

# Corrosion inhibition studies of copper in highly concentrated NaCl solutions

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**Abstract** The influence of the concentration of sodium succinate (SS) on the corrosion and spontaneous dissolution of copper in aerated non-stirred highly concentrated (5.0 M) NaCl solutions was studied at different temperatures (10–60 °C). The investigations involved weight loss as well as potentiodynamic polarization and impedance measurements. The inhibition efficiency increases with increase in the concentration of SS and decreases with temperature. The inhibition mechanism involves adsorption of SS on the copper surface. An adherent layer of inhibitor is postulated to account for the protective effect. Energy dispersion X-ray (EDX) examinations of the electrode surface confirmed the existence of such an adsorbed film. The potential of zero charge (pzc) of copper was studied by the ac impedance technique and the mechanism of adsorption is discussed.

**Keywords** Copper · NaCl solution · Sodium succinate · Corrosion inhibition · Adsorption · EIS

## 1 Introduction

Copper is commonly used as a material in heating and cooling systems. Scale and corrosion products have a negative effect on heat transfer, causing a decrease in heat transfer efficiency, which is why periodic de-scaling and cleaning in hydrochloric acid pickling solutions are necessary. Thus, corrosion of copper and its inhibition in chloride solutions have attracted the attention of a number of investigators [1–12].

It is generally accepted that anodic dissolution of copper in chloride environments is influenced by the chloride concentration and the acidity of the medium. At chloride concentrations lower than 1 M, copper dissolution occurs through the formation of CuCl, which is not protective enough and is converted to soluble  $\text{CuCl}_2^-$  by reacting with excess chloride [2]. According to Bacarella and Griess [3], the anodic dissolution of copper is under mixed control by the electro-dissolution of copper and the diffusion of soluble  $\text{CuCl}_2^-$  from the Helmholtz plane into the bulk solution. On the other hand, at concentrations higher than 1 M, higher cuprous complexes such as  $\text{CuCl}_3^{2-}$  and  $\text{CuCl}_4^{3-}$  are formed in addition to ones with fewer chlorides such as CuCl and  $\text{CuCl}_2^-$  [13].

The main object of the present work is to investigate the ability of sodium succinate (SS) to inhibit the corrosion of copper in aerated stagnant 5.0 M NaCl solution under the influence of various experimental conditions. For this purpose, gravimetric (weight loss) and electrochemical (potentiodynamic polarization and impedance) measurements have been used complemented with some EDX observations.

## 2 Experimental

### 2.1 Solutions

Sodium succinate (SS),  $\text{C}_4\text{H}_4\text{O}_4\text{Na}_2$  (> 99%) was purchased from Merck (Darmstadt, Germany). The electrolytes were prepared using analytical grade reagents (Merck) and triply distilled water. Sodium succinate was dissolved at concentrations in the range 0.001–0.10 M in 5.0 M NaCl solutions.

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## 2.2 Weight loss measurements

For weight loss measurements, corrosion tests were performed using coupons measuring 1 cm × 3 cm × 0.1 cm prepared from pure copper. These coupons were mechanically polished with aluminum powders of different grain sizes down to 0.05 μm, using water as lubricant, and was then repeatedly rinsed with water, dried, and then etched in a 7 M HNO<sub>3</sub> solution for 30 s. The etched electrode was rapidly rinsed with deionized water, followed by immediate rinsing with absolute ethanol. The nitric acid etching method provided a fresh and active (oxide-free) copper surface. The coupons were dried and kept in a desiccator. Such pretreatment of the coupons was repeated after each run.

The weight loss (in mg cm<sup>-2</sup>) was determined at different immersion times (from 0.50 to 6.0 h) at 30 °C by weighing the cleaned samples before and after hanging the coupon in 100 ml of the corrosive solution, namely aerated 5.0 M NaCl solution in the absence and presence of various concentrations of sodium succinate (SS). After the time elapsed, the cleaning procedure consisted of wiping the coupons with a paper tissue and washing with distilled water and acetone, followed by oven drying at 110 °C.

## 2.3 Electrodes and apparatus

The working electrodes were made of spec pure copper. Experiments were carried out in a three-compartment glass cell. Electrode potentials were measured and reported against a saturated calomel electrode with NaCl solution. A platinum wire was used as auxiliary electrode. Reference and auxiliary electrodes were individually isolated from the test solution by glass frits.

