From Food Preservation to Surface Protection:
Enhanced Corrosion Protection by Fatty Acid Salts

YAIR EIN-ELI
Department of Materials Engineering, Technion—Israel Institute of Technology, Haifa 32000, Israel

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Abstract. The ability of dissolved monocarboxylate salts, often used as food preservatives, to produce surface passivation and to inhibit aqueous corrosion of metals and alloys is discussed. Electrochemical measurements indicate that the inhibiting efficiency of these compounds, with a general formula C_{n-1}H_{2n-1}COOK or C_nK (n = 3...12), is dependent on the hydrocarbon chain length. Inhibiting efficiency was higher for a longer hydrocarbon chain of n-alkanoic acid. Copper corrosion protection level was found to increase with an increase in fatty acid salt concentration; the optimum concentration of potassium dodecanoate (C_{12}K) in sulfate solutions was found to be 70 mM. Protective layers formed at the copper surface subsequent to exposure in various n-alkanoate solutions were characterized by an electrochemical impedance spectroscopy, X-ray photoelectron spectroscopy, Fourier transform infrared reflection spectroscopy, and contact angle measurements. Observed copper passivation is attributed to the growth of a protective film on the copper surface, containing both copper oxides and copper carboxylate compounds. 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.

I. INTRODUCTION

Unsaturated aliphatic monocarboxylic acids and their salts were discovered in the late 1930s and mid-1940s to be effective at inhibiting the growth of microorganisms. Following this discovery, the use of the acid salt, e.g., 2,4-hexadienoic acid potassium salt (K-sorbate), in the food industry increased rapidly. Short chain fatty acids and their salts have been used for their antimicrobial activity, causing cell stasis or lag phases in growth, rather than killing microbe cells. The attractive features of this type of material, namely preserving food against yeast and fungus growth, without leaving traces of odor or taste, led to an extensive use of these materials in food technology.

The growing interest in advanced materials capable of efficiently protecting metal and alloy surfaces from degradation, and in addition satisfying the demand of being non-toxic, benign, and even biodegradable, is driving many research groups to search for such materials. These benign materials are being used in various applications such as atmospheric and environmental metal corrosion and batteries. For example, it is known that 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. The effectiveness of these heterocyclic molecules is based on their ability to form a polymer-like film that 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 suspected of being carcinogenic materials. Moreover, benzotriazole, one of the most widely studied compounds, has the disadvantage of reacting with chlorine, which is normally used as a water bactericidal agent. In addition, most environmentally friendly inhibitors are targeted to protect a specific metal or alloy, while a nonspecific, highly efficient corrosion inhibitor group of materials has not been reported, until now. For these reasons, researchers are searching for new corrosion inhibitors having all the desired characteristics, such as being nontoxic, being easily biodegradable, and above all, being environmentally friendly. Here, we fully report on the capabilities of this group of materials to act as efficient metal corrosion inhibitors.

2. EXPERIMENTAL

Electrochemical characterization, namely, passivation currents ($i_p$) and breakdown potential ($E_b$), were evaluated by polarization measurements, while the physical properties of the protective layer formed at the copper surface by different $n$-alkanoic acid potassium salts were evaluated by electrochemical impedance spectroscopy (EIS). The hydrophobicity of a copper surface modified by a length of $n$-alkanoic acid potassium salts was determined by contact angle measurements using a droplet of water. Characterization of copper surface subsequent to immersion in $n$-alkanoic acid potassium salts was 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

