{-1}\) was attributed to the symmetric carboxylate vibration \(\nu_{s}(\text{COO}^-)\).34 The presence of both peaks in substantial intensity suggests that the carboxylate head group binds to the surface at an angle so that both transition dipoles have a significant component along the surface normal. The \(\Delta\nu(COO^-)\) of 142 cm\(^{-1}\) can be attributed to a copper binuclear complex with symmetrically bound carboxylate groups via a bridging bidentate divalent structure.34,40–42

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![Figure 6](image-url)
phase element (CPE) should be used. A constant phase element has been used to model oxide film formation.\textsuperscript{44} On the basis of Deflorian and co-workers\textsuperscript{48} studying the protective organic coatings on carbon steel, a general equivalent circuit for a carboxylate-covered copper electrode was established (see circuit in the Figure 6a inset).

The impedance plot can be described with the equivalent circuit model depicted in Figure 6a, where \( R_s \) is the solution resistance between the working and reference electrodes, the corrosion process is characterized by the charge-transfer resistance \( R_{ct} \) corresponding to the corrosion reaction at the metal substrate/solution interface, and \( Q_0 \) is the double layer constant phase element (CPE). The properties of the surface layer are characterized by the layer resistance \( R_L \) and the \( Q_f \) layer (CPE), which reflects the protective properties of the carboxylate-modified copper film. Admittance and impedance of a CPE are, respectively, defined as

\[
Y_Q = Y_0(j\omega)^n
\]

and

\[
Z_Q = \frac{1}{Y(j\omega)^n}
\]

where the subscript \( Q \) represents a CPE, \( Y_0 \) represents the modulus, \( \omega \) represents the angular frequency, and \( n \) represents the phase.\textsuperscript{49,50}

The quality of the carboxylate-modified copper electrode can be evaluated by \( R_L \) and \( Q_f \). The more densely packed the protective film, the larger the \( R_L \) values and the lower the \( Q_f \) values. The value of \( n \) for the \( Q_f \) element can be used as an index to determine whether protective film acts as a pure capacitor. The protective film tends to be an ideal capacitor when the \( n \) value approaches \(-1\).

As one can see from the Nyquist plot (Figure 6a), the diameter of the capacitive loop (\( R_L \)) is associated with the corrosion resistance ability of the protective layer, increased with hydrocarbon chain length. This implies that a denser packaging of the organic layer formed at the copper surface with a longer hydrocarbon chain. Values of copper passive layer resistance (\( R_L \)) and capacitance (\( C_f \)), as a function of the hydrocarbon chain length of potassium carboxylate salts, were obtained by fitting an equivalent circuit as shown in Figure 6a (inset), and they are presented in Figure 6c and d. The quality of the organic protective layer can be evaluated via the \( R_L \) and \( C_f \) values.\textsuperscript{51,52} By comparing the values of \( C_f \) and \( R_L \) (different hydrocarbon chain lengths), it is suggested that longer hydrocarbon chains of potassium carboxylate salt provide better copper corrosion protection, due to an increase in \( R_L \) values and a decrease in \( C_f \) values. Therefore, it is evident from Figure 6 that longer hydrocarbon chains provide higher protection of the copper surface. In corrosion science, a CPE’s \( n \) value reflects a roughness of the electrode surface.\textsuperscript{53} The deviation from unity is ascribed to a surface roughness of the copper electrode caused by the corrosion reactions, whereas most CPE’s \( n \) values obtained in different hydrocarbon chain length solutions were over 0.91. This indicates that an electrode

surface modified by n-alkanoic acid potassium salts (n = 4...10) remains uniform due to enhanced corrosion protection.

Impedance studies indicated that films with longer hydrocarbon chain length potassium carboxylates provide an enhanced physical barrier to the diffusion of ionic species present in the aqueous phase. The superior barrier properties of these films are attributed to the densely packed organic layer that separates the underlying copper from the external environment.

3.4.1. Effect of Immersion Time on Film Formation. A series of EIS measurements corresponding to different immersion times were measured at OCP in 0.07 M C\textsubscript{12}K solution containing 1 g L\textsuperscript{-1} K\textsubscript{2}SO\textsubscript{4}. Nyquist impedance spectra are presented in Figure 7a. The spectra were analyzed with the use of the equivalent circuit shown in Figure 7b. The surface layer properties are characterized by the film resistance \( R \), a layer CPE \( Q \), and the Warburg impedance attributed to mass transport during corrosion reactions \( Z_w \). The Warburg impedance is related to the diffusion process of copper ions from the electrode surface to the bulk solution or the diffusion of dissolved oxygen or aggressive anions (Cl\textsuperscript{-}) from the bulk solution to the electrode surface. O represents the Warburg element.\textsuperscript{44-46,54,55} the term O in the circuit represents dimensional diffusion through a layer of finite thickness. From an electrical point of view, it is equivalent to the impedance of a finite length transmission line given by

\[
Z_w = Z_\Omega(j\omega)^{-n} \tanh[B(j\omega)n]
\]

where \( B \) depends on the (chemical) diffusion coefficient \( D_{\text{Cu}} \) and the layer thickness \( d \). The value \( Z_\Omega \) (O\textsuperscript{-1}) contains both the diffusion constant and concentration of copper (defects) in the protective film, as well as the physical dimension of the system under study.

Figure 7c and d presents the resistivity and capacitance, respectively, of a copper protective layer calculated by fitting the experimental data shown in Figure 7a, using the equivalent circuit depicted in Figure 7b. An increase in immersion time caused a decrease in capacitance \( (C_\ell) \) of the copper electrode and an increase in film resistivity \( (R_f) \). These results indicate the formation of an enhanced protective film at the copper surface with a longer exposure time of the copper electrode. Moreover, an increase in the \( n \) values with immersion time indicates that the carboxylate protective layer tends to behave as a perfect capacitor. Therefore, we estimate that the protective layer being

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An increase in the \( R_f \) corrosion resistance element values was obtained for a longer hydrocarbon chain length; thus, the formation of a more densely packed and thicker organic layer at the copper surface is suggested.

XPS and FTIR spectroscopies confirmed the existence of a well characterized surface film formed on the copper surface in n-alkanoic acid potassium salt solutions. The proposed model that emerged from these studies suggests a copper surface having a copper oxide covered with an organic layer. FTIR spectroscopy indicates the formation of a copper binuclear complex with symmetrically bound carboxylate groups via a bridging bidentate divalent structure.

Carboxylates salts (based on short chain n-alkanoic acids) are found to be highly efficient copper corrosion inhibitors. The use and applications of such advanced materials can range from additives in cooling systems, utilizing metals such as copper, to the application of such a protective material as a robust copper passivator in the ultra large system integrated (ULSI) micro-electronic industry.

4. Conclusions

Protective characteristics of n-alkanoic acid potassium salts (C\textsubscript{n}K\textsubscript{....}C\textsubscript{12}K) were investigated and reported in this study. Copper immersed in solution media containing n-alkanoic acid potassium salts with a chain length higher than six carbons has been observed to develop hydrophobic surface films at the copper surface. The length of the hydrocarbon chain has a dramatic influence on copper corrosion protection; longer hydrocarbon chain lengths provide better corrosion protection, which is expressed by lower anodic current densities under polarization conditions.

A general equivalent circuit, \( R_c(Q(R_f(Q_d(R_d)))) \), for a short chain n-alkanoic acid-covered copper electrode is proposed. An increase in the \( R_c \) corrosion resistance element values was obtained for a longer hydrocarbon chain length; thus, the formation of a more densely packed and thicker organic layer at the copper surface is suggested.

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