For electrochemical measurements the investigated materials were cut as cylindrical rods, welded with Cu-wire for electrical connection and mounted in glass tubes of appropriate diameter using Araldite to offer an active flat disc shaped surface of (0.75 cm<sup>2</sup>) geometric area to contact the test solution. Prior to each experiment the surface pretreatment of the working electrode mentioned in weight loss measurements was performed. The measurements were carried out in aerated non-stirred 5.0 M NaCl solutions with and without various concentrations (0.001–0.10 M) of SS at the required temperature (± 1 °C) using a water thermostat.

The potentiodynamic current/potential experiments were carried out at a scan rate of 1.0 mV s<sup>-1</sup>. Impedance measurements were carried out using AC signals of amplitude 5 mV peak to peak at the open circuit potential in the frequency range 100 kHz–1.0 Hz. A Potentiostat/Galvanostat (EG&G model 273), lock-in amplifier (model 5210) and M352 corrosion software and M398 impedance software from EG&G Princeton Applied Research were

used for the polarization and impedance measurements, respectively. All impedance data were fitted to appropriate equivalent circuits using the computer program EQUIV-CRT [14].

The composition of the corrosion products formed on the Cu surface in 5.0 M NaCl in the absence and presence of 0.01 M SS were tested at different immersion times by EDX analysis using a Traktor TN-2000 energy dispersive spectrometer. The Cu samples were finally washed thoroughly and submitted to 5 min of ultrasonic cleaning in order to remove loosely adsorbed ions.

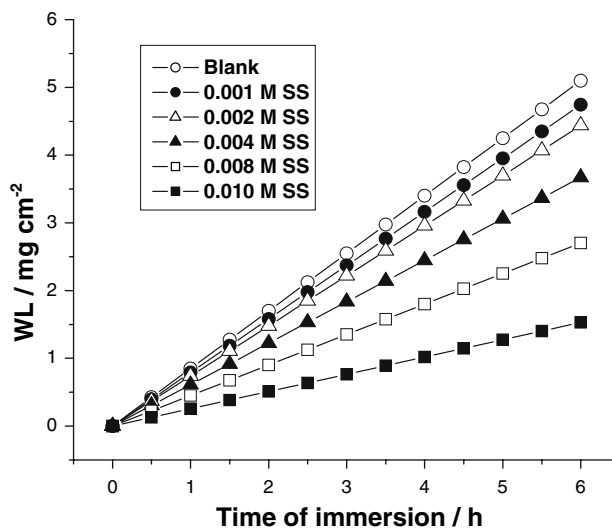
## 3 Results and discussion

### 3.1 Weight loss measurements

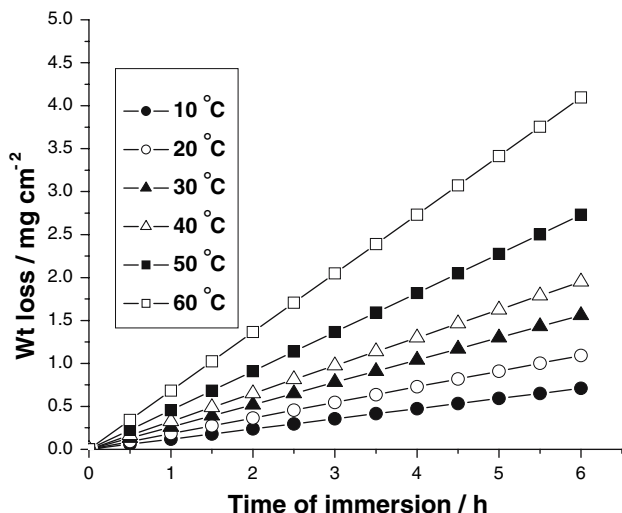
The variation of the weight loss (in mg cm<sup>-2</sup>) of copper with the immersion time in 5.0 M NaCl solution in the absence and presence of various concentrations (0.001–0.10 M) of SS at 30 °C was studied. Some results are presented in Fig. 1. Figure 2 shows the effect of temperature (10–60 °C) on the variation of the weight loss of copper with immersion time in (1.0 M NaCl + 0.01 M SS) solution. It is obvious from Fig. 1 that the weight loss decreased, and therefore the corrosion inhibition increased with increase in inhibitor concentration. This results from the fact that adsorption and surface coverage increases with increase in concentration [15].