Salts of $n$-alkanoic acid ($C_nH_{2n+1}COOK$, $C_nAK$, $C_nK$), with aliphatic chain length of $n = 3$..12 carbon atoms, were prepared via the reaction of the corresponding $n$-alkanoic acid with potassium hydroxide, followed by neutralization. Electrolytes used in the electrochemical studies contained 1 g L$^{-1}$ K$_2$SO$_4$ with the addition of different concentrations of $n$-alkanoic acid potassium salts (10 and 70 mM). Solution pH values were adjusted to 10 by the addition of diluted potassium hydroxide. For $n > 12$, $n$-alkanoic acid potassium salt was immiscible, and thus, no experiments could be realized in these solutions. A pencil-type specimen made of 5-mm-diameter copper (99.999 wt%), aluminum (6061), carbon steel (1020), and stainless steel (316 L) rods mounted in a room-temperature-curing-epoxy were used in the electrochemical measurements. Subsequent to polishing with 1200-grit SiC paper, the samples were carefully degreased with acetone and rinsed with de-ionized (DI) water. Electrochemical measurements were conducted with 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 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 a 273A EG&G potentiostat (Princeton Applied Research) and an EG&G frequency response detector model 1025. A copper rod electrode (99.999 wt%; $A = 0.2$ cm$^2$) sealed in epoxy resin served as the working electrode, while a round stainless steel (316) and a saturated calomel electrode were used as the counter and reference 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 and 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 done 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 and then washed in DI water. Prior to the immersion of the copper electrode into the potassium dodecanoate solution, it was immersed in diluted H$_2$SO$_4$ to remove air formed copper oxides. Afterward, the Cu electrode was washed with DI water 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 with nitrogen flow, and then it was put directly in the XPS chamber.

2.2.1.2. Reference sample—Copper disc electrode (99.999 wt%) was mechanically polished up to 1 µm, 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$(RCO_2)_4$ [denoted Cu$_4$(C$_{12}$H$_{25}$)$_4$], where R is C$_7$H$_{15}$, 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 (10 mM) solution with a potassium dodecanoate (20 mM) solution. The blue solid precipitates were filtered, rinsed with DI water, and dried in desiccators.

2.2.2. Contact angle measurements

Wetting characteristics of the copper modified surfaces were evaluated via measurements of the contact angle, using the captive bubble method. In this method, a droplet of water was formed by manipulation of a micrometer syringe is placed in contact with a solid surface, and the contact angle is measured by photographing the drop profile with a camera.

2.2.3. X-ray photoelectron spectroscopy (XPS)

XPS spectra were collected using a VG Scientific Micro-
lab III and a Thermo VG Scientific Sigma Probe spectrometer with monochromated Al Kα radiation (\(hν = 1486.8\) eV). Emitted photoelectrons were detected by a hemispherical analyzer providing both high sensitivity and high resolution. The operating pressure in the sampling chamber was below \(1 \times 10^{-6}\) Pa. Detailed spectra of Cu 2p, O 1s, and C 1s photoelectron lines were measured with pass energy of 20 eV and 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.

The addition of C to the sulfate solution significantly increases, indicating an active copper dissolution at potentials above 0.08 V. Further potential shift reveals a narrow region of copper passivity, while at a potential of –0.12 V, 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–Lorenzian 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 400–000 cm\(^{-1}\) and reported in absorbance units. 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-Salt-Based Solutions

Potentiodynamic curves shown in Fig. 1 demonstrate the electrochemical behavior of copper in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) containing different concentrations of potassium decanoate salt (C\(_{10}\)K) at a pH value of 10. Both cathodic and anodic polarization curves were obtained individually by shifting the potential in the negative and positive directions, respectively. In addition, the bold black line in Fig. 1 depicts, for comparison, the electrochemical behavior of copper in a 1 g L\(^{-1}\) K\(_2\)SO\(_4\) organic-free solution (pH value of 10 was adjusted by KOH addition). As can be seen, the onset of anodic current in organic-free solution containing only 1 g L\(^{-1}\) K\(_2\)SO\(_4\) was obtained at a potential of –0.12 V\(_{SCE}\). Further positive potential shift reveals a narrow region of copper passivity, while at potentials above 0.08 V\(_{SCE}\) the anodic current gradually increases, indicating an active copper dissolution. The addition of C\(_{10}\)K to the sulfate solution significantly affects the electrochemical behavior of copper. Addition of 10 mM C\(_{10}\)K to the sulfate solution shifted the onset of anodic currents to slightly lower values, –0.14 V\(_{SCE}\). Further positive potential shift revealed a region of copper passivity up to 0.15 V\(_{SCE}\) characterized by low anodic currents, 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 10 mM C\(_{10}\)K, revealed a marked hysteresis, indicating that the copper electrode surface suffers from localized corrosion attacks. At higher concentrations of C\(_{10}\)K (50 and 70 mM), no breakdown of copper passivity was detected up to a potential of 1 V\(_{SCE}\). Current density values measured in the 70 mM C\(_{10}\)K solution were significantly lower in comparison with those in the 50 mM solution. It should be noted that current density values measured during positive potentiodynamic sweeps in 70 mM C\(_{10}\)K were in the region of copper passivity, and they are in the order of a tenth of \(\mu A/cm^2\), indicating enhanced copper passivity. The cathodic branch of the polarization curves reveals that addition of C\(_{10}\)K to the sulfate solution (pH 10) did not alter the cathodic current characteristics. Therefore, capric acid potassium salt (C\(_{10}\)K) acts as a highly efficient copper anodic inhibitor.