The inhibition efficiency (IE%) was calculated from the total weight loss by the Eq. [16, 17]:

$$IE\% = [1 - (WL/WL^0)] \times 100 \quad (1)$$



**Fig. 1** Variation of the weight loss (in mg cm<sup>-2</sup>) with immersion time of a Cu electrode in 5.0 M NaCl solution in the absence and presence of various concentrations of SS at 30 °C



**Fig. 2** Variation of the weight loss (in mg cm<sup>-2</sup>) with immersion time of a Cu electrode in 5.0 M NaCl solution containing 0.01 M SS at different temperatures

where WL<sup>o</sup> and WL are the weight losses of specimens without and with inhibitor. In the present work, the values of IE% were calculated for copper in 5.0 M NaCl solution containing various concentrations of SS at different temperatures. Some data are listed in Tables 1 and Table 2. At a given temperature, the inhibition efficiency increases with increasing SS concentration. Moreover, at a given SS concentration the inhibition efficiency decreases with rise in temperature. These results may be attributed to the decrease in adsorption strength at higher temperature, suggesting that physical adsorption occurs [16, 17].

3.2 Polarization measurements

3.2.1 Effect of inhibitor concentration and temperature

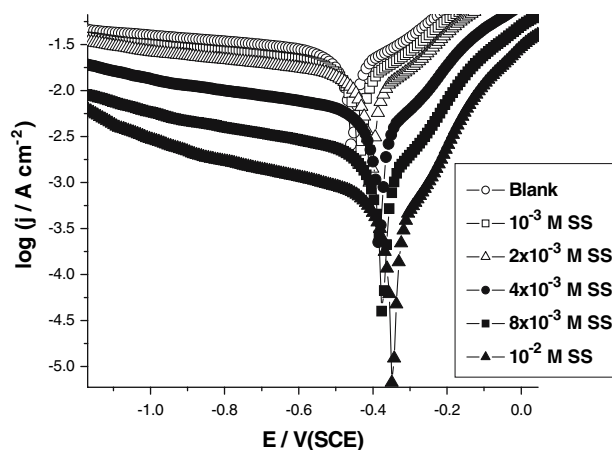
Figure 3 shows the effect of SS concentration (0.001–0.10 M) on the anodic and cathodic polarization curves of

**Table 1** IE% values, calculated from weight loss, polarization and impedance measurements, recorded for Cu in 5.0 M NaCl solution containing different concentrations of SS at 30 °C

IE%			
C <sub>inhib</sub> /M	Weight loss	Polarization	Impedance
0.001	7.40	7.49	7.62
0.002	13.75	13.78	13.76
0.004	28.88	29.02	28.65
0.008	48.45	48.76	47.94
0.010	72.12	72.25	70.90
0.020	87.20	88.00	86.28
0.040	89.65	89.97	88.20
0.080	89.94	90.98	89.75
0.100	91.35	91.49	91.05

**Table 2** IE% values, calculated from weight loss, polarization and impedance measurements, recorded for Cu in 5.0 M NaCl solution containing 0.01 M SS at different temperatures

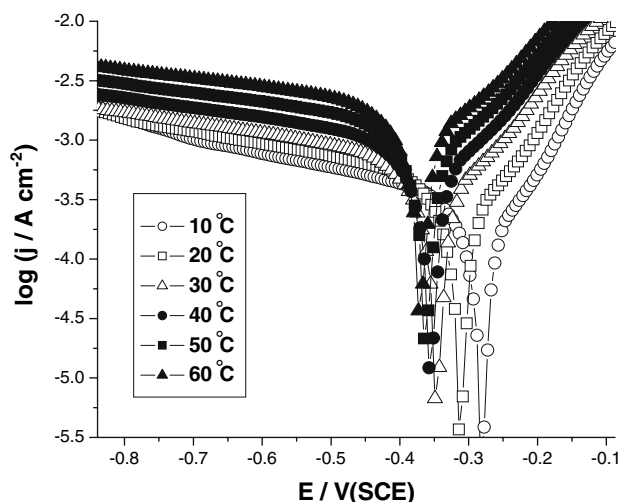
IE%			
T/K	Weight loss	Polarization	Impedance
283	79.44	79.65	78.96
293	75.15	75.35	75.08
303	72.12	72.25	70.90
313	58.98	59.75	58.87
323	55.25	55.38	55.16
333	44.05	44.22	43.97



**Fig. 3** Potentiodynamic anodic and cathodic polarization curves of a Cu electrode in 5.0 M NaCl solution in the absence and presence of various concentrations of SS at a scan rate of 1.0 mV s<sup>-1</sup> and at 30 °C. (1) Blank; (2) 1 × 10<sup>-3</sup> M; (3) 2 × 10<sup>-3</sup> M; (4) 4 × 10<sup>-3</sup> M; (5) 8 × 10<sup>-3</sup> M; (6) 1 × 10<sup>-2</sup> M

copper in 5.0 M NaCl solution at a scan rate of 1.0 mV s<sup>-1</sup> and at 30 °C. The effect of temperature (10–60 °C) on the anodic and cathodic polarization curves of copper in 5.0 M NaCl solution containing 0.01 M SS was examined at a scan rate of 1.0 mV s<sup>-1</sup>, and the results are depicted in Fig. 4. From Fig. 3, by comparing polarization curves in the absence and presence of various concentrations of SS, it is observed that an increase in SS concentration shifts the corrosion potential (E<sub>corr</sub>) in the positive direction and reduces both the anodic and cathodic current densities. Thus the presence of SS inhibits both the anodic and cathodic processes (mixed inhibitor). The action of SS may be related to adsorption and formation of a barrier film on the copper surface. The formation of such a barrier film is confirmed by EDX analysis of the electrode surface (as will be discussed later).

The electrochemical parameters (j<sub>corr</sub>, E<sub>corr</sub>, b<sub>a</sub> and b<sub>c</sub> and R<sub>p</sub>) associated with polarization measurements for copper at different SS concentrations and temperatures were simultaneously determined from the polarization



**Fig. 4** Effect of temperature (10–60 °C) on the potentiodynamic anodic and cathodic polarization curves of a Cu electrode in (5.0 M NaCl + 0.01 M SS) solution at a scan rate of 1.0 mV s<sup>-1</sup>

curves in the potential range ( $E_{\text{corr}} \pm 20$  mV) using M352 corrosion software from EG&G Princeton Applied Research and are listed in Tables 3 and Table 4, respectively. The slopes of the anodic ( $b_a$ ) and cathodic ( $b_c$ ) Tafel lines remain almost unchanged upon addition of inhibitor. Thus the adsorbed inhibitor acts by simple blocking of active sites for both anodic and cathodic processes. In other words the inhibitor decreases the surface area for corrosion without affecting the corrosion mechanism and only causes inactivation of a part of the surface with respect to the corrosive medium [16, 17].

Figure 4 clearly shows that an increase in solution temperature slightly shifts  $E_{\text{corr}}$  in the negative direction and enhances both the anodic and cathodic current densities. The  $j_{\text{corr}}$  values were used to calculate IE% of SS at different concentrations and temperatures (see Tables 1 and 2), using the Equation:

$$\text{IE}\% = 100 \times [(j_{\text{corr}}^{\circ} - j_{\text{corr}})/j_{\text{corr}}^{\circ}] \quad (2)$$

**Table 3** The electrochemical parameters ( $j_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $b_c$  and  $b_a$  and  $R_p$ ) associated with polarization measurements of Cu electrode in 5.0 M NaCl solution in the absence and presence of different concentrations of SS at 30 °C

$C_{\text{inhib}}/\text{M}$	$j_{\text{corr}}/\text{mA cm}^{-2}$	$E_{\text{corr}}/\text{V(SCE)}$	$b_a/\text{V dec}^{-1}$	$b_c/\text{V dec}^{-1}$	$R_p/\Omega \text{ cm}^2$
Blank	15.75	-0.45	0.075	-0.125	175.00
0.001	14.57	-0.44	0.074	-0.126	189.19
0.002	13.58	-0.43	0.075	-0.127	202.90
0.004	11.18	-0.42	0.076	-0.125	246.48
0.008	8.07	-0.40	0.077	-0.124	341.46
0.010	4.37	-0.38	0.074	-0.125	630.63
0.020	1.89	-0.37	0.075	-0.126	1458.33
0.040	1.58	-0.36	0.076	-0.124	1750.00
0.080	1.42	-0.34	0.073	-0.125	1944.44
0.100	1.34	-0.32	0.074	-0.128	2058.82

**Table 4** The electrochemical parameters ( $j_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $b_c$  and  $b_a$  and  $R_p$ ) associated with polarization measurements of Cu electrode in 5.0 M NaCl solution containing 0.01 M SS at different temperatures