The impact of n-alkanoic chain length is shown in Fig. 2, which presents anodic potentiodynamic curves obtained from copper polarization in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solutions containing 70 mM of various n-alkanoic acid potassium salts \((n = 3…12)\), and in a 1 g L\(^{-1}\) K\(_2\)SO\(_4\) organic-free solution for comparison. All solutions were adjusted to a pH value of 10. The number of carbon atoms (chain length) in dissolved carboxylate salts was...
longer hydrophobic tails having formed at the copper surface, which prevents penetration of water and aggressive anions such as \( \text{SO}_4^{2-} \) or \( \text{Cl}^- \).

The corrosion inhibition of aluminum, copper, stainless and carbon steels in the presence of K-sorbate was evaluated and studied in solutions containing 100–1,000 ppm of chloride solutions. Figure 3 reveals that in the presence of 1% potassium sorbate (10 g/L) in chloride-containing solutions (KCl in concentrations of 100–1,000 ppm), all studied metals and alloys exhibited a passivity state in a wide range of potential. In the absence of the short chain fatty acid salt, all metals and alloys are actively dissolved upon anodic polarization in the aggressive chloride solutions. The decrease in anodic currents observed in chloride solutions, from values of 1 mA/cm\(^2\) at high anodic potentials (0.0 V for Al and carbon steel, 0.1 V for Cu, and 0.6 V for stainless steel) to less than a few \( \mu \text{A/cm}^2 \) in chloride solutions containing sorbate ions, at the same anodic potentials, demonstrates that potassium sorbate is a versatile, non-selective, and powerful corrosion inhibitor, capable of providing passivity to metals in a wide potential window of \( \pm 1.2 \) V, without any evidence of pitting (no hysteresis in the cyclic polarization curve, Fig. 3c). The passivity potential range can be further extended by an increase in the K-sorbate concentration (for example, 50 g/L), as demonstrated in Fig. 3d. It is important to note that prior to the introduction of a passivity stage, one can observe the appearance of an anodic peak, at potentials higher by only 50–100 mV from the open circuit potential (OCP) (easily observed in Fig. 3b and d), related to oxide film formation.

Evaluation of sorbate’s superiority over other anodic inhibitors is demonstrated by a comparative study between a well-known copper corrosion inhibitor, benzotraizole (BTA), and sorbate. Such a study was performed in equimolar solutions, containing 70 mM of each inhibitor and 1,000 ppm of sulfate ions, as illustrated in Fig. 4. As can be seen in Fig. 4, the anodic potentiodynamic polarizations obtained from polarizing copper in both solutions reveal that while both materials passivate copper surface, the potential range of copper passivation is considerably extended with the use of sorbate, up to a potential of 1 V. Potentiostatic evaluations of copper in BTA and K-sorbate acid salt solutions at different anodic potentials shown in Fig. 5 reveal two important features of sorbate inhibition: (i) passive films obtained in the sorbate solution are constructed faster than BTA passive film (Fig. 5a,b); and (ii) the protective film produced in the sorbate solution is highly stable at high anodic potential, in contrast to Cu–BTA film destruction at a potential of 0.5 V and above it (Fig. 5c).

Fig. 2. Anodic polarization curves obtained from copper immersed in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solutions containing 70 mM \( n \)-alkanoic acid potassium salts of different hydrocarbon chain length \((n = 3…12)\) at pH 10. Solid line represents anodic polarization curves obtained from copper immersed in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solutions adjusted to pH 10.

between 3 and 12. Salts with longer hydrocarbon chain lengths could not be dissolved, and immiscible crystals were present in those solutions.