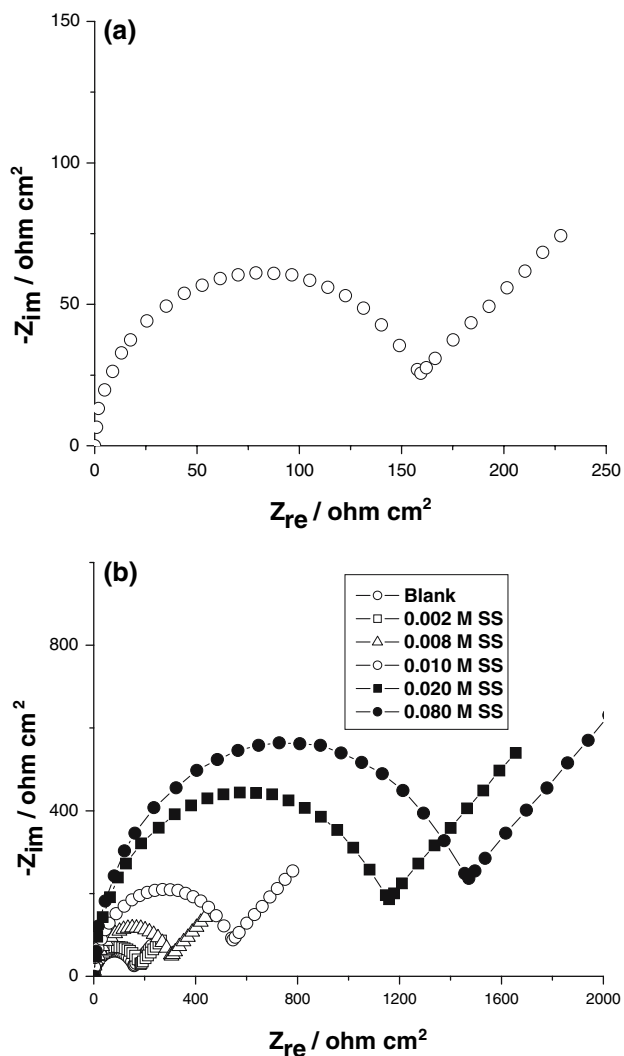
T/K	$j_{\text{corr}}/\mu\text{A cm}^{-2}$	$E_{\text{corr}}/\text{V(SCE)}$	$b_a/\text{V dec}^{-1}$	$b_c/\text{V dec}^{-1}$	$R_p/\Omega \text{ cm}^2$
283	1.75	-0.34	0.075	-0.123	875.00
293	3.00	-0.36	0.076	-0.124	750.00
303	4.37	-0.38	0.074	-0.125	630.63
313	6.25	-0.39	0.073	-0.124	500.75
323	8.15	-0.40	0.075	-0.126	388.80
333	11.88	-0.42	0.074	-0.125	225.00

where  $j_{\text{corr}}^{\circ}$  and  $j_{\text{corr}}$  are the corrosion current densities for uninhibited and inhibited solutions, respectively.

### 3.3 Impedance measurements

#### 3.3.1 Effect of inhibitor concentration and temperature

Figure 5 shows Nyquist plots for copper in 5.0 M NaCl solution at 30 °C without (Fig. 5a) and with various concentrations of SS at the respective corrosion potentials (Fig 5b). The influence of solution temperature on the impedance response in (5.0 M NaCl + 0.01 M SS) solution was studied at OCP; results are depicted in Fig. 6. Figure 5 shows a high frequency (HF) semicircle followed by a straight-line portion in the low-frequency (LF) region. The HF semicircle is attributed to the time constant of charge transfer and double-layer capacitance [18, 19]. This semicircle makes an angle approaching 70° with the real axis and its intersection gives a value of 1.35  $\Omega \text{ cm}^2$  for the resistance of the solution ( $R_s$ ) enclosed between the working electrode and the counter electrode. The intercept of the HF charge transfer semicircle with the real axis gives the charge transfer resistance ( $R_{\text{ct}}$ ) value [20]. The LF linear portion is generally believed to be a Warburg type impedance related to the diffusion of soluble copper species from electrode surface to bulk solution [13,18, 19]. To



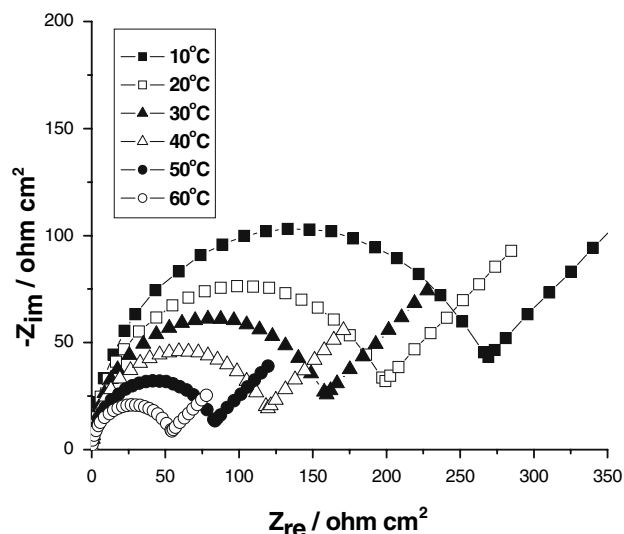
**Fig. 5** Impedance response of a Cu electrode in 5.0 M NaCl solution in (a) absence and in (b) presence of various concentrations of SS solution at the respective corrosion potentials and at 30 °C

obtain the double layer capacitance ( $C_{dl}$ ), the frequency ( $f_{max}$ ) at which the imaginary component of the impedance is maximal was found and used in Eq. (3):

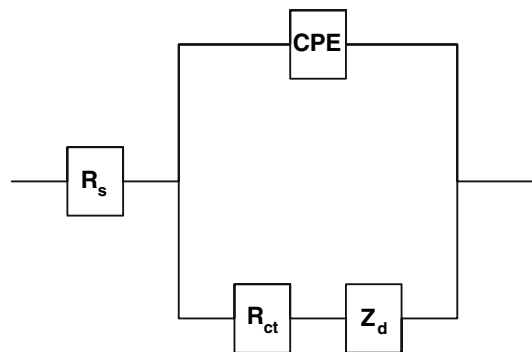
$$C_{dl} = 1/2\pi f_{max} R_{ct} \tag{3}$$

The large semicircle observed from high to low frequencies in the presence of inhibitor indicates that the charge-transfer resistance became dominant in the corrosion process due to the formation of an SS film on the copper surface. However, the Warburg impedance in the LF region is still visible at all SS concentrations, indicating that the corrosion process is controlled by mixed charge-transfer and diffusion in solution.

The impedance data were interpreted according to the equivalent circuit depicted in Fig. 7. This equivalent circuit was used to simulate the EIS data displaying a Warburg



**Fig. 6** Influence of solution temperature (10–60 °C) on the impedance responses of a Cu electrode in 5.0 M NaCl solution containing 0.01 M SS at the respective corrosion potentials



**Fig. 7** Equivalent circuit used to fit the EIS data

impedance. In this circuit,  $R_s$  is the solution resistance,  $R_{ct}$  is the charge transfer resistance,  $C_{dl}$  is the double-layer capacitance, and  $Z_d$  represents the diffusion impedance appearing in the LF region.

One constant phase element (CPE) is substituted for the capacitive element to give a more accurate fit [21], as the capacitive loop is a depressed semi-circle rather than regular one. The CPE is a special element whose immittance value is a function of the angular frequency ( $\omega$ ), and whose phase is independent of frequency. Its immittance and impedance are, respectively, expressed as :

$$Y_{CPE} = Y_0(j\omega)^n \tag{4}$$

and

$$Z_{CPE} = (1/Y_0) [(j\omega)^n]^{-1} \tag{5}$$

where  $Y_0$  is the magnitude of the CPE,  $\alpha$  is the phase angle of the CPE and  $n = \alpha/(\pi/2)$ . The factor  $n$  is an adjustable



parameter that usually lies between 0.50 and 1.0 [22]. The CPE describes an ideal capacitor when  $n = 1$ . Values of  $\alpha$  are usually related to the roughness of the electrode surface. The smaller the value of  $\alpha$ , the higher the surface roughness [21, 22]. The complex plane impedance plot is similar to that calculated by the equivalent circuit models. The points in Figs. 5b and 6 represent the experimental data while the solid curves represent the best fits.

The inhibition efficiency was evaluated from  $R_{ct}$  and  $C_{dl}$  values of the impedance (see Table 5). The more densely packed the inhibitor surface film, the larger the diameter of the semicircle, which results in higher  $R_{ct}$  and lower  $C_{dl}$  values. Data presented in Table 5 showed that the  $R_{ct}$  values increase with increasing SS concentration, while the  $C_{dl}$  values tend to decrease. The decrease in  $C_{dl}$  values is due to the adsorption of SS on the metal surface [23, 24]. The reverse changes were produced by increasing temperature as shown in Fig. 6. The  $R_{ct}$  values were used to calculate the IE% of SS at different concentrations and temperatures (see Tables 1 and 2), using Eq. (6).

$$IE\% = 100 \times [(R_{ct} - R_{ct}^0)/R_{ct}] \quad (6)$$

where  $R_{ct}^0$  and  $R_{ct}$  are the charge transfer resistances for uninhibited and inhibited solutions, respectively. The inhibition efficiency increases with increasing inhibitor concentration. Moreover, the inhibition efficiency decreases with increasing temperature, confirming the suggestion that physical adsorption occurs. It is worth noting from Tables 1 and 2 that the inhibition efficiencies obtained from impedance measurements are comparable and run parallel with those obtained from weight loss and potentiodynamic polarization methods.