Addition of \( n \)-alkanoic acid salts to 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solution led to a major change in the electrochemical behavior of copper. A decrease of anodic currents was obtained with the addition of 70 mM C\(_3\)K and C\(_4\)K to the sulfate solutions up to a potential of \( +120 \) mV, similar to copper behavior in organic-free solution. Active dissolution of copper was observed in both solutions once the copper potential was higher than 120 mV, indicating an active copper dissolution. With a further increase in the hydrocarbon chain length \((n > 4)\), a wide range of copper passivity was obtained, from OCP to 1 V. Moreover, a further increase in the fatty acid chain length decreased the passivation currents significantly. For example, the copper passivation current at 0.4 V in C\(_6\)K was 4 \( \mu \text{A/cm}^2 \), while in C\(_{12}\)K it was 1 order of magnitude lower, 0.42 \( \mu \text{A/cm}^2 \). The decrease in the anodic currents obtained for longer hydrocarbon chains of \( n \)-alkanoic acid potassium salts may be explained by
Fig. 3. Polarization curves obtained from polarizing metals in sorbate (1 wt%) and sorbate-free solutions. (a) Aluminum 6061 in a solution containing 100 Cl\(^-\) ions. (b) Copper in 1,000 ppm Cl\(^-\) ions. (c) Stainless steel 316 L in 1,000 ppm Cl\(^-\) ions; cyclic polarization of stainless steel 316 L indicates a stable passive film up to 1 V. (d) Carbon steel 1020 in 1,000 ppm of Cl\(^-\) ions. Increase in K-sorbate concentration to 5 wt% leads to increase in the passive potential range up to 1.0 V. Arrows indicate the electrochemical scan direction.

Fig. 4. Anodic polarization of copper in sulfate solutions (Na\(_2\)SO\(_4\), 1 %wt) in the presence of 70 mM benzotriazole (BTA) and K-sorbate. Passive film formed on copper is stable up to 0.5 V in BTA-based electrolyte, while passive film formed in K-sorbate is stable up to 1 V.

3.2. Contact Angle Measurements

Hydrophobic characteristics of copper surfaces, subsequent to 24 h immersion in a solution of 1 g L\(^{-1}\) K\(_2\)SO\(_4\) containing 70 mM n-alkanoic acid potassium salts with different hydrocarbon chain lengths, were visualized using contact angle measurements of water droplets. Figure 6 presents recorded images of a water droplet on copper surfaces prior (a) and subsequent to copper surface modification for 24 h in C\(_6\)K (b), C\(_8\)K (c), and C\(_{12}\)K (d). The contact angle of the fresh copper surface is estimated to be 50° (Fig. 6a). The contact angle did not change significantly subsequent to treatment for 24 h in C\(_6\)K solution (55°, Fig. 6b). However, a further increase in n-alkanoic 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 for 24 h in C\(_8\)K solution. The contact angle was measured to be 110° subsequent to treatment in C\(_8\)K solution (Fig. 6c).
3.3. Surface Characterization

Characterization of the copper passive layer formed in potassium dodecanoate \((\text{C}_{12}\text{K})\) solution was performed by 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 \(\text{C}_{12}\text{K}\) solution. Identification of surface species subsequent to exposure at OCP and \(0.2 \text{ V}_{\text{SCE}}\) was studied. Figure 7 presents high-resolution XPS C 1s, O 1s, and Cu 2p\(_{3/2}\) core levels obtained from copper samples. The data in Fig. 7a were obtained from a copper surface subsequent to 1 h exposure at \(0.2 \text{ V}_{\text{SCE}}\) in \(1 \text{ g L}^{-1} \text{K}_{2}\text{SO}_{4}\) 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.\(^{27-32}\) The ratio between the C–C and COO\(^{-}\) peaks is close to that of the theoretical value of potassium dodecanoate, (being 11:1, based on a ratio in dodecanoic acid). 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 \(\text{C}_{11}\text{COO}^{-}\) occurred at the copper surface subsequent to \(0.2 \text{ V}_{\text{SCE}}\) exposure for 1 h in a solution containing \(\text{C}_{12}\text{K}\). In addition, the presence of copper dodecanoate at the copper surface can be realized from the Cu 2p\(_{3/2}\) and O 1s lines. The O 1s spectrum (Fig. 7b, black) obtained from copper electrode was resolved into two components; the main peak was located at 530.6 eV (peak 1) and attributed to \(\text{Cu}_{2}\text{O}\), and the second peak was located at a higher binding energy, 532.05 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 \(\text{Cu}_{2}\text{O}\) (cuprous oxide), metallic copper (Cu\(^{0}\)), or both species.\(^{33-35}\) 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 carboxylate group at the copper surface.\(^{26,36,37}\)

It was previously reported that the O 1s line at 532.8 eV is present in the XPS spectra of Cu(2,4-pentanedione).\(^{38}\) Thus 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 indicated that the O 1s line at 532.0 ± 0.2 eV was assigned to oxygen in the \(\text{Zr}–\text{O}–\text{C}\) bond of bis(acetylacetonate) zirconium.\(^{39}\) To fully understand the origin of peak 2 (Fig. 7a) in the Cu 2p\(_{3/2}\) and O 1s XPS spectrum, we synthesized copper...
Fig. 6. Water droplet contact angle on copper electrode interfaces that were previously immersed for 24 h in 1 g L\(^{-1}\) K\(_2\)SO\(_4\) solution, containing \(n\)-alkanoic acid potassium salts with different hydrocarbon chain lengths: (a) reference; (b) C\(_6\)K; (c) C\(_8\)K; (d) C\(_{12}\)K.

Fig. 7. XPS spectra of (a) C 1s, (b) O 1s, (c) Cu 2p\(_{3/2}\) core level obtained from copper surface subsequent to 2 h exposure at 0.2 V\(_{\text{SCE}}\).
dodecanoate in our laboratory (the reader is directed to Section 2.2.1. for more details). High-resolution XPS C 1s, O 1s, and Cu 2p\textsubscript{3/2} spectra of copper dodecanoate are presented in Fig. 4b, while the reference electrode spectrum is presented in Fig. 7c, 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{27, 29–32} The reference sample spectrum reveals some organic contaminations (peak at 285 eV), however, the peak at 288.6 eV was not obtained, indicating that no carboxylic groups are present. The O 1s spectra (Fig. 7b) is resolved into two components (black curve); the main peak was located at 532.05 eV and attributed to oxygen in the carboxylate group, while the second peak at 533.8 eV can be attributed to the adsorbed water. In the Cu 2p\textsubscript{3/2} 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{3}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 peak 2 energies, in both the O 1s and Cu 2p\textsubscript{3/2} spectra (Fig. 7a) corresponded well with the peaks obtained from the synthesized copper dodecanoate compound (Fig. 7b). Therefore, the XPS results suggest that the protective layer formed at the copper surface subsequent to 0.2 V\textsubscript{SCE} polarization in potassium dodecanoate solution mainly consists of Cu\textsubscript{2}O and copper dodecanoate at the surface.

Characteristics of the bonding in copper dodecanoate were studied by AR-FTIR (attenuate reflectance-FTIR). Figure 8a 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 \(\nu_{as}(\text{CH}_3)\) and symmetric \(\nu_{s}(\text{CH}_3)\) modes, respectively; the bands at 2921.6 and 2850 cm\textsuperscript{-1} are assigned to the asymmetric \(\nu_{as}(\text{CH}_2)\) and symmetric \(\nu_{s}(\text{CH}_2)\) modes, respectively.\textsuperscript{36,37,40–44} The bands at 1590 and 1418 are associated with the asymmetric \([\nu_{as}(\text{COO}^-)]\) and symmetric \([\nu_{s}(\text{COO}^-)]\) carboxylate stretches, respectively, while the bands at 1467 and 1435 cm\textsuperscript{-1} are attributed to \(\delta(\text{CH}_2)\) scissoring and \(\delta_{as}(\text{CH}_3)\) antisymmetric bandings, respectively.\textsuperscript{40–44}

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 CO bonds of the carboxylic group, whereas, the carboxylate ion has strong antisymmetric \(\nu_{as}(\text{COO}^-)\) and relatively strong symmetric \(\nu_{s}(\text{COO}^-)\) carboxylic stretches, respectively. It has been proposed that the relative positions of the asymmetric \([\nu_{as}(\text{COO}^-)]\) and symmetric \([\nu_{s}(\text{COO}^-)]\) carboxylic bands can be used to shed light on the type of

![Fig. 8. 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{SCE} in 1 g L\textsuperscript{-1} K\textsubscript{2}SO\textsubscript{4} solution containing 70 mM potassium dodecanoate.](image-url)
carboxylate-to-metal complexation structure in a given metal carboxylate. Three common coordination modes for metal carboxylates are described and illustrated in Scheme I: monodentate (structure I), bridging bidentate (structure II), and chelating bidentate (structure III). Band separations are generally 350–500 cm$^{-1}$ for monodentate binding, 150–180 cm$^{-1}$ for bridging bidentate coordination, while chelating bidentate structures usually give rise to $\Delta \nu (\text{COO}^-) \approx 100$ cm$^{-1}$.

The difference between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ for the copper dodecanoate compound correlates quite well with the carboxylate coordination. The difference of 172 cm$^{-1}$ is attributed to a copper binuclear complex with symmetrically bound carboxylate groups, having a bridging bidentate valent structure, as illustrated in Scheme II. A good correlation exists between the FTIR spectroscopy and XPS results. XPS results suggest that copper is present in two valence states in the copper dodecanoate and that the atomic concentration ratio of copper and oxygen in this compound is 4. This is in a good agreement with the proposed model of the copper dodecanoate molecule derived from FTIR measurements. Thus, XPS and FTIR results strongly indicate that copper dodecanoate (Cu$_2$(C$_{11}$H$_{23}$COO)$_4$) possesses a bidentate divalent structure.

Figure 8b presents an infrared spectrum of 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 70 mM potassium dodecanoate. A broad band positioned at 3265 cm$^{-1}$ originates from the stretching behavior of water and/or hydroxyl groups incorporated or adsorbed at the surface film. Peaks positioned at 2960 and 2916 cm$^{-1}$ are due to the asymmetric stretching vibrations of CH$_3$ groups and CH$_2$ groups, respectively. The peaks positioned at 2874 and 2848 cm$^{-1}$ are due to the symmetric stretching of these groups. The peak positioned at 1588 cm$^{-1}$ was assigned to the asymmetric stretch of $\nu_{\text{as}}(\text{COO}^-)$ and peak at 1447 cm$^{-1}$ was attributed to the symmetric carboxylate vibrations $\nu_{\text{sym}}(\text{COO}^-)$. The presence of both peaks in substantial intensity suggests that the carboxylate headgroup binds to the surface at an angle so that both transition dipoles have a significant component along the surface normal. The $\Delta \nu (\text{COO}^-)$ of 142 cm$^{-1}$ can be attributed to a copper binuclear complex with symmetrically bound carboxylate groups via a bridging bidentate divalent structure.

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) 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 has been widely used to evaluate the barrier properties of inhibitors. Figure 9 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 70 mM of n-alkanoic acid potassium salts with different chain lengths (C$_n$K, $n = 4...12$) at a pH value of 10. Figure 9b illustrates that $\log Z$/ against log f curves show three distinctive segments. In the higher frequency region, the $\log Z$/ against log f curve tends to become zero with phase angle values falling rapidly toward 0°. This is typical of resistive behavior and corresponds to a solution resistance. The medium- and low-frequency ranges show that (i) the pure capacitive behavior, which is characterized by the slope of the $\log Z$/ against log f curve, is equal to -1, and (ii) the phase angle at lower frequencies deviates from the line approaching 0°. Such behavior indicates that a mass transport occurring through the phase layer must be taken into account and that the protective film formed on the metal surface did not act as a pure capacitor, and a constant phase element (CPE) should be used. A constant phase element has been used to model oxide film formation. A general equivalent circuit for a carboxylate-covered copper electrode was established (see circuit in the Fig. 9a inset) based on the work of Deflorian and coworkers, who studied protective organic coatings on carbon steel.

The impedance plot can be described with the equiv-
alent circuit model depicted in Fig. 9a, where $R_s$ is the solution resistance between the working and reference electrodes, the corrosion process is characterized by $R_{dl}$, the charge-transfer resistance corresponding to the corrosion reaction at the metal substrate/solution interface, and $Q_{dl}$ is the double layer constant-phase element (CPE). The properties of the surface layer are characterized by $R_f$, the layer resistance 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

$$Y_Q = Y_o (j\omega)^{n}$$

and

$$Z_Q = \frac{1}{Y_Q} (j\omega)^{-n}$$

where the subscript $Q$ represents a CPE, $Y_o$ represents the modulus, $\omega$ represent the angular frequency, and $n$ represents the phase.\textsuperscript{54,55} The quality of the carboxylate-modified copper electrode can be evaluated by $R_f$ and $C_f$. The more densely packed the protective film, the larger the $R_f$ values and the lower the $C_f$ 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 (Fig. 9a), the diameter of the capacitive loop ($R_f$), which 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 \((R_f)\) 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 Fig. 9a (inset), and they are presented in Fig. 9c,d. The quality of the organic protective layer can be evaluated via the \(R_f\) and \(C_f\) values.\(^{56,57}\) By comparing the values of \(C_f\) and \(R_f\) (different hydrocarbon chain lengths), it is suggested that longer hydrocarbon chains of potassium carboxylate salt provide better copper corrosion protection, due to increase in \(R_f\) values and a decrease in \(C_f\) values. Therefore, it is evident from Fig. 9 that longer hydrocarbon chains provide higher protection of the copper surface.

In corrosion science, CPE’s \(n\) value reflects a roughness of the electrode surface.\(^{58}\) 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 crystalline hydrocarbon 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 was measured at OCP in 70 mM \(C_{12}K\) solution containing 1 g L\(^{-1}\) \(K_2SO_4\). Nyquist impedance spectra are presented in Figure 10a. The spectra were analyzed with the use of the equivalent circuit shown in Fig. 10b. The surface layer properties are

![Fig. 10.](image-url)

**Fig. 10.** (a) Nyquist plots and (b) equivalent circuit with (c) corresponding resistance and (d) capacitance values of the passive layer of a copper electrode in 1 g L\(^{-1}\) \(K_2SO_4\) solutions containing 70 mM \(C_{12}K\) at pH 10. Impedance plots were obtained subsequent to different immersion periods at OCP.

Ein-Eli / From Food Preservation to Surface Protection
characterized by the film resistance, $R_f$, layer CPE $Q_f$, 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 ($\text{Cl}^-$) from the bulk solution to the electrode surface. $O$ represents the Warburg element; 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

$$Z_w = Z_o (j\omega)^{-n} \tan h [B(j\omega)n]$$

where $B$ depends on the (chemical) diffusion coefficient $D_{Cu}$ and the layer thickness $d$. The value $Z_o$ ($O^-$) 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 10c,d presents the resistivity and capacitance, respectively, of a copper protective layer calculated by fitting the experimental data shown in Fig. 10a, using the equivalent circuit depicted in Fig. 10b. An increase in immersion time caused a decrease in capacitance ($C$) 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 formed on the copper electrode repairs itself with time, while a denser and homogenous film is formed at a prolonged immersion time.

4. CONCLUSIONS

Protective characteristics of $n$-alkanoic acid potassium salts (C,K,…C$_8$K) were investigated and reported in this study. $n$-Alkanoates, such as 2, 4-hexadienoate potassium salt (K-sorbate), are found to be—in addition to their frequent use in the food industry as preservative materials—superior advanced materials, serving as non-selective corrosion inhibitors for metals and alloys. Copper immersed in solution media containing $n$-alkanoates 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 the metal (copper in this case) corrosion protection; longer hydrocarbon fatty acid chain lengths provide better corrosion protection, which is expressed by lower anodic current densities under polarization conditions. A general equivalent circuit, $R_f(Q(R_f(Q_fR_w)))$, for a short chain fatty acid-covered copper electrode is proposed. An increase in $R_f$ corrosion resistance element values was obtained for a longer hydrocarbon chain length; thus, the formation of more densely packed and thicker organic layer at the copper surface is suggested.

XPS and FTIR measurements confirmed the existence of a well-characterized surface film formed on the copper surface in $n$-alkanoate 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 divergent structure. The copper soap-like film, in the form of copper-alkanoate, adheres to the copper metal surface via a binding to an oxide film with the carboxylate end group, forming a thin film with advanced protection capabilities. Impressive stability of the metal/protective film interfaces in aggressive media, containing chloride and sulfate ions, was found to be in a wide range of potentials, up to 1.2 V (vs. SCE reference electrode). Hence, a possibly versatile and advanced new family of metal and metal alloy inhibitors based on short chain fatty acid salts should be considered. The use of these materials, capable of protecting several metals without any selectivity (unlike most inhibitor materials), is most appealing. The use and applications of such agents can range from additives in cooling systems utilizing metals such as aluminum and copper, through the application of such a protective material as a robust copper passivating the ULSI (ultra large system integrated) microelectronic industry.

REFERENCES AND NOTES