**Table 5** Values of  $R_{ct}$  and  $C_{dl}$  recorded for Cu electrode in 5.0 M NaCl solution in the absence and presence of different concentrations of SS at 30 °C

$C_{inhib}/M$	$R_{ct}/\text{ohm cm}^2$	$C_{dl}/\mu\text{F cm}^{-2}$
Blank	170.00	15.00
0.001	183.47	13.90
0.002	196.54	12.97
0.004	237.55	10.73
0.008	325.59	7.83
0.010	582.37	4.38
0.020	1235.47	2.06
0.040	1436.89	1.77
0.080	1568.91	1.63
0.100	1644.45	1.55

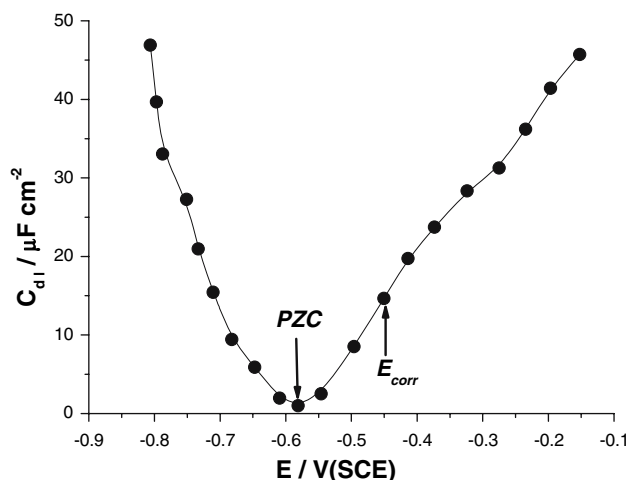
### 3.3.2 Determination of the PZC of copper in NaCl solutions and the mode of adsorption of SS on the copper surface

Adsorption of charged species (like SS in this study) on a corroding metal depends mainly on the charge of the metal surface, the charge or the dipole moment of the charged species, and the adsorption of other ionic species if it is electrostatic in nature [25]. The potential of zero charge (PZC) plays a very important role in the electrostatic adsorption process. The ac impedance study was used to evaluate the potential of zero charge (PZC) [26, 27]. A plot of  $C_{dl}$  values recorded for copper in 5.0 M NaCl solution at each applied potential is shown in Fig. 8; this is a parabola with a minimum capacitance at about  $-0.58$  V(SCE). This value is the PZC of copper in 5.0 M NaCl solution, which is more negative than the corrosion potential [ $-0.45$  V(SCE)]. This means that the copper surface is positively charged at the corrosion potential.

These results suggest that the inhibitive action of SS in NaCl solution results from physical (electrostatic) adsorption of the negatively charged succinate ions to the positively charged copper surface forming a barrier on the copper surface. When the immersion time and SS concentration increase, more succinate anions adsorb electrostatically on the copper surface. The barrier becomes more compact and protective with adsorption of more succinate anions. Thus the inhibition efficiency increases with increase in immersion time and concentration.

### 3.4 EDX analysis of the electrode surface

EDX survey spectra were used to determine which elements were present on the copper surface before and after



**Fig. 8** Relationship between  $C_{dl}$  values and the applied potential for a copper electrode in 5.0 M NaCl solution at 30 °C

exposure to the inhibitor solution. Figure 9 presents spectra for copper samples exposed for 30, 60 and 120 min in 5.0 M NaCl with and without added inhibitor (0.01 M). In uninhibited NaCl solutions, the EDX spectra (Fig. 9a) confirm the existence of cuprite crystals ( $\text{Cu}_2\text{O}$ ), as indicated by the Cu and O signals. However, in inhibited NaCl solutions (Fig. 9b–d), the spectra showed an additional line characteristic of the existence of C (due to the carbon atoms of SS). In addition, the O signal is significantly enhanced due to the two oxygen atoms present in the carboxylate group of SS. These data show that a carbonaceous material containing oxygen atoms has covered the electrode surface. This layer is undoubtedly due to the inhibitor, because the carbon signal and the high contribution of the oxygen signal are not present on the copper surface exposed to uninhibited NaCl solutions after 30 min immersion (see Fig. 9a). In addition, the intensity of the carbon and oxygen signals increase with immersion time (see Fig. 9b–d), since more succinate anions will electrostatically adsorb on the fresh copper surface. This may imply that IE% improved with time. This is in accordance with the IE% values calculated from weight losses in absence and presence of 0.01 M SS after 30, 60 and 120 min (see Fig. 1).

The spectra of Fig. 9b–d show that the Cu peaks are suppressed relative to the samples prepared in NaCl solution and this suppression increases with immersion time. The suppression of the Cu lines occurs because of the overlying inhibitor film. These results confirm those from polarization measurements which suggest that a surface film inhibits the growth of copper oxide, and hence retards the reduction of dissolved oxygen in the NaCl solution. The

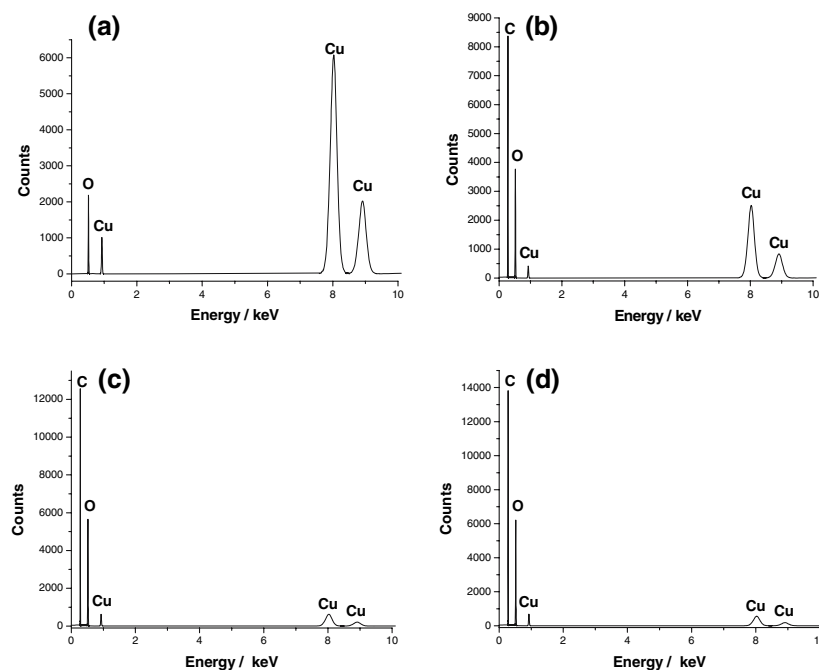
inhibitor surface film acts as a barrier to the diffusion of oxygen molecules from solution to copper substrate, which may increase the overpotential of cathodic reduction of dissolved oxygen, as shown in Fig. 3. This surface film also increases the charge transfer resistance of the anodic dissolution of copper (Fig. 5b), reducing the corrosion rate.

#### 4 Conclusion

Weight loss, electrochemical polarization, AC impedance and EDX measurements were used to study the corrosion inhibition of copper in aerated stagnant 5.0 M NaCl solution at the corrosion potential using sodium succinate (SS). The principle conclusions are

- (i) The corrosion of copper in NaCl solutions is significantly reduced with addition of SS.
- (ii) Electrochemical polarization studies revealed that SS functions as a mixed-type inhibitor.
- (iii) Inhibition efficiency increases with increasing SS concentration, while it decreases with temperature.
- (iv) Physisorption is proposed as the mechanism of corrosion inhibition.
- (v) EDX analysis showed that a film of inhibitor is formed on the electrode surface. This film retards the reduction of dissolved oxygen and inhibits the growth of copper oxide.
- (vi) The inhibition efficiencies obtained from weight loss, electrochemical polarization and impedance measurements are in good agreement.

**Fig. 9** EDX spectra of copper specimens (a) after 30 min of immersion in 5.0 M NaCl solution. (b) after 30 min of immersion in (5.0 M NaCl + 0.01 M SS) solution. (c) after 60 min of immersion in (5.0 M NaCl + 0.01 M SS) solution. (d) after 120 min of immersion in (5.0 M NaCl + 0.01 M SS) solution